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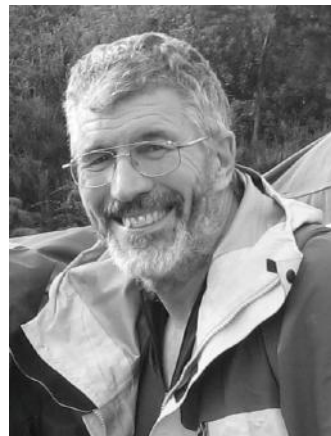
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Comment from the President



This issue I'd like to comment on three themes of specific and current importance to our profession in New Zealand.

In our July issue I noted that the Royal Society of New Zealand was to consider forming an expert panel to examine the future science technician workforce. I can now confirm that the RSNZ Council has supported

this action and that the Science Technicians Workforce Panel will be chaired by Professor Jim Johnston of Victoria University. The terms of reference for the panel are to identify a national approach to science technicians' careers and training in New Zealand, with a number of specific questions to be addressed. Jim and the other panel members, including myself, will be seeking input from an expert reference group of eleven, and also from the wider New Zealand community across the many faces of the science, business and education sectors. The detailed terms of reference for the panel will appear on the RSNZ website in due course. Your input, either formally via the RSNZ or informally via Jim and I, will be very welcome.

My second comment is to express sadness that ongoing instability in the AgResearch funding model continues to play havoc with the careers, morale and delivery of our colleagues in the agricultural science community, with the impending loss of some 80 scientific and technical staff positions. I've seen at first hand the impacts of funding loss on project teams who believed that they were doing relevant and appropriate research to benefit New

Zealand but whose vision was not accepted by the funding agencies. There is no 'plan B' for such research teams and once they are they dispersed, they cannot be reassembled. The options at an individual level are few. Some will retrain, often in fields distant from their core skills. Those who are more mobile or motivated may leave New Zealand. The outcome in all cases is a loss of critical mass in the particular research field, a waste of educational and taxpayer investment in training highly skilled staff and in a number of cases a direct loss of this capability to competing offshore economies with all of the inherent and serious risk of loss of New Zealand's intellectual property. I am alarmed at the 'red flag' message that this gives our younger researchers and those considering a research career in the government science agencies. With our agricultural exports being challenged or threatened in the world market place it is the time to support innovation in this key science sector and not crush it.

To finish on a much more positive note, I'd like to publicise that three of our prominent chemists have been appointed to key leadership roles in IUPAC for the coming year. Richard Hartshorn (University of Canterbury) has been elected as IUPAC Secretary General while Greg Russell (University of Canterbury) and Margaret Brimble (University of Auckland) will head the 'Polymer' and 'Organic and Bioorganic' divisions respectively (that is, two of the eight IUPAC divisions). This is a superb personal recognition of Richard, Greg and Margaret and the strongest possible acknowledgement of the quality of our New Zealand chemical scientists on the world stage in the discipline of chemistry.

Ian Brown
Callaghan Innovation
NZIC President 2015

Comment from the Editor



As we reach the last issue of our journal for 2015, I am very pleased to be able to reflect on the fact that the major problem I have encountered this year has been one of juggling content to keep within our space and cost constraints. There has been quite a variety of article topics and an increase in the

number of new contributors contacting me with enquiries about publishing in *Chemistry in New Zealand* which I hope will continue into next year. This is your journal, so keep those submissions coming in.

In this issue, we have an item discussing the skills and attributes required of new chemistry graduates from the perspective of an employer in industry. It would be interesting to know what readers think of some of the points raised, and to hear the views of those involved in teaching at undergraduate level. Correspondence on this or any other topic is always welcome.

Finally, we will be conducting a salary survey early in 2016. All NZIC members will be asked to participate and I hope we will get a good response rate. A salary survey has not been carried out since 2006 so it will be timely to review what has changed over the past 10 years.

Cath Nicholson

New Zealand Institute of Chemistry

supporting chemical sciences

October News

2015 NZIC Prizes

Easterfield Medal

Dr **Justin Hodgkiss**, School of Chemical and Physical Sciences, Victoria University of Wellington.

Maurice Wilkins Centre Prize for Chemical Science

Assoc. Prof. **Shane Telfer**, Institute of Fundamental Sciences, Massey University.

Shimadzu Applied and Industrial Chemistry Prize

Jointly awarded Dr **Paul Benjes**, GlycoSyn, Callaghan Innovation and Dr **Phillip Rendle**, Ferrier Research Institute, Victoria University of Wellington.

ABA Resources Denis Hogan Prize for Chemical Education

Dr **Sheila Woodgate**, School of Chemical Sciences, University of Auckland.

FNZIC

The following members have been accepted as Fellows of NZIC:

Dr **Simon Hinkley**, Dr **Olga Zubkva**, Dr **Ralf Schwoerer**, Ferrier Research Institute, Victoria University of Wellington; Dr **Mattie Timmer**, Dr **Bridget Stocker**, Dr **Joanne Harvey**, School of Chemical and Physical Sciences, Victoria University of Wellington; Dr **Timothy Kemmitt**, Callaghan Innovation.

2015 Hatherton Award

Lujia (Luke) Liu, a PhD student at Massey University, Palmerston North, received the 2015 Hatherton Award from the Royal Society of New Zealand. This award recognises the best scientific paper by a PhD student at any NZ university in physical sciences, earth sciences and mathematical and information sciences. Luke's paper, describing a method

of constructing metal-organic frameworks from four components, was published in the *Journal of the American Chemical Society*, vol 137, pp 3901-3909. Luke is a student of Assoc. Prof. **Shane Telfer** who won the Maurice Wilkins Prize for Chemical Science.

Branch News

AUCKLAND

The University of Auckland

Centre for Green Chemical Science

The School of Chemical Sciences at the University of Auckland has established a Centre for Green Chemical Science to facilitate research, education and outreach in green chemical science and to develop innovative green solutions to sustainability issues that face the global chemistry community.

The Centre opened with a Green Chemistry Symposium on 8 September at the Conference Centre, University of Auckland. Distinguished speakers at the symposium included Professor **Milton Hearn**, Director of the Green Chemistry Centre at Monash, **Malcolm Rands**, CEO of Ecostore, **Chris Mulcare** from Pure Advantage and Professor Paul Kilmartin from the University of Auckland. The symposium provided a forum for attendees to learn about sustainable chemical research at the University of Auckland, hear keynote addresses from experts in the area and make new contacts. There was also an informal networking session to help establish new relationships and research partnerships between university researchers and industry.

Congratulations

Congratulations to Distinguished Professor **Margaret Brimble** for her selection as a Senior Fellow of the International Society of Heterocyclic Chemistry (ISHC). The announce-

ment was made at the International Congress of Heterocyclic Chemistry in Santa Barbara in August.

Professor Brimble was also awarded the RSC Australasian Lectureship for 2015.

The picture below shows Professor Brimble (right) with **Mark Cesa**, IUPAC President and **Natalia Tarasova**, IUPAC Vice-President at the IUPAC awards function for Distinguished Women in Chemistry held in South Korea in August (see news item in the July issue of CINZ).



Congratulations to PhD student **Matias Kinzurik** who won the top poster prize at the wine chemistry conference, *In Vino Analytica Scientia 2015*. His poster, entitled *H₂S production causes the accumulation of sulfur volatiles associated with cooked onion aroma during winemaking*, was selected among a field of 58 student posters from all around the world. Matias's research is funded by NZ Winegrowers and the Bragato Trust



and jointly supervised by Dr *Bruno Fedrizzi*, SCS, and Professor *Richard Gardner*, SBS, at the University of Auckland.

PhD students Wan-Ting Chen and Andrew Chan have both been awarded AINSE Post Graduate Research Awards by the Australian Institute of Nuclear Science and Technology. Each PGRA award offers a stipend (AUD 7,500 p.a.) as a top up on their primary UoA PhD scholarships and funds to use ANSTO facilities (AUD 10,000 p.a.). AINSE provides PGRA awards for postgraduate students whose research projects involve nuclear science or which require the use of facilities at the Australian Nuclear Science & Technology Organisation (ANSTO), Lucas Heights, Australia.

Faculty of Science pedometer challenge

The Faculty of Science staff team pedometer challenge kicked off on 25 May and ran for eight weeks. Teams from all around the Faculty participated, including the School of Chemical Sciences staff members.

Winners from the School of Chemical Sciences were Associate Professor *Gordon Miskelly*, who won 'Most Steps in a Day' with his 113,943 steps. Dr *Ivanhoe Leung* and his team, who won in the 'Best Graph' and 'Best Leader' categories.

Congratulations to the winning staff members and teams!

The New Zealand Institute of Advanced Study (NZIAS), Massey University, Auckland

Massey University agreed to build a new science building on the East Precinct of the Albany Campus to house chemistry, part of biological sciences and possibly physics. A newly arrived NMR machine will be moved to this new location. There will be a new position opening for an inorganic chemist at the beginning of next year. Professor *Peter Schwerdtfeger* started his Rutherford lecture tour with sold-out events in Wellington. He gave a keynote lecture on new carbon materials at the pulp and paper conference in Taupo. He was also in Poland attending a nuclear physics

meeting talking about the chemistry of superheavy elements.

CANTERBURY

NZIC Seminars

Prof. *Gregory F. Metha* (Department of Chemistry, University of Adelaide) presented a seminar on 9 June entitled *Musings on energy and climate change, and the role of chemistry*. At least 97% of actively publishing climate scientists agree that the climate-warming trend over the past century is very likely due to human activities. Yet rising energy consumption and increasing CO₂ emissions continues unabated, whilst governments and policy-makers flounder to make decisions on how to stop the planet's temperature from increasing beyond 2 °C, generally regarded as the point of dangerous climate change. From a chemistry perspective, this presentation involved, the relationship between global energy demand, fossil fuel consumption, rising greenhouse gas emissions and climate change and the issue of energy storage from intermittent, non-dispatchable electricity sources such as wind and solar. Professor Metha ended his presentation by highlighting some of the conflicting political and commercial interests at play, including climate change denial, and suggested that the time has arrived for all scientists to take a more active role in demanding change from our governments. Professor Greg Metha is a visiting Erskine Fellow in the University of Canterbury with a strong interest in the impact of chemistry on the world around us.

Derek Wann (University of York, UK) presented a seminar on 29 July entitled: *Making molecular movies*. At the heart of chemistry is a desire to understand better the functions of molecules. Key to that is having an ability to accurately measure molecular structure which, in turn, informs us about structure-function relationships. Electron diffraction has been a staple technique in determining the structures of molecules for nearly a century. However, until recently most electron diffraction experiments used a continuous electron

beam, which restricted us to studying static structures of molecules. As molecules are constantly moving, this time-averaged information is essentially a "blurred" image, like a photograph of a fast moving object taken with a long-exposure camera.

With the availability of Ti:sapphire lasers, it is now possible to capture sharp, near-instantaneous diffraction images from molecular species using a pulsed electron beam. By combining the laser pump and electron probe techniques one can watch molecular structures as they evolve over a period of time: the so-called "molecular movie". Dan's talk presented an overview of advances that have been made in the field of electron diffraction to the point where one can now observe the motions of atoms in molecules yielding the first true molecular movies.

University of Canterbury

Awards and appointments

Congratulations to *Antony Fairbanks* and *Sarah Masters* for making it to the second round of their Marsden applications.

Congratulations to our new PhDs who successfully defended their theses recently: *Pragya Priyanka* supervised by Antony Fairbanks and co-supervised by *Peter Steel*, and *Sandra Atkinson* supervised by Sarah Masters and co-supervised by *Bryce Williamson*.

Congratulations to the following students who have successfully completed their MSc theses: *Emma Livingstone*, *Ethan Lankshear* and *Evonne Ruegg*.

Congratulations to *Gemma Wadworth* and *Alex McNeill* for winning first and third place in the Postgraduate Students' Association Research Roulette Competition on 26 May. Postgraduate students from across the University were given one minute to tell each of the other contestants about their research in an "elevator pitch".

Congratulations to *Alexandra McNeill* from the Downard Group, supervised by *Alison Downard* and co-supervised by *Martin Allen*. Alex

has received a 2015 Fulbright Science and Innovation Award. Alex is going to undertake a year-long research visit to **Robert Hamser's** lab at the University of Wisconsin-Madison researching surface modification of zinc oxide.

Thesis in Three

On 28 July the Department held its heat for the UC Thesis in Three competition. Nine MSc thesis and doctoral students presented their work in this special, short format rapid fire seminar. The students had just three minutes to describe WHAT (they are doing); WHY (they are doing it – the importance/impact of the research) and HOW (they are doing it). Only a single PowerPoint slide (no slide transitions) could be used, with no additional electronic media, e.g. sound and video files, and no additional props, e.g. costumes, instruments (musical, laboratory), etc.. After a strong round of presentations, **Will Kerr**, **Alex McNeill** and **David Lim** went forward to the College of Science final, held on 6 August, with 12 MSc thesis and doctoral students participating. The standard of the presentations was extremely high, and the judges had some tough deliberation prior to announcing the results.

Huge congratulations to Will Kerr who won the College final and went forward to the UC grand final along with Sarah Davies and Kerstin Erffmann (from the Department of Communication Disorders). The UC Thesis in Three final took place on 13 August. There were 17 presentations across the five colleges, and competition was fierce with an incredibly high standard. Will Kerr emerged victorious, with his presentation *Enforcing a chemical handshake*.

Visitors

Welcome to **Dinga Wonanke**, who will be working in the Department as a PhD student. Dinga is from a small town in Cameroon called Dschang. Dinga studied at the University of Dschang completing an MSc in theoretical and computational chemistry. Dinga's MSc research was on density function theory investigation of the different orientation of hydrogen bonding in a complex of

transdiaquabis(N-benzylidene-2-hydroxybenzohydrazide)iron(II). In his spare time Dinga enjoys studying the bible with friends and choral singing.

Dr Derek Wann visited the department from the University of York, UK, between 9 July and 22 August. As an Erskine visitor he spent time lecturing undergraduate students (at 300- and 400-level) and delivered research lectures in UC and in other New Zealand universities. Derek's research interests include computational chemistry as well as electron diffraction and while in the department he reacquainting himself with Sarah Masters' electron diffraction apparatus on which he performed his PhD work when Derek and Sarah were both at the University of Edinburgh. Derek's current research focusses on developing methods for performing time-resolved electron diffraction, where a femtosecond Ti:sapphire laser is used both to excite structural changes of interest, as well as to produce short pulses of electrons.

Sarah Kessans earned her PhD in 2011 from Arizona State University, where she worked to develop a plant-based vaccine against HIV-1. Arriving in New Zealand in 2012, she has spent the last few years in UC's School of Biological Sciences with **Renwick Dobson**, gaining biochemistry experience in enzyme evolution and characterisation. She is now returning to her molecular biology roots, working with **Emily Parker's** group to develop fungal factories for biosynthesis of high value industrial bioproducts for commercial applications. Outside of the lab, Sarah can be found kayaking down rivers, biking in the mountains, running around the ultimate frisbee pitches, and generally exploring the natural wonders for which New Zealand is famous.

OTAGO

The Otago branch of the NZIC again sponsored the Aurora Otago Science & Technology Fair. Prizes were awarded to:

Meg Christophers (*Zap that zit*), **Hannah Paton** (*SoapAsalt – Investigating the salt curve*), **Madyson Witehira** (*Chlorine vs temperature*), **Lucy**

Matehaere (*Salt in the harbour*) and **Ben Rowley** (*How does storage of apple juice at various temperatures affect vitamin C concentration?*).

University of Otago, Department of Chemistry

The past few months have been a busy time in the department for PhD completions. Successfully negotiating their oral defence in the period late May-August have been: **Antonia Seidel** (Jameson group), **Dylan Hegh** (Tan group), **Warrick Lo** and **Sree Vellas** (Crowley group), **Holly van der Salm** (Gordon group), **Reece Miller** (Brooker group), **Kiattipoom (Mart) Rodpun** (Meledandri group), **Alastair Lee** (Larsen group), **Sruthi Rajasekharan Nair Sreelatha** (Sander group), and **Amandine Sabadel** (Frew group). Mart and Holly, along with **Mattias Fellner** (Jameson group) all graduated in person at the ceremony on 15 August.

Christopher Larsen (Gordon and Lucas groups) won the sciences heat of the Otago 3-Minute Thesis competition and went on to speak in the university final held on 26 August. His presentation was entitled *Molecular lego: designing functional material*. Chris finished the week with the submission of his PhD thesis on the synthesis and spectroscopy of donor-acceptor materials.

Attending the 10th International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC) 28 June-2 July 2015 in Strasbourg were a contingent of staff and students from the department including **Sally Brooker**, **James Crowley**, **Dave McMorran**, **Synøve Scottwell**, **Dan Preston**, and **Komal Patil**.

Reece Miller who successfully completed his PhD, is currently completing more papers to add to his CV. PhD student **Hannah Davidson** (pictured) has just spent a week working in London testing complexes with collaborators for their potential as greener catalysts for a range of polymerisations. **Sally Brooker** has been awarded the 2015 University of Otago Distinguished Research Medal (pictured with her team: photo by Sharron Bennett). Sally was in Europe mid-year, visiting a

number of collaborators, presenting department seminars, and participating in ISMSC (Strasbourg) and the Asian Coordination Chemistry Conference (ACCC, Hong Kong). PhD student *Santi Rodriguez* is currently in Spain to present his



Hannah Davidson

spin crossover work at the European Conference on Molecular Magnetism (ECMM). J *Hrudka*, a PhD student from Florida State University, is on a collaborative research visit with us for six months.

New PhD student *Olu Babaranti* joined Rob Middag's research group in July. Olu is from Nigeria and has come to New Zealand to study the distribution of dissolved trace elements in the ocean and their impact on ocean productivity and climate change.

Plant & Food Research and the University of Otago celebrated the opening of the refurbished Plant Extracts Research Unit in Dunedin on 22 August. "PERU" was first opened in 1991 as a collaboration between the University of Otago and MAF Technology. This unit is located within the Department of Chemistry and

currently has four PFR staff: *Elaine Burgess*, *Catherine Sansom*, *John van Klink* and *Nigel Perry* (PFR Bio-actives team leader and UO Associate Professor). *Bruce Smallfield* (PFR Lincoln) is a regular guest, working at PERU on various projects, including taramea with Ngai Tahu and mānuka nectar quality for honey. Two UoO students are working in PERU at present: *Oliver Watkins* (PhD) and *Alistair Richardson* (BSc Hons).

Our new laboratories and offices will boost our efforts on identifying new bioactive natural products from introduced crops and New Zealand native plants and animals; developing fast analytical methods and collaborating with research biologists and industry partners to translate the results into commercial developments.

WAIKATO

NZIC Analytical Chemistry Competition 2015

This annual event was held on 17 June. Invitations were sent to schools in the wider Waikato/Bay of Plenty region to send teams of four students to the university for the day to carry out an analysis. A total of 23 teams competed in the event.

The task was to analyse a sample of $\text{NiSO}_4 \cdot n\text{H}_2\text{O}$ using a gravimetric procedure for Ni^{2+} and a volumetric method for SO_4^{2-} to allow the value of n to be calculated in the empirical formula by difference. This was a demanding task in the time available but some excellent results were achieved.

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

First Prize: Hamilton Boys' High School 1

(Hayden Lee, Christopher Mayo, Visharn Sathiyakumar, Lucas Sherlock)

Second Prize: St Peter's School

Sam Frengley, Erin Gatenby, Shenaz Husain, Rishi Kumar



Sally Brooker (second from right) with her team. Image by Sharron Bennett.



Photo: Guests and staff in the modernised Plant Extracts Research Unit main laboratory, from left to right: Catherine Sansom, PFR Dunedin; Mary Gower, Research and Enterprise, UO; Nigel Perry (obscured), PFR Dunedin and UO Chemistry; Richard Macknight, UO Biochemistry and PFR Dunedin; Kieran Elborough, PFR General Manager Breeding & Genomics; Richard Blaikie, UO DVC Research and Enterprise; and Lyall Hanton, UoO Head of the Chemistry Department. Image by John van Klink, PFR Dunedin



Prize winners: Hamilton Boys' High School's Christopher Mayo, Visharn Sathiyakumar, Lucas Sherlock and Hayden Lee were the winners of the 2015 NZIC Analytical Chemistry Competition (shown here with competition judge and chief organiser Dr Michèle Prinsep (far left)).



Two of the competing teams

Third Prize: Tauranga Girls' College

Nell Ager, Jessica Crockett, Emma Dalton, Sophie Godden

Fourth Prize: Pukekohe High School

Jack Boulton, Ryan Le Quesne, Jacqui Smith, Bailee-Jayne Waller

Fifth Prize: Mount Maunganui College

(Monique Frost, George Maltby, Tim Scott, Kayla Waters

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

SCION

Warren **Grigsby** recently returned

from Japan having taken up a Japan Society for Promotion of Science Invitational Fellowship. During his stay Warren worked with colleagues at the Forest & Forest Products Research Institute (FFPRI) on a collaborative project to assess volatile organic compounds arising from wood panels produced using bioadhesives. Analysis included compounds emitted during panel manufacture and released over time, and those produced by specific adhesive ingredients.

University of Waikato

PhD student **Raymond Onyekachi** was selected as one of the winners for the AMP Ignite programme - a competition in which PhD students across New Zealand pitched their research as an entertaining performance in front of a live business audience in Auckland. He went on to win the finalist prize of \$1000. Raymond was also the 2014 University of Waikato 3 Minute Thesis winner and will represent the university in the Trans-Tasman Finals in October, in Queensland, Australia.

WELLINGTON

Joan (Matteringley) Cameron, Hon FNZIC, a longstanding member of the Wellington Branch died on July 27. She had been in the care of the staff of Eldon Lodge, Paraparaumu for several years (see her obituary page 199).

On 10 June, over 130 Year 12 and 13 students from 17 schools participated in the 2015 Branch Chemistry

Quiz. The night was a great success with the students and helpers getting involved and having a good time. First place was taken by *See you at the bottom of the burette* from Newlands College, second place was *Technetium (Tc)* from Tawa College. Third was *Alkynes of Trouble* from Paraparaumu College, who also won the team name, and had one member win a prize for reciting the periodic table furthest from memory (as far as rhodium!). Other spot prizes included adding the elements to a blank periodic table (*Technetium* won that one as well) and drawing the most even and accurate seven-membered ring. Thanks to the student helpers on the night, and the SCPS staff and academics who helped with the organisation.

There was no Branch meeting as such in July because of the visit of UK chemist Dr **Peter Wothers** (Teaching Fellow, Cambridge University) (organised by Dr **Suzanne Boniface** and brought to New Zealand by the *New Zealand Institute of Chemistry for the International Year of Light*) who gave public demonstration lectures on *The chemistry of light* as part of International Programme, as well as public talks on *The secret life of shampoo* here, in Palmerston North and Auckland between July 3 and 14. Peter is a Fellow of St Catharine's College, Cambridge and heavily involved in promoting chemistry to young students and members of the public. He has fronted the lectures at the department for the Cambridge Science Festival for more than 15 years and is known nationally and internationally for his demonstration lectures. In 2012 he presented *The modern alchemist* as the Royal Institution Christmas Lectures. He created the popular Cambridge Chemistry Challenge, an international online competition, and he has authored a number of popular textbooks including *Organic Chemistry* (with Clayden, Greeves and Warren), and *Chemical Structure and Reactivity* (with Keeler). Peter was awarded an MBE for Services to Chemistry in the 2014 Queen's Birthday Honours.

His 'sold out' *Chemistry of light* show provided a remarkable display of

chemistry in action as the history of light was portrayed in words and spectacular chemical reactions accompanied by a very interesting commentary that was especially useful for students of chemistry. They were popular with families with primary school children who were entranced by the colour, flashes and bangs and the older students and adults enjoyed the connections between the chemistry, light and history. Although a lot of work to set up, the event inspired both adults and children alike by illustrating the everyday value of chemistry and the importance of having a better understanding of the world around us. Peter's visit was sponsored by the Institute, Victoria University, Massey University, RSNZ, RSC and the MacDiarmid Institute.

The Branch was also involved in supporting the *Chemistry Education Conference* combined for the first time with the Biology Educators' conference *BioLiveChemEd* at Victoria University over July 5-8. The delegates, about 250 in all, attracted a number of international guests, including three members of the IUPAC Committee on Chemistry Education. The conference opened with Dr Peter Wother's *Chemistry of light show* (see above) who also spoke about the strange history behind the names of the ingredients in everyday substances. Other keynote speakers included: Professor Roy Tasker (University of Western Sydney), who talked about molecular-level visualisation for a deeper understanding of chemistry and cell biology; Mrs. Laura Trout from the US Process Oriented Guided Inquiry Learning (POGIL) project who introduced and modelled the project strategy; and Professor Ian Shaw (Canterbury University) spoke about *Molecules and Mimicry*. Victoria University academics described their research and delegates were given opportunities to visit local science institutions and places in the local community where science is used. The conference also provided opportunities for teachers to showcase and share best practice in teaching and learning in chemistry and biology.

Among the international visitors were ten sponsored (UNESCO, NZAid

and IUPAC) teachers from the South Pacific countries of Samoa, Vanuatu (3), Cook Islands, Tonga (2), Kiribati, Tuvalu and Niue. They arrived in NZ a few days ahead of the conference to observe science classes in some Wellington high schools, and visited places around Wellington that provided useful backgrounds for their teaching. They all attended the POGIL workshop at the conference. Now home, the teachers are sharing their learning with others in their school and wider community. The conference has given them the tools and confidence to make changes to the way they work.

The August meeting, held later in the month than usual, had Professor **Ian Shaw** (Professor of Toxicology and Director of Biochemistry, University of Canterbury) address us on *Molecular mimicry – undercover chemistry in a biological world*. He reminded us that cells are driven and controlled by highly specialised proteins, including receptors and enzymes that have remarkable approaches to ensure that only the right molecules fit into their binding sites because it is these molecules that determine what happens in the cell. If the wrong molecule fools an enzyme or receptor protein the cell could behave in ways that it should not. Such molecules have attributes that interact with enzymes and receptors in a way that initiates the complex chemistry leading to cellular responses – just like the 'real' molecules do. These molecules are the sleuths of the biochemistry world and are having a significant impact on creatures large and small, including humans. He then explored the world of proteins, looked at how molecules bind to them and then unravelled a catalogue of molecules that interact with proteins by mimicking their 'natural' counterparts causing untold, but often esoteric, mayhem.

Victoria University – SCPS

Professor **Thomas Nann** took up his position as Director of the MacDiarmid Institute and Alan MacDiarmid Chair of Chemistry in mid-August. He studied chemistry at the Albert-Ludwig University in Freiburg, Germany and then held several academic positions at universities in Germany, the

UK and Australia. His research on nanomaterials and their applications has always been highly interdisciplinary and focussed on energy conversion/storage and nanomedicine. In recent years, he has become increasingly active in research management and leadership and was Director of the South Australian node of the Australian National Fabrication Facility prior to joining the MacDiarmid Institute.



Professor Thomas Nann

Dr **Suzanne Boniface** has been appointed as Lecturer in Chemistry Education. She joined the School in 2008 as a Senior Teaching Fellow and in this role substantially raised the standard of teaching practice and the quality of educational outcomes for our school.

Dr **Anna L. Garden** (University of Otago) visited and presented her seminar *From fertilisers to fuels – a computational approach to heterogeneous catalysis* in late May last. She explained how heterogeneous catalysis encompasses the class of catalytic reactions in which the phase of the catalyst is different to that of the reactants. Typically the catalyst is a solid while the reactants are either liquids or gases. Such catalysis plays a vital role in e.g. fertiliser production, fuel cells and catalytic converters in automobiles, with some 90% of all reactions in the chemical industry relying on heterogeneous catalysis. Furthermore, heterogeneous catalysis represents the key to unlocking dream reactions to achieve a sustainable future, such as photocatalytic water splitting and

synthetic enzymes. However, given that the catalytic reactions of interest are often complex, multi-step processes and there are a vast number of potential catalysts, finding the optimum one for a given reaction is a daunting task.

Professor **Ivar Reimanis** (Metallurgical and Materials Engineering Department, Colorado School of Mines) also visited in early June. He was hosted by Professor **Ken McKenzie**, his group and other staff members, and gave a seminar that provided *A taste of ceramics research at Colorado School of Mines with a highlight on mechanical behaviour of an unusual ceramic – β -eucryptite (LiAlSiO₄).*

At the end of July Dr **Ivan Leung** (School of Chemical Sciences, University of Auckland) visited, met with staff and students and presented his lecture on *NMR studies of 2-oxoglutarate oxygenases*.

After illustrating that NMR spectroscopy is a well-established technique for the studies of ligand binding to proteins, he outlined some of its broad applications as a probe to investigate biochemical pathways in the development of new enzyme inhibitors and protein ligands design. Such NMR techniques generally fall into two classes: *ligand-based NMR*, in which the behaviour of the ligand (usually a small molecule) itself is monitored, and *protein NMR* in which the resonances of isotopically labelled proteins are detected. For example, ligand-observed techniques have been used extensively for the screening and quantification of ligand binding to protein receptors, whilst protein-observed methods allow the mapping of protein-ligand binding interfaces and the monitoring of protein dynamics at an atomic level. 2-oxoglutarate-dependent (2OG) oxygen-

ases are ubiquitous in plants, microorganisms and animals. In humans, they are involved in a diverse range of important biological roles that include oxygen sensing, fatty acid metabolism and epigenetic regulation. Many 2OG oxygenases are current inhibition targets for treatments of diseases such as cancer, ischemia and anaemia. Ivan reviewed the NMR methods routinely applied to study 2OG oxygenases and highlighted the information that these methods provide in order to help further our understandings from mechanistic and inhibition perspectives.

Recent PhD completions have included: **Thomas Nilsson** (*Scale-up of the synthesis of gold nanoparticles – wool fibre composites*); Professor **Jim Johnston** in late May and **Omar Alsager** (*Development of aptasensors for steroidal hormones*); Dr **Justin Hodgkiss** in mid-July.

Conference Calendar

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.

pacifichem.org

Chemistry, Chemical engineering and Chemical Process (CCECP 2016)

Hotel Fort Canning, Singapore

18-19 January 2016

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 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.

chemistry-conf.org/index.html

Notice of the NZIC Annual General Meeting

The Annual General Meeting of the New Zealand Institute of Chemistry will be held on Wednesday 11 November 2015 at 6pm in the Laby Building, LB118, University of Victoria, Wellington.

Agenda:

1. Apologies
2. Minutes of 2014 AGM held on 16 November 2014 at the University of Waikato
3. Matters arising
5. Announcement of prize winners
4. Financial report including auditor's report
5. Election of Officers. Nominations:

President

1st Vice-President

2nd Vice-President

Treasurer

Honorary General Secretary

Nominations for these positions close with NZIC administration on 31 October 2015

6. Other Business

The simultaneous determination of hydroxyproline and pentosidine in avian skin tissue

Matthew R. Campion

Landcare Research, PO Box 69040, Lincoln (email: campionm@landcareresearch.co.nz)

Keywords: *hydroxyproline, pentosidine, avian age, HPLC*

Introduction

The measurement of age is an important tool for providing insight into wildlife population demographics and management of endangered species. This includes information such as the effect of age on behaviour, susceptibility to disease, onset of sexual maturity, and age specific fecundity.^{1,2} Aging of birds can be difficult in species that exhibit few morphological changes beyond adulthood, with current information on bird aging primarily reliant on the labour intensive technique of banding.^{3,4}

One potentially useful technique is the use of 'advanced glycation end-products' (AGES) as a biomarker of aging. These compounds form through a non-enzymatic process known as the Maillard reaction, with the compound pentosidine specifically investigated in a range of mammalian and avian species.^{5,6} Comprised of an arginine and lysine residue bound by a pentose sugar, pentosidine is a stable, fluorescent and irreversible collagen crosslink.⁷ It is found in many different tissues and organs, e.g. skin, and accumulates throughout the lifetime of the individual, which makes it a potentially useful biomarker for chronological age.⁸

The analysis of pentosidine has been used as a reliable method of aging in a number of bird species. These include domestic poultry,⁹ ruffed grouse,¹⁰ double-crested cormorants,^{10,11} and various species of wild birds.⁶ It is worth noting, however, that this technique may not be useful in all species, as in the case of common gulls reported by Rattiste *et al.*¹²

The method described here involves the preparation of a collagen lysate from a sample of avian skin, followed by simultaneous determination of hydroxyproline and pentosidine (structures shown in Fig. 1) using reverse-phase HPLC analysis with fluorescence detection. In the past, both assays have typically been carried out separately; however, this represents a significant investment of time and consumption of laboratory resources. Hydroxyproline determination has been carried out via colorimetric methods,¹³ with derivatisation and analysis via reverse-phase HPLC being an alternative.¹⁴⁻¹⁷ Analyses of pentosidine have remained largely unchanged since the method first described by Sell and Monnier,⁷ with further refinements being made in the years following.

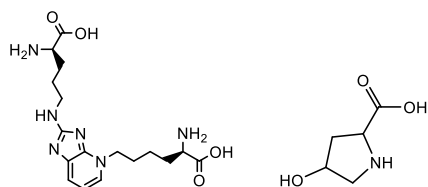


Fig. 1. Structures of pentosidine (left), and hydroxyproline (right)

There were several challenges involved in combining the two assays. These include the disparity in concentration between the two analytes, their reactivity with respect to the derivatising reagent, and their different fluorescent properties. These were overcome by making modifications to the method where necessary, and determining experimentally the most appropriate reaction and HPLC conditions.

Pentosidine concentrations can be measured directly in the sample; however, the determination of hydroxyproline requires a pre-column derivatisation step. Total collagen amount is calculated on the assumption that hydroxyproline represents 14% of total collagen.¹⁸ Results are expressed as the amount of pentosidine as a proportion of the total amount of collagen ($\mu\text{g}/\text{mg}$ or $\text{pmol}/\mu\text{g}$).

A sample of skin or collagen was prepared via a process similar to that described by Sell *et al.*¹⁹ This involved removal of excess muscle and adipose tissue, followed by delipidation in chloroform/methanol. After reconstitution in distilled water the samples were hydrolysed in culture tubes for a period of 18 hours using 6 M HCl at 110 °C. Evaporation of the acid was carried out in a heating block at 120 °C under a stream of air, followed by reconstitution of the sample in distilled water.

An aliquot was taken and further diluted, followed by hydroxyproline derivatisation using 4-chloro-7-nitrobenzofurazan (NBD-Cl) in accordance with the method described by Vázquez-Ortiz *et al.*¹⁶ The reaction was quenched by addition of 1 M HCl, with an aliquot taken and returned to the original lysate. Further reaction of the derivatising reagent with hydroxyproline does not continue on account of the decreased pH (Fig. 2).

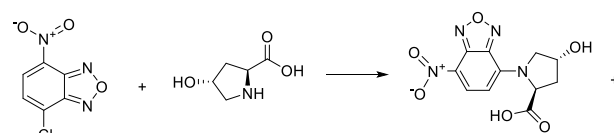


Fig. 2. The reaction of hydroxyproline with NBD-Cl

Analysis of pentosidine and derivatised hydroxyproline in the sample is carried out via reverse-phase HPLC with a C18 5 μm column, using gradient elution with a mobile phase comprised of an ion-pairing reagent, heptafluorobutyric acid (HFBA), in acetonitrile and water.

Materials and methods

For the purposes of setting up and validating the method, collagen from bovine Achilles tendon was purchased from Sigma (St Louis, MO, Item #: C9879) and used as a surrogate for skin tissue. Kakapo (*Strigops habroptilus*) patagium skin biopsy samples from birds of varying, known

age were provided by the New Zealand Department of Conservation. Pentosidine was sourced from Cayman Chemical (Ann Arbor, MI, Item #: 10010254) and stored at -20 °C upon receipt. The derivatising reagent (NBD-Cl) was sourced from Sigma (St Louis, MO, Item #: 25455). To assess the extent and efficiency of collagen hydrolysis, a suitable hydroxyproline-containing tripeptide (H-Gly-Ala-Hyp-OH; Fig. 3) was sourced from Bachem (Bubendorf, Switzerland, Item #: H-3260.0250). All other chemicals were of analytical or HPLC grade.

Apparatus

Collagen hydrolysis was carried out using a Ratek (Victoria, Australia) dry block heater equipped with an air blowdown manifold. HPLC analyses were performed on an Agilent (Santa Clara, CA) 1200 series HPLC consisting of a quaternary pump (G1311A), degasser (G1322A), automatic liquid sampler (G1329A), thermostatted column compartment (G1361A), and fluorescence detector (G1321A). It is important to note that this model of fluorescence detector is capable of switching fluorescence parameters during the course of a chromatographic run, a vital function for the implementation of this method.

Preparation of solutions

Stock solutions (1000 µg/ml) of pentosidine and hydroxyproline were prepared in DMSO and sodium tetraborate buffer, respectively. NBD-Cl was prepared at a concentration of 5 mg/ml in methanol. HFBA mobile phase solutions were separately prepared in both water and acetonitrile, at a concentration of 0.01M. Sodium tetraborate buffer (0.025M) and HCl (1M and 6M) were prepared in accordance with standard laboratory procedure.

Preparation of collagen lysate

Samples of skin were scraped with a scalpel blade (where necessary) to remove excess muscle and adipose tissue, and then finely minced. For further delipidation, 5 ml of 2:1 chloroform/methanol was added and the tubes placed on a horizontal shaker overnight. They were then centrifuged at 3000 rpm for 5 minutes and the supernatant decanted. When using bovine collagen (approx. 20 mg), the first step was omitted, proceeding straight to delipidation.

The samples were reconstituted in 2 ml 1:1 methanol/distilled water and placed on a horizontal shaker for 10 minutes. They were then centrifuged at 3000 rpm for 5 minutes, and the supernatant decanted.

N₂-flushed 6M HCl (5 ml; 1 ml per 10 mg skin/collagen) was added to each tube, which was then securely capped. Tubes were placed in a heating block at 110 °C for 18 hours. After cooling, the lids were carefully removed and the samples blown down at 120 °C under air to facilitate complete evaporation of HCl. Nitrogen blowdown was not used as it caused samples to condense on the blowdown needles.

Samples were then reconstituted in 2 ml distilled water, filtered with a 0.45 µm filter and transferred to amber vials for hydroxyproline derivatisation. If further analysis

was not to be carried out immediately, the samples were stored at -20 °C.

For each assay, duplicate spikes were prepared by addition of 200 µl 1 µg/ml pentosidine to approximately 50 mg of collagen, yielding a concentration of 0.01 µg/mg. Tissue (collagen) and reagent blanks were also run. Duplicate samples were run at a rate of 1 in 10, or as sample numbers allowed. Approximately 5-10 mg of H-Gly-Ala-Hyp-OH tripeptide was used to assess the efficiency of collagen hydrolysis.

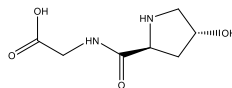


Fig. 3. Structure of H-Gly-Ala-Hyp-OH tripeptide

Hydroxyproline derivatisation

Lysate (50 µl) was diluted to 1 ml in pH 10.2 sodium tetraborate decahydrate buffer. A 250 µl aliquot was added to an amber vial with 200 µl 5 mg/ml NBD-Cl solution. The vials were mixed and placed in a 65 °C (±2 °C) water bath for 30 minutes. Upon removal from the water bath, 50 µl of 1M HCl was added and the vials mixed well, then cooled at -20 °C for 5 minutes.

For HPLC analysis 50 µl of the derivatised sample was added to 450 µl of the original lysate. Samples were stored at -20 °C until ready for HPLC analysis.

Chromatography

HPLC parameters are detailed below:

Column: Alltima C18 5µm (250 mm × 4.6 mm)

Flow rate: 1.2 ml/min

Gradient parameters:	0 min:	5% A; 95% B
	0–5 min:	5% A; 95% B
	5–20 min:	30% A; 70% B
	20–25 min:	50% A; 50% B
	25–27 min:	5% A; 95% B
	27–32 min:	5% A; 95% B

Run time: 32 min

Injection vol: 10 µl

Mobile phase: (A) 0.01M HFBA in acetonitrile; (B) 0.01M HFBA in MQ water.

Detector parameters:

Hydroxyproline Ex: 465 nm Em: 535 nm (0–20 min)

Pentosidine Ex: 325 nm Em: 390 nm (20–32 min)

The retention time for pentosidine is approximately 18.9 minutes and for the hydroxyproline derivative approximately 20.7 minutes.

Method validation

Initial method validation was based upon the same principles as those described by the American Public Health Association.²⁰ This involved the analysis of eight replicates at three concentrations; the highest value likely, 5 × the estimated limit of detection, and a mid-range value.

To ensure the analysis approximated the assay of real samples, collagen from bovine Achilles tendon was used as the spiking matrix. An assay was conducted to establish baseline values for both pentosidine and hydroxyproline, with spiking of collagen replicates weighing ~20 mg carried out thereafter. Average baseline concentrations were then subtracted from the values for the spiked samples to calculate analyte recoveries. Pentosidine is the main analyte of concern with respect to limits of detection, given that hydroxyproline analysis required 400-fold dilution prior to assay. Method validation with respect to the latter is more focussed on ensuring that results are reproducible.

Spikes were carried out using 0.5, 5 and 10 mg of hydroxyproline and 0.04, 4 and 1 µg of pentosidine.

The baseline hydroxyproline content of the bovine collagen was 12.54% w/w, with a standard deviation of 0.47%. This takes into account the moisture content, which was 10.6%. The baseline pentosidine concentration was 0.0021 µg/mg collagen, with a standard deviation of 0.00021 µg/mg. Note that conversion of pentosidine from µg/mg to pmol/mg can be achieved by applying a conversion factor of 2642.5.

The hydroxyproline amount in the sample is given by:

$$\text{Hydroxyproline (mg)} = (P_x \times C_s / P_s) \times 0.4$$

Where:

P_x is the peak area for the sample

C_s is the concentration of the relevant standard in µg/ml

P_s is the peak area of the standard

The factor of 0.4 takes into account the 400-fold dilution factor and the conversion from µg to mg. The amount of collagen in the sample is given by multiplying the amount of hydroxyproline by a factor of 7.14.¹⁸

The pentosidine content of the samples is given by:

$$\text{Pentosidine (µg)} = 1.11 \times P_x \times C_s / P_s$$

Where:

P_x is the peak area of the sample

P_s is the peak area of the standard

C_s is the concentration of the relevant standard in µg/ml

The factor of 1.11 takes into account the addition of 50 µl derivatised hydroxyproline solution prior to assay.

Data for the method validation is given below:

Pentosidine

Concentration (µg/mg):	0.002	0.02	0.05
Bias:	8%	9%	6%
Precision (cv):	13%	2%	3%
Method uncertainty: (95% confidence interval)	19%	2%	4%
Method detection limit:	0.0005 µg/mg		

Hydroxyproline

Spiking amount (mg):	0.5	5	10
Bias:	5%	-2%	-3%
Precision (cv):	10%	2%	3%

Recoveries for both pentosidine and hydroxyproline were approximately 100% at all concentrations. Linearity charts for both analytes are shown in Figs. 4 and 5.

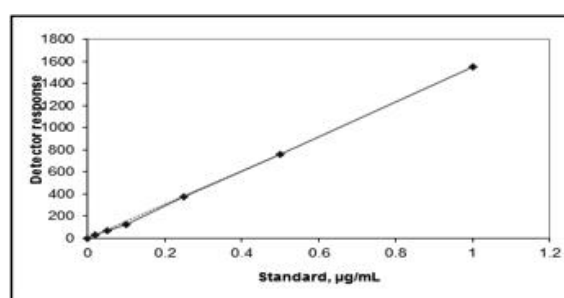


Fig. 4. Pentosidine standard curve, linearity fit ($r^2 = 0.998$). Gain = 10

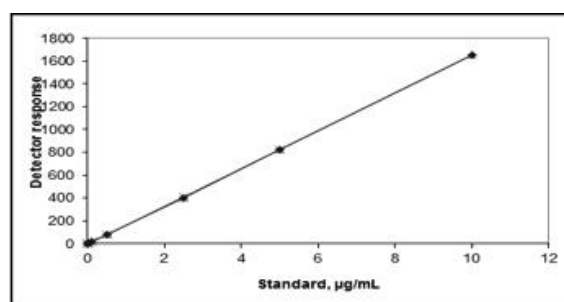


Fig. 5. Hydroxyproline standard curve, linearity fit ($r^2 = 0.999$). Gain = 10

Upon analysing the kakapo skin samples it was discovered that the method lacked sufficient sensitivity, and was unable to adequately detect either hydroxyproline or pentosidine. Despite the weight of these samples being 5–20 mg, they were comprised of only very small amounts of collagen, with this also being reflected in the pentosidine concentration. In order to compensate for this, the gain on the fluorescence detector photomultiplier tube was increased from the default value of 10 to 16. This served to amplify the signal, resulting in a 50-fold increase in sensitivity. Whilst this has the potential to adversely affect the signal to noise ratio the cleanliness of the samples reduced this impact. The increase in sensitivity is shown in the revised linearity charts in Figs. 6 and 7.

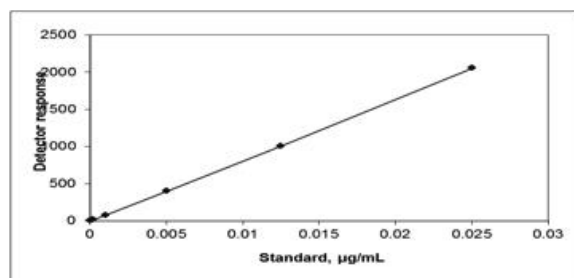


Fig. 6. Pentosidine standard curve, linearity fit ($r^2 = 0.998$). Gain = 16

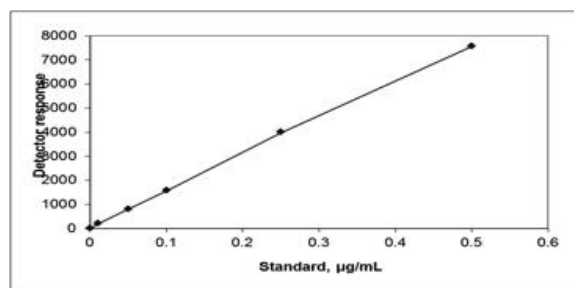


Fig. 7. Hydroxyproline standard curve, linearity fit ($r^2 = 0.998$). Gain = 16

HPLC profiles for bovine collagen, kakapo skin and the hydroxyproline/pentosidine standard are shown in Figs. 8, 9 and 10 respectively.

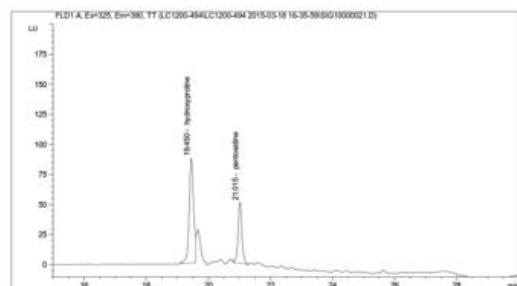


Fig. 8. HPLC profile of 20mg of bovine collagen

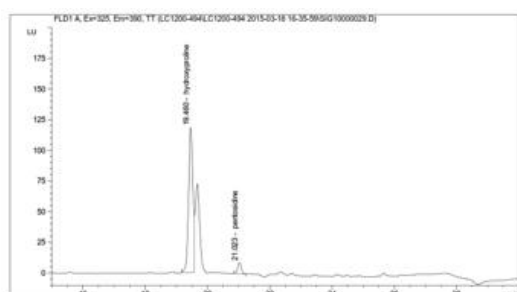


Fig. 9. HPLC profile of kakapo skin sample

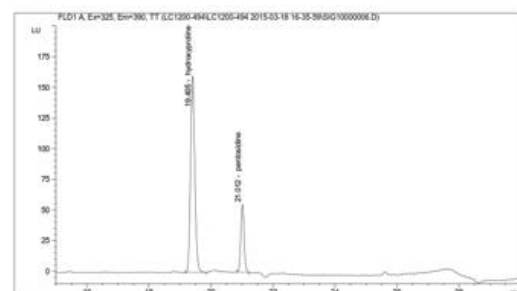


Fig. 10. HPLC profile of 0.1 µg/mL hydroxyproline and 0.005 µg/mL pentosidine standards

In both the collagen and kakapo samples a co-eluting peak was observed adjacent to hydroxyproline. The identity of this component was unknown, but is likely to be an additional derivatised amino acid. Despite modifications to the mobile phase gradient, baseline resolution of these peaks proved difficult. The lowest point between the two was selected and the peaks split to allow for integration.

To determine the efficiency of the collagen hydrolysis, a small quantity (4-5 mg) of the tripeptide H-Gly-Ala-Hyp-OH was assayed. Assuming complete hydrolysis (Fig. 11), this yields 1 M of hydroxyproline per 1 M of tripeptide. When prepared and assayed using the described method, duplicate samples returned an average of 92% of the nominal value.

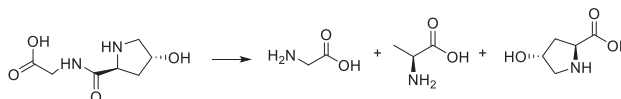


Figure 11: Hydrolysis of H-Gly-Ala-Hyp-OH tripeptide

Given that the initial pentosidine method validation was performed using significantly higher concentrations of collagen (approx. 20 mg) than that found in the kakapo skin samples, it would be beneficial to revalidate the method to reflect this. Using 2 mg of collagen as a starting point, the lowest pentosidine spike of 0.002 µg/mg would then correspond to 0.004 µg as opposed to 0.04 µg. It is also likely that using a spiking matrix containing moderate amounts of both analytes has contributed to measurement uncertainty, hence the loss of precision at the lowest spike value.

Results and discussion

The method described here eliminates the need for two separate assays in determining the amount of pentosidine versus total collagen. It uses the analysis of pentosidine as previously described with the addition of a pre-column derivatisation step for hydroxyproline. The disparity in concentrations between the two analytes is overcome via considerable dilution of an aliquot of the lysate prior to derivatisation. This requires estimating the likely amount of collagen in the sample; this estimation is acceptable as the detector response to the hydroxyproline is linear over a wide range.

The hydroxyproline derivative and pentosidine have different fluorescent properties; however, it is possible to analyse both at their respective maxima by utilising the fluorescence switching capabilities of the Agilent fluorescence detector.

The derivatising reagent, NBD-Cl, is able to react with both analytes, as demonstrated by the disappearance of the peak upon derivatising a 0.05 µg/ml solution of pentosidine under the specified experimental conditions. The addition of 50 µl of 1 M HCl to the derivatised collagen quenches the derivatisation reaction and inhibits any further reaction upon its addition to the original lysate. This is despite an excess of NBD-Cl remaining in the sample. The pH values of the injected samples were 1-2;

therefore, any reaction with NBD-Cl was significantly inhibited, as basic conditions are required for the reaction to proceed. If any further derivatisation was to occur, the observed hydroxyproline concentration would be higher, and the pentosidine concentration lower. Given that the spike recoveries for both analytes were close to 100%, it is reasonable to conclude that this does not occur. Samples of the lysate only were also run, without the addition of derivatised hydroxyproline. These gave similar peak area values to those containing the hydroxyproline derivative, further indicating that continued reactivity is not a concern.

The fundamentals of the hydroxyproline assay were the same as those described by Vasquez *et al.*,¹⁶ with the exception of some chromatographic parameters (mobile phase, elution gradient). These did not adversely affect hydroxyproline analysis.

Further improvements to this method could be made. These include the use of UHPLC in conjunction with a column of smaller particle size (<5 µm) and greater specificity. This would reduce the time taken for chromatographic analysis. Collagen hydrolysis as described by Tsugita *et al.*²¹ may also introduce a significant time saving. By using a combination of trifluoroacetic and hydrochloric acids at high temperatures they reduced the time taken for hydrolysis to 30 minutes, compared to 18-24 hours using the conventional method. Obtaining the fluorescence spectra of the derivatised pentosidine may also be useful if it exhibits increased fluorescence, potentially allowing increased sensitivity.

Overall, this method allows for the simultaneous analysis of hydroxyproline and pentosidine, the two compounds associated with the estimation of avian age.

Acknowledgements

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opment of this method (Authorisation number: 39183-DOA).

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The analysis of polyphenolic compounds in selected turmeric, green tea and fruit products as a measure of potency and authenticity

Darren A. Saunders,^{1*} Shirley Jones,¹ Sophia Baumann,² Ellen Ashmore¹

¹The Institute of Environmental Science & Research (ESR) Ltd, 27 Creyke Road, Ilam, Christchurch,

²Otto-von-Taube Gymnasium, Gauting, Germany (email: Darren.Saunders@esr.cri.nz)

Keywords: polyphenols, turmeric, green tea, anthrocyanidin, anthrocyanin

Biography

Darren Saunders obtained his undergraduate degree in chemistry from Canterbury University and an MSc in pharmacology from Otago University. Prior to working at ESR, he spent 10 years as the scientific officer for the clinical pharmacology department at the Christchurch School of Medicine, primarily involved in developing methods for the analysis of drugs and endogenous compounds in clinical samples. Since 1998 he has worked in the ESR Christchurch Science Centre's food chemistry laboratory as laboratory manager and, currently, as technical manager performing chemical food analyses and conducting research on behalf of the NZ Food Safety Authority (now the Ministry of Primary Industries) and other clients. His work encompasses basic nutritional assays, food forensics and analytical method development, especially for analyses rarely performed by other laboratories and frequently involving the active ingredients of natural products.

Introduction

Over the last two years our laboratory has experienced increasing interest in the analysis of natural products whether produced locally or imported. Examples include assaying locally grown ginseng for its active ingredients, and determining whether imported grapefruit seed extract was indeed what it was purported to be and of the claimed potency. More recently turmeric supplements have been marketed heavily for their beneficial active components. The research conducted studied natural products, many of which are polyphenolic in nature, specifically turmeric curcuminoids and green tea catechins. Anthrocyanidin profiles of fruit-containing products were also studied as a measure of their authenticity, i.e. whether they actually contain the fruit the ingredient list states and to determine the effect of processing, e.g. canning, fermentation, etc, on these profiles.

Polyphenols

Polyphenols are compounds ubiquitous in plants located throughout most plant tissues with key roles in pigmentation, reproduction and growth together with

resistance to pathogens and predators due to their potent astringency. More than 8000 different polyphenolic compounds have been identified in various plant species (see Figs 1 and 2 for polyphenol subclasses and their generic structures). Plant polyphenols are important components of the human diet having anti-oxidant activity and free radical-scavenging abilities. Some polyphenolic compounds also exhibit antibiotic, anti-inflammatory, anti-ulcer and anti-diarrheal activity, as well as conferring protection against cancer, diabetes and cardiovascular and neurodegenerative disease (see Table 1 for important plant sources of polyphenols). As molecules, polyphenols are products of secondary metabolism and can vary from simple phenolic compounds to highly polymerised molecules such as tannins. Polyphenols exist primarily in a conjugated form with one or more sugar residues (most frequently glucose) linked to one or more hydroxyl groups. The most common and important low molecular weight compounds are simple phenolic derivatives and flavonoids, the latter constituting the bulk of naturally occurring dietary polyphenols.^{1,2}

Table 1. Polyphenolic categories, polyphenols and important sources¹⁻³

Polyphenol class	Polyphenols (examples)	Important sources
Phenolic acids	Gallic, caffeic, chlorogenic, ferulic, sinapic acids	Blueberry, kiwifruit, cherry, plum, coffee
Stilbenes	Resveratrol	grapes
Lignans	Secoisolariciresinol	linseed
Flavonoids		
Flavonols	Quercetin, kaempferol, myricetin	Tomato, broccoli, blueberry
Flavanones	Hesperidine, naringenin	Orange, grapefruit, lemon
Flavans	Catechin, epicatechin	Chocolate, black and green teas, red wine
Flavones	Apigenin, luteolin	Capsicum, celery
Anthrocyanins/ anthrocyanidins	Cyaniding, pelargonidin, peonidin, delphinidin, malvidin	Blueberry, blackcurrant, blackberry, cherry, black grape, rhubarb, aubergine, strawberry
Isoflavones	Daidzein, genistein, glycitein	Soy beans, miso, tofu,

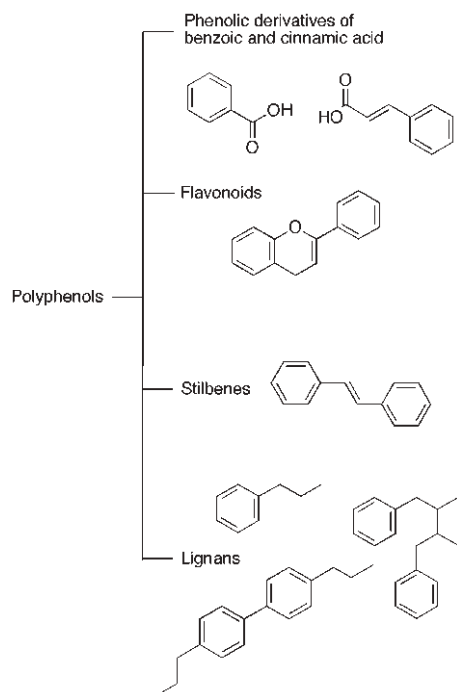


Fig. 1. Main core of various polyphenol subclasses

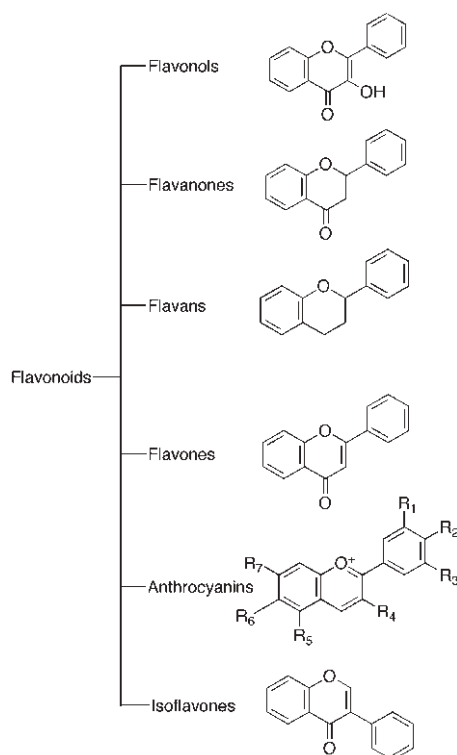


Fig. 2. Cores of flavonoid subclasses

Turmeric

Introduction

Turmeric (*Curcuma longa*) is a rhizomatous herbaceous perennial plant of the ginger family, native to Southwest India. The rhizomes, if not used fresh are boiled, oven dried and ground to a powder for subsequent use as a dye or as a spice and colouring agent in cuisine. Turmeric is also used in Ayurvedic medicine to aid digestion and liver function, relieve arthritis and has been directly applied to the skin for eczema and wound healing.⁴ The primary bioactive component and the compound that

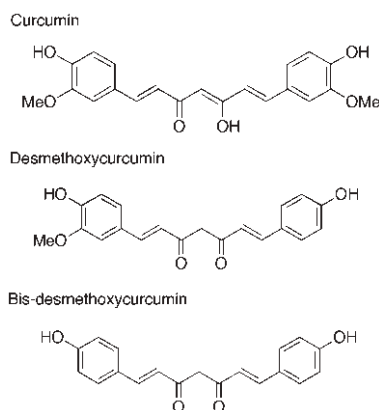


Fig. 3. Curcuminoids

imparts turmeric's bright yellow colour is curcumin, along with lesser amounts of desmethoxycurcumin and bis-desmethoxycurcumin (polyphenolic curcuminoids, see Fig. 3 for molecular structures).⁵ Curcumin has been found to suppress the initiation, promotion and metastasis of a wide variety of tumour cells as well as being a potent anti-oxidant and anti-inflammatory agent.⁶

Experimental

A variety of turmeric products were purchased from local supermarkets and health food shops in Christchurch, New Zealand, including four different brands of turmeric spice (seven samples in total) and four different varieties of turmeric extract in lozenge or capsule form of various claimed potencies. The total curcumin, desmethoxycurcumin and bis-desmethoxycurcumin content of these samples were determined by HPLC.

Method - sample extraction

Approximately 0.1 g of turmeric powder or homogenised supplement was accurately weighed into a 50 ml disposable centrifuge tube and extracted with 20 ml of 70% v/v ethanol in water at 80 °C for 30 minutes with frequent shaking. Extracts were subsequently diluted by 1/10th with methanol.⁷

HPLC

Column: 220 x 4.6 mm i.d. Applied Biosystems 5 µm RP-18 with a 15 x 3.2 mm i.d. Applied Biosystems 7 µm RP-18 guard column; mobile phases "A" 20% CH₃CN, 80% 0.01M H₃PO₄ pH 5.0 and "B" 80% CH₃CN, 20% 0.01 M H₃PO₄ pH 5.0; flow rate 1.5 ml/min; gradient 0 to 20 min 100% "A" to 100% "B", 20 to 21 min 100% "B" to 100% "A" end at 30 min. Detection: UV-VIS @ 428 nm. Injection volume: 20 µl.

Results

Results for turmeric are presented in Table 2.

Discussion

Several studies have shown that soil factors, including nutrients and acidity as well as genetics may affect the content of curcumin in turmeric plants. Consequently the curcumin content is reported to vary from one batch of turmeric powder to another. Tayyem *et al.* 2006 found an the curcumin content in commercially available turmeric averaged 1.51% (w/w) (n=9) with the lowest at 0.58%

Table 2. Content of curcuminoids and curcumin in turmeric spice and supplements purchased locally

Producer	Total curcuminoids* mean % (w/w)	Total curcumin % (w/w)
Spices		
#1	2.69	1.49
#2	2.46	1.54
#3	2.43	1.38
#4	1.41	0.90
Supplements		
	Total curcuminoids* (mg)/tablet or capsule	Label claim curcumi- noids* (mg)/tablet or capsule
#1	430	600
#2	80	100
#3	112	Not stated
#4	114	120

*Curcuminoids = curcumin, desmethoxycurcumin and bis-desmethoxycurcumin

(w/w) and the highest 3.14% (w/w).⁸ Our results (Table 2) were consistent with these findings. To put these figures in more familiar terms, one teaspoon (5 ml) of turmeric powder was found to weigh approximately 2.6 g. The average curcuminoid content of the four commercially available spices examined was 2.2% (w/w) which equates to 57 mg of curcuminoids per teaspoon of spice powder. Hence each capsule in the supplements above contain the equivalent as curcuminoids of approximately 2 teaspoons of turmeric powder, while supplement #1 contained the equivalent as curcuminoids of 10-11 teaspoons of turmeric per tablet.

Green tea

The water extract of the dry leaves of the plant *Camellia sinensis*, an evergreen shrub of the Theaceae family, commonly known as tea, is the most consumed beverage in the world next to water. The world's total amount of tea produced is approximately 78% black, 20% green and < 2% oolong tea.

Green, black and oolong tea undergo different manufacturing processes. To produce green tea, freshly harvested leaves are quickly steamed or fried to inactivate enzymes, preventing fermentation and producing a dry, stable product. Epicatechin polyphenols are the main compounds in green tea accounting for its characteristic colour and flavour. To produce black and oolong teas, fresh leaves are allowed to dry to approximately 55% (w/w) moisture concentrating the leaf polyphenols. The leaves are then rolled and crushed initiating fermentation of polyphenols to produce theaflavins and thearubigins. Oolong tea is considered to be approximately half as fermented as black tea.⁹⁻¹²

Approximately 2% of the materials formed by photosynthesis in plants are transformed into flavonoids whose role is to protect the plant from ultraviolet light and bacteria. The flavonoid chalcone is first formed and then transformed into various flavonoids including catechin, epicatechin, etc.¹⁰ Green tea is characterised by a high flavonoid content with catechins accounting for 20-30%

of dry weight which impart a bitter taste and astringency to green tea infusions. The major catechins are: epicatechin (EC), epigallocatechin gallate (EGCG), epigallocatechin (EGC), epicatechin gallate (ECG), catechin (C), galocatechin (GC) and galocatechin gallate (GCG). EGCG is regarded as the most important tea catechin because of its abundance (~40% of total catechin in tea, see Fig. 4 for structures).^{10,13}

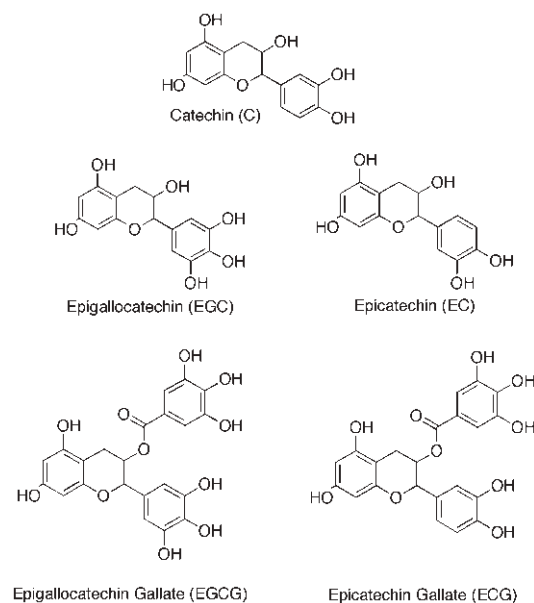


Fig. 4. Green tea catechins investigated in this study

The health benefits of green tea have been known for centuries. Modern studies have demonstrated anti-inflammatory, anti-proliferative, anti-atherosclerotic activity as well as the ability to reduce cholesterol and enhance weight loss. These health benefits have led to the inclusion of green tea extracts in supplements, nutraceuticals and functional foods.⁹⁻¹³

The amount of catechin in green tea varies according to cultivar, climate and cultivation practices. Kodama *et al.* 2010 found the total phenolic content as catechin equivalents in 1 cup of different green teas varied from 90 to 341 mg.¹⁰ The catechin content in green tea extracts depends on the methodologies employed during extraction, concentration and preservation. Quality control of these extracts involves the determination of the total catechin content as well as that of the individual isomers.¹⁴

Experimental

All tea samples were prepared as per product instructions; generally teabags were steeped in 220 ml of boiling water for 2-3 minutes and the solution tested directly for catechins. Diet preparations were dissolved in water. Green tea extracts or supplements were ground and approximately 1 g accurately weighed and extracted three times into separate 40 ml aliquots of 80% methanol/20%, 3% v/v HCl. The extracts were combined prior to analysis.

HPLC

Column: 220 x 4.6 mm i.d. Applied Biosystems 5 μ m RP-18 with a 15 x 3.2 mm i.d. Applied Biosystems 7 μ m RP-18 guard column; mobile phases "A" 5% CH₃CN, 95% 0.3% v/v formic acid and "B" 90% CH₃CN, 10%, 0.3% v/v formic

acid; flow rate 1.5 ml/min; gradient 0 to 5 min 100% "A", 5 to 20 mins 0% to 25% "B", 20 to 25 mins 25% to 100% "B", 25 to 30 min 100% "B" to 100% "A" end at 40 min. Detection: UV-VIS @ 270 nm. Injection volume: 50 μ l.^{13,14}

Results

Results for green tea are presented in Table 3.

Discussion

Kodama *et al.* 2010 found infusions prepared from tea bags had varying contents of total catechins ranging from 96 to 201 mg/200 ml.¹⁰ Engelhardt *et al.* 2000 gives a range for total catechins in green tea of between 8.5 and 20.6 % (w/w).¹⁵ Comparison of the results in Table 3 with these literature values should be done with caution as many of the tea bag products examined also contained other herbaceous material such as dried fruit or fruit leaves. Brewing conditions also influence the final antioxidant capacity of green tea as consumed, with approximately 84% of the total antioxidant activity solubilised within 5 minutes of brewing.¹⁰ The presence of other herbaceous material and the different brewing times recommended may explain in part why our results appear lower than those found by some other investigators. With regards to the supplements and diet products, product #1 conformed within experimental variation to the label claim of 20% (w/w) catechins. Each sachet of product #2 claimed to contain the equivalent of 5 g of dry green tea leaf, the total catechin in the sachets examined amounted to an average of 36 mg which is low even when the lowest concentration of 8.5% catechins in dried tea is used (this equates to 425 mg of catechin in 5 g of dried tea).¹⁵ The total catechin content of product #3 was not explicitly stated on the label. The ingredients list states *inter alia* "Green Tea Extract (90% Polyphenols), Acai...". Catechins are a subset of polyphenols hence although we found the product contained an average of 2.69% (w/w) total green tea catechins, the labelling cannot be said to be inaccurate as acai berries are known to have a high polyphenolic content. Regardless, the individual sachets in both diet products contained similar amounts of green tea catechins as found in a single tea bag.

Subsequent to these investigations, our laboratory successfully adapted the method above to the detection of catechins in wine that are responsible in part for its astringency, bitterness and mouthfeel as well as reacting with anthocyanins to modify wine colour.

Fruit anthocyanidins and authenticity

The word 'anthocyanin' is derived from the Greek word *anthos* (flower) and *kyanos* (blue). Anthocyanins are responsible for the red, orange, blue and purple colours of most fruits, flowers, herbs, grains and vegetables.

Anthocyanins are the mono- and di-glycosylated forms of anthocyanidins with the most common carbohydrates on anthocyanins being glucose, galactose, rhamnose and arabinose. The six most commonly occurring anthocyanidins are pelargonidin, cyanidin, delphinidin, peonidin, petunidin and malvidin (see Fig. 5 and Table 4 for chemical structures).

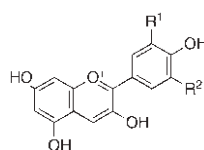


Fig. 5. Anthocyanidin basic structure

Table 4. Commonly occurring anthocyanidins

Anthocyanidin	R1	R2
Pelargonidin	-H	-H
Cyanidin	-OH	-H
Delphinidin	-OH	-OH
Peonidin	-OMe	-H
Petunidin	-OMe	-OH
Malvidin	-OMe	-OMe

Anthocyanins not only impart colour to many plants, they also act as biological control agents, optical filters protecting molecules from visible light and are excellent scavengers of free radicals especially those of oxygen. The latter activity of anthocyanins with regards to health benefits has been extensively studied. Anthocyanins have been shown to improve visual acuity, protect from heart at-

Table 3. Weight of individual and total catechins extracted from green tea bags, supplements and sachets prepared as per product instructions (results are means of n=3 individual tea bags or supplements)

Green Tea Teabags	ECG (mg)	C (mg)	EC (mg)	EGCG (mg)	EGC (mg)	Total catechins (mg)	Catechin % (w/w)
#1 Organic green tea 85 g	35	2	10	53	14	116	6.7
#2 Green tea 30 g	20	2	6	34	11	76	6.3
#3 Green tea 34 g	23	1	8	30	8	72	4.1
#4 Green tea 36 g	27	3	10	60	20	122	7.8
#5 Green tea 43 g	18	2	5	21	9	56	2.9
Green tea supplement/ diet products							
#1 (tablet)	27	7	14	116	22	186	18.5
#2 (sachet)	12	2	3	18	<1	36	1.19
#3 (sachet)	15	2	8	55	<1	81	2.69

ECG = epigallocatechin, C = catechin, EC = epicatechin, EGCG = epigallocatechin gallate, EGC = epicatechin gallate

tacks (especially in the form of grape juice and red wine) and aid in the prevention of diabetes and obesity.¹⁶⁻²⁰

Unlike the turmeric and green tea analyses described above in which we aimed to quantitate the active polyphenolic components primarily for determination of potency, we investigated anthocyanidins as markers of authenticity. Because of their health benefits, fruit juices and extracts especially from fruit high in anthocyanins, for example pomegranate, blueberry, blackcurrant, are valuable commodities and as such are at risk of adulteration with less expensive but similarly coloured fruit juices and extracts. Pomegranate has been found to be diluted with red grape juice.²¹⁻²³

The anthocyanin content and composition of fruit shows significant variations among cultivars of the same species. Since the analysis of anthocyanins poses analytical difficulties due to the sheer number of anthocyanins and expense of primary standards, we decided to investigate the anthocyanidin profile of various fruit juices (Table 5) and other products by removing the sugar molecules from the anthocyanins by acid hydrolysis, reducing them to their anthocyanidin "parent" molecules. The distribution of the most important anthocyanidins in common fruits can serve as a marker of authenticity.²⁰ In addition to determining the anthocyanidin profile of genuine fruit samples and comparing this to the anthocyanidin profiles of fruit juices purportedly from the same source to check the veracity of the label claim, we also aimed to ascertain if the anthocyanidin profile of a given fruit was conserved in different matrices after various forms of processing e.g. juicing, preserving (jam), canning (canned

fruit) and fermentation (alcoholic beverages) in order to determine if the profile could be employed as an authenticity marker in these products.

Experimental

Genuine raw fruit samples were homogenised and approximately 5 g extracted into 20 ml of 3% v/v conc. HCl in methanol. Fruit juice, jams, canned fruit etc. were homogenised, dissolved in water where necessary and 5 ml of solution extracted into a suitably prepared C18, 300 mg Solid Phase Extraction (SPE) column. Sugars were washed off the column with 5 ml of water and the retained anthocyanins eluted with 1ml of methanol 0.1% v/v HCl. Extracts of raw fruit (5 ml) and methanol SPE eluents of fruit products were then treated with 1.5 ml of conc. HCl and placed in a water bath at 90°C for 20 mins. This had the effect of removing the sugar units from the anthocyanins converting them to their basic anthocyanidin form. The anthocyanidin profiles for the different fruit products were then determined by HPLC and the results for individual anthocyanidins expressed as % of total chromatographic anthocyanidin peak area.

HPLC

Column: 220 x 4.6 mm i.d. Applied Biosystems 5 µm RP-18 with a 15 x 3.2 mm i.d. Applied Biosystems 7 µm RP-18 guard column; mobile phases "A" 10% formic acid, 10% CH₃CN and "B" 10% formic acid, 50% CH₃CN; flow rate 1.5 ml/min; gradient 0 to 20 mins, 0 to 100% "B", 20 to 25 mins 100% "B", 25 to 30 mins 100% to 0% "B" end 40 mins. Detection: UV-VIS @ 520 nm. Injection volume: 20 µl.^{17,24}

Table 5. Anthocyanidin profiles of common fruits, adapted from Goulas *et al.* 2012. "+" = present²⁰

Fruits	Cyanidin	Delphinidin	Petunidin	Pelargonidin	Peonidin	Malvidin
Blackberry	+	+	+	+	+	+
Blueberry	+	+	+		+	+
Cheery, sweet	+			+	+	
Cranberry	+	+	+	+	+	+
Currant, black	+	+	+	+	+	
Grape, red	+	+	+		+	+
Plum	+				+	
Pomegranate	+	+		+		
Raspberry	+			+	+	
Strawberry	+		+	+		

Table 6. Anthocyanidin profiles of various fruits and fruit products as % total peak area of individual anthocyanidins in anthocyanidin chromatographic profiles

Sample No/matrix	Label claim	Dp	Cy	Pt	Pn	Pg	Ma
Pomegranate							
#1 juice	Pomegranate 100%	31.2	64.2	0.0	2.4	2.2	0.0
#2 juice	Pomegranate 100%	35.1	59.6	0.0	3.2	2.1	0.0
#3 juice	Pomegranate 100%	36.9	58.3	0.0	2.9	2.0	0.0
#5 sauce	Pomegranate 100%	31.9	51.4	4.0	4.4	2.7	5.7
Pomegranate mixtures							
#4 juice	Pomegranate 6%, aronia berry 5%	2.2	71.8	9.9	6.2	6.1	3.9
#21 juice	pomegranate 85%, blueberry 15%, cranberry 12%	38.1	55.7	4.0	2.2	0.0	0.0

Sample No/matrix	Label claim	Dp	Cy	Pt	Pn	Pg	Ma
#22 juice	Pomegranate 10%, raspberry 3%	5.5	67.1	2.7	1.0	22.9	0.9
#64 tea	Pomegranate, acai	56.9	43.1	0.0	0.0	0.0	0.0
#65 tea	Pomegranate 4%, grape 2%	54.3	38.4	6.5	0.0	0.2	0.6
Cranberry	raw	0.4	52.9	2.0	0.0	43.9	0.9
#6 juice	Cranberry 12%	0.4	51.7	12.1	0.0	30.1	6.0
#8 juice	Cranberry 18%	5.7	51.3	4.2	2.0	26.5	10.4
#10 juice	Cranberry 18%	3.3	50.6	3.8	1.5	35.7	5.2
#16 juice	Cranberry 18%	4.9	51.8	4.8	0.9	32.4	5.4
#56 cider		2.3	45.2	16.0	1.3	32.2	3.1
Cranberry mixtures							
#11 juice	Cranberry 2%, black carrot	3.3	50.6	3.8	1.5	35.7	5.2
#67 tea	Cranberry 1%, blackcurrant 1%, Goji 1%, acai 1%	62.2	32.1	5.0	0.0	0.6	0.0
#68 tea	Cranberry, elderberry	57.4	36.0	6.1	0.0	0.5	0.0
Blackcurrant	raw	42.6	56.3	0.1	0.5	0.6	0.0
#13 juice	Blackcurrant 5.7%	47.3	46.9	3.4	0.6	1.0	1.0
#15 juice	Blackcurrant 10%	36.1	58.4	5.7	0.0	0.0	0.0
#19 syrup	Blackcurrant 30%	54.2	45.2	0.0	0.2	0.4	0.0
#23 juice	Blackcurrant 2.6%	58.5	39.6	0.0	0.0	1.8	0.0
#25 syrup	Blackcurrant 50%	54.0	45.4	0.0	0.2	0.4	0.0
#33 juice	Blackcurrant 5%	52.0	47.7	0.0	0.2	0.1	0.0
#40 juice	Blackcurrant 10%	53.6	42.7	2.8	0.2	0.6	0.0
#43 juice	Blackcurrant 5%	42.7	48.6	5.0	0.0	3.7	0.0
Blackcurrant mixtures							
#18 syrup	Blackcurrant 31%, raspberry 17%	50.3	49.1	0.0	0.2	0.3	0.0
#26 syrup	Blackcurrant 29%, boysenberry 13%	44.1	52.1	0.0	3.4	0.5	0.0
Raspberry	raw	0.0	92.5	2.8	2.3	2.5	0.0
#48 tinned	Raspberries 54%	0.0	96.6	0.0	3.4	0.0	0.0
#57 cider		0.0	89.6	4.0	0.0	6.5	0.0
Blueberry	raw	20.2	8.3	20.7	0.3	2.6	48.0
#46 tinned	Blueberries 55%	27.2	10.6	21.0	0.0	1.8	39.4
#71 tea	NZ blueberry powder 2%, blue- berry powder 0.5%	49.5	50.5	0.0	0.0	0.0	0.0
#72 tea/syrup	Blueberry 50% from concentrate	0.0	48.4	0.0	0.0	0.0	51.6
Blueberry mixtures							
#70 tea	Blueberry 0.2%, strawberry 0.2%, raspberry 0.2%, blackberry 0.2%	64.8	30.3	4.6	0.0	0.3	0.0
Strawberry	raw	0.0	9.0	0.1	84.6	6.4	0.0
#61 tinned		0.0	18.5	8.1	64.0	9.4	0.0
Strawberry mixtures							
#12 juice	Strawberry 5%, kiwifruit 5%	0.0	91.8	5.5	0.0	2.7	0.0
#39 smoothie	Strawberry 26%, boysenberry 10%, blackberry 2%	0.0	81.1	0.0	18.5	0.5	0.0
Boysenberry	raw	0.0	92.8	1.7	1.5	4.1	0.0
#47 tinned	Boysenberry 62%	0.7	91.1	8.2	0.0	0.0	0.0
#49 tinned	Boysenberry 66%	0.0	99.2	0.0	0.3	0.5	0.0
#53 cider		0.5	95.6	3.1	0.7	0.0	0.0

Sample No/matrix	Label claim	Dp	Cy	Pt	Pn	Pg	Ma
Boysenberry mixtures							
#38 juice	Boysenberry 6%, blueberry 2%	0.0	98.5	0.0	0.4	1.1	0.0
#41 smoothie	Boysenberry 10%, strawberry 10%, blackberry 5%, blueberry 3%, raspberry 2%	0.7	91.1	8.2	0.0	0.0	0.0
Plum	raw	1.4	96.4	0.4	1.1	0.6	0.3
#44 tinned	Plums 58%	0.0	94.3	5.4	0.0	0.3	0.0
#45 tinned	Plums 58%	0.0	93.5	5.7	0.4	0.4	0.0
Plum mixtures							
#62 cider	Plum, blackberry	24.2	45.1	30.8	0.0	0.0	0.0

Dp = Delphinidin, Cy = Cyanidin, Pt = Petunidin, Pn = Peonidin, Pg = Pelargonidin, Ma = Malvidin

Results

Results for fruit anthocyanidins are presented in Table 6.

Discussion

Broadly speaking, the anthocyanidin profiles given in Table 6 are consistent with literature findings of anthocyanidin presence-absence summaries in Table 5. However, the latter gives no information about the relative abundance of each anthocyanidin in any given fruit species while the former approach allows discerning between fruits such as pomegranate and blackcurrant that contain high levels of the same anthocyanidins (delphinidin and cyanidin) but different ratios of each. While the anthocyanidin profiles of most single fruit products including juices, teas, fruit ciders and syrups were remarkably consistent between products and when compared to genuine fruit samples either frozen, fresh or tinned, the anthocyanidin profile of blueberry products stood out as being more variable than that of the other fruits examined. Blueberries have one of the highest concentrations of polyphenols compared to other fruits, contain a variety of anthocyanidins and are a high value commodity. While raw and tinned blueberries (sample #46) gave similar profiles to one another, products #71 and #72 have profiles that differ greatly from the unambiguous raw and tinned samples for which the identity of the fruit was not in question. The complete absence of malvinidin from sample #71 (and mixed products #38, #41, #70) is of interest as blueberries have this anthocyanidin in great abundance compared with all other fruits. Conversely while #72 has high levels of malvinidin and cyanidin found in abundance in the raw and tinned blueberry samples, the delphinidin which was also expected on the basis of raw fruit findings was almost completely absent. The differences between raw and tinned blueberry profiles and that of the tea products could be due to processing, although the other fruit varieties examined did not display such a degree of variability based upon processing or lack of it. While the number of blueberry samples examined was small, the variability of their anthocyanidin profiles compared with the other fruit products examined justifies further investigation of blueberry products to determine if the profile variability is the result of processing or something more nefarious.

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RACI National Congress

R Janadari Kariyawasam

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140
(email: rasika.karivawasam@pg.canterbury.ac.nz)

I was extremely lucky to participate in the RACI national congress held in Adelaide, Australia, in December 2014. It was an amazing experience to meet so many chemists and to learn about their research experiences. As a chemist, it was good to be surrounded by people who appreciate and understand my research.

The Congress ran from 7-12 December at the Adelaide Convention Centre. Each day started with a plenary lecture from a renowned scientist, who presented recent fascinating research achievements. They talked about their greatest discoveries as well as their research journey.

I was grateful that I was able to participate actively in the congress and communicate my PhD research project with the attending scientists and researchers in the same field, as well as to represent the University of Canterbury. My research project is in the field of photoactivated cytotoxins. I presented my research at the synthetic chemistry and chemistry in health poster session.

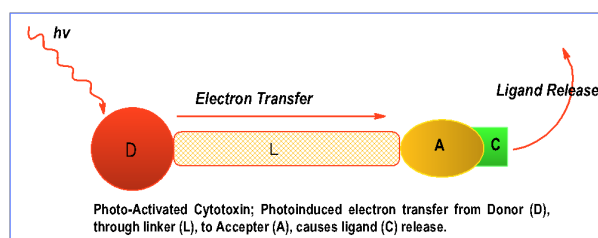
It was also a pleasure to be chosen as one of the top six students to participate in and contest the Stranks award presentation series. The contestants for this award were selected by poster abstracts submitted prior to the conference. The Don Stranks Awards commemorate Don Stranks' substantial contribution to inorganic chemistry in Australia, and particularly his nurture and encouragement of students. Don Stranks Awards are open to student members of RACI and affiliated societies, and recognise outstanding performance in research within a current PhD candidature. The awards are made at national conferences of the Inorganic Chemistry Division.

During my presentation I talked about my achievements during my PhD research. The feedback and questions definitely helped to re-evaluate my research and direct it onwards.

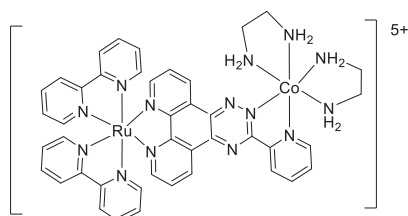
The poster session was very relaxed and enjoyable. It was surprising how scientists got interested in my research, and answering their questions was very enjoyable; I also got to explain the research achievements and future goals. The senior scientists with similar research backgrounds brought up valuable ideas and held great discussions.

Photoactivated cytotoxins are new class of anticancer compounds. Here, we use light energy to trigger release of the cytotoxic nitrogen mustard compounds, in order to achieve selective cytotoxic activity. This will help to minimise the side effects.

Model studies for this type of complex were studied previously in the Hartshorn research group by Alan Downward.¹



Graphical representation of photo-induced ligand release



Ru(II)-Co(III) heterodinuclear model system

He synthesised the heterodinuclear complex shown below, and demonstrated that photo induced ligand release can be achieved in these systems.

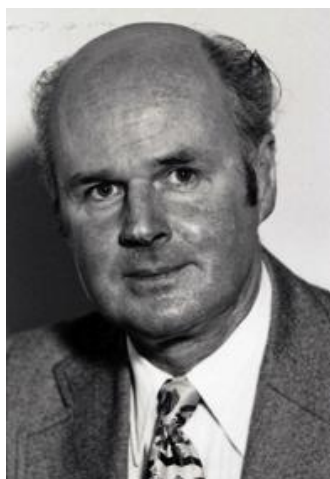
In my research, a major challenge is the synthesis of a nitrogen mustard ligand on an inert cobalt(III) metal centre.² So far in the literature, the complexation of a nitrogen mustard involves the free handling of the nitrogen mustard ligand.^{3,4,b} In our research we are looking at a safer synthetic approach.

I have synthesised and characterised cobalt(III) complexes containing nitrogen mustard ligands containing either one or two chloroethyl arms as potential alkylating agents. These cobalt(III) complexes will be used to synthesise heterodinuclear metal complexes before we examine whether they exhibit photoactivated cytotoxicity.

I am thankful toward my supervisor, Prof. Richard Hartshorn for his guidance, as well as the financial support I received from the NZIC travel grant and Evans Fund to attend the conference.

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Wilfred E. (Bunt) Dasent (1926-2015)



Bunt Dasent and right: Lecturing in Easterfield 006 (modified from VUW 2-145 with permission)

Wilfred Effingham Dasent never used his given names preferring the nickname 'Bunt' given him by his elder sister. He was born in Wellington and lived in the same house in Nottingham Street, Karori, until he and his wife Barbara moved into a retirement home. Bunt attended Karori School and then Wellington College, which he enjoyed. After three years he entered employment with the firm of Accountants Watkins, Hull, Wheeler and Johnson, but after three years decided that life must offer more than endlessly adding up columns of pounds, shillings and pence. With the help of a small legacy from an aunt he changed the direction of his life, enrolling for a BSc at Victoria University College. His first foray into the world of chemistry led to a fail in the course. However, he persevered, passed the following year, and continued to complete a BSc, majoring in the subject. This was followed by study for an MSc. For his research project Bunt studied reaction kinetics with Professor P.W. Robertson as supervisor and one of his last students. Bunt completed the examinations and submitted his thesis in 1949 (*Halogen addition to acetylenic compounds*), and was duly awarded First Class Honours in Chemistry. This work was included in the publication *Kinetics of halogen addition. XVII. Acetylenic compounds* (Robertson, Dasent, and Olive, *J. Chem. Soc.* 1950, 1628), and is typical of Robertson's work, requiring only pipettes, burettes and a thermostatted water bath. Bunt graduated in the same year as Nobel Prize winning Alan Macdiarmid. In 1951, Bunt was appointed Junior Lecturer in Chemistry under Stanley Slater as Professor and Head of Department. Undergraduate classes were of similar size to now, so teaching loads were high. Bunt was promoted to Lecturer (1954) and Senior Lecturer (1966). He was an extremely competent lecturer and in later years many former students have described him as the best teacher of their university years.

At that time inorganic chemistry was taught largely as 'preps and props', a more or less systematic study of the chemistry of the elements. Bunt was fascinated not simply by the regularities, but particularly by the irregularities in these properties, and attempted to rationalise

these by considering factors such as bond energies, lattice energies, etc., and published these ideas in *J. Chem. Educ.* (1963, 40, 130). Over 1964-1965, Bunt took sabbatical leave at Florida State University in Tallahassee, where he fleshed out his ideas into a book, *Nonexistent Compounds* [*Compounds of Low Stability* (Marcel Dekker, 1965). It was during the disturbing years of interracial tensions, yet Bunt was able to appropriately consider why some apparently rational compounds had then not been observed, e.g. why is there no silicon equivalent of ethylene, why the oxyacids of fluorine are unknown and why the inert gases form no compounds? Some of his examples remain unknown, while ways of making others, such as the xenon compounds, have been found. These ideas were extended into a widely acclaimed more general text *Inorganic Energetics* (Cambridge University Press, 1970).

Bunt's life changed in 1964 with a part-time appointment as Assistant to the Vice Chancellor, making use of his accountancy skills to straighten out the university's finances, which were in something of a tangle. This progressed into his appointment as part-time Bursar, but he was so frustrated with working in the university administration that he returned to chemistry as Reader in 1972. After reorganisation of the administration, Bunt was persuaded to accept appointment as Registrar in 1973 and as Pro-Vice-Chancellor in 1978.

The success of *Inorganic Energetics* led the Cambridge Press to persuade him to update it for a second edition. Bunt was dubious, thinking that his move to administration had removed him from developments in chemistry, but he was persuaded by the offer of a Fellowship at a Cambridge College and the second edition, rewritten and updated, was published in 1982. Bunt formally retired at 60 years of age in 1986.

Bunt was a scholar rather than a researcher, had few students and wrote few research papers, a problem when promotions became largely tied to publications. Study leave at York University in 1973 led to an interest in us-

ing infrared spectroscopy to characterise inorganic compounds, which resulted in several publications. In 1999, the University recognised his major contributions to VUW by conferring on him the Award for Distinguished Service.

Bunt married Barbara in 1950. They had daughter Helen, who died in 1990 and son Peter, who has a successful career in music based in Sydney. Bunt was a classical intellectual with wide ranging interests. He enjoyed music,

regularly attended concerts and had an extensive collection of classical and jazz music on vinyl. He was interested in art and had some talent as a water-colourist. He fancied himself as a gourmet cook and was interested in wines.

Bunt became a Member of the Institute in 1951 and a Fellow in 1971.

Brian Halton & Neil Curtis, with thanks to Peter Dasent

IUPAC and nomenclature: brief guides and 2D (QR) InChI barcodes

Richard Hartshorn

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140
(email: richard.hartshorn@canterbury.ac.nz)



The International Union of Pure and Applied Chemistry (IUPAC, <http://iupac.org/>) is **the** organisation, worldwide, that is most closely identified with nomenclature, and I have been working on nomenclature projects with IUPAC for some 15 years now. The key publications that pull together the IUPAC nomenclature recommendations are the “colour” books. The “Blue Book” (*Nomenclature of Organic Chemistry – IUPAC Recommendations and Preferred Names 2013*, H. A. Favre, W. H. Powell (Eds.), Royal Society of Chemistry, Cambridge, U.K., ISBN 978-0-85404-182-4) covers the nomenclature of organic chemistry, while the “Red Book” (*Nomenclature of Inorganic Chemistry – IUPAC Recommendations 2005*, N. G. Connelly, T. Damhus, R. M. Hartshorn, A. T. Hutton (Eds.), Royal Society of Chemistry, Cambridge, U.K., ISBN 0-85404-438-8) deals with inorganic nomenclature, and the “Purple Book” (*Compendium of Polymer Terminology and Nomenclature – IUPAC Recommendations 2008*, R. G. Jones, J. Kahovec, R. Stepto, E. S. Wilks, M. Hess, T. Kitayama, W. V. Metanomski (Eds.), Royal Society of Chemistry, Cambridge, U.K., ISBN 978-0-85404-491-7) with polymer nomenclature.

These books are not small documents – the “Blue Book” runs to over 1500 pages, which perhaps gives a sense of the complexities and subtleties that may arise. Inorganic chemists may think they have it easy, by comparison, as the “Red Book” contains only 350 or so pages. Of course that neglects the fact that organic nomenclature is often also required to name inorganic compounds!

Fortunately, however, the basics of nomenclature are nowhere near as complicated, and it is possible to condense them into a much shorter document. I am involved with a project that seeks to do this for each of inorganic and organic nomenclature. The final four-page document covering inorganic nomenclature is included with this article,

and the equivalent organic document is in preparation. It is intended that these brief guides can be republished in other journals and included in textbooks and other such publications, thereby achieving consistent presentation and wide dissemination of the fundamentals of chemical nomenclature. This is the first such republication of the original version that appeared in the August 2015 issue of Pure and Applied Chemistry.

Recently I have worked with a task group setting up a project to investigate and consult on possibilities for a QR code (2D barcode) version of the International Chemical Identifier (InChI). The InChI is a text string that encodes chemical structure and provides a means to search databases for the structure. IUPAC and the InChI Trust (<http://www.inchi-trust.org/>) are examining development of a QR code version of the InChI. We are consulting with industry/regulatory/academic sector users to identify and prioritise additional information that could/should be included in the QR code at a series of workshops.

The additional information will enhance the value and commercial utility of the QR InChI and perhaps provide a mechanism to improve aspects of health and safety and inventory control. Possible additions to the QR code InChI to be evaluated and elaborated upon include: health/safety information (UN GHS and/or safety data URL); catalog code; batch number; inventory information; sample composition/purity. This project is complementary to another user-focused project that is developing the InChI for states and mixtures. More information on this project can be found at: [http://www.iupac.org/nc/home/projects/project-db/project-details.html?tx_wfqbe_pi1\[project_nr\]=2015-019-2-800](http://www.iupac.org/nc/home/projects/project-db/project-details.html?tx_wfqbe_pi1[project_nr]=2015-019-2-800), and feedback, in case you would like to comment on the possibilities for the QR code InChI can be sent to me at: richard.hartshorn@canterbury.ac.nz.



Brief Guide to the Nomenclature of Inorganic Chemistry

R. M. Hartshorn (New Zealand),* K.-H. Hellwich (Germany), A. Yerin (Russia), T. Damhus (Denmark), A. T. Hutton (South Africa). *E-mail: inorganic.nomenclature@iupac.org, Sponsoring body: [IUPAC Division of Chemical Nomenclature and Structure Representation](http://www.iupac.org/publications/pac/).

PREAMBLE

The universal adoption of an agreed chemical nomenclature is a key tool for communication in the chemical sciences, for computer-based searching in databases, and for regulatory purposes, such as those associated with health and safety or commercial activity. [The International Union of Pure and Applied Chemistry \(IUPAC\)](http://www.iupac.org/) provides recommendations on the nature and use of chemical nomenclature.¹ The basics of this nomenclature are shown here, and in companion documents on the nomenclature systems for [organic chemistry](http://www.iupac.org/)² and [polymers](http://www.iupac.org/),³ with hyperlinks to the original documents. An overall summary of chemical nomenclature can be found in [Principles of Chemical Nomenclature](http://www.iupac.org/).⁴ Greater detail can be found in the [Nomenclature of Inorganic Chemistry](http://www.iupac.org/), colloquially known as the Red Book,⁵ and in the related publications for [organic compounds](http://www.iupac.org/) (the Blue Book)⁶ and [polymers](http://www.iupac.org/) (the Purple Book).⁷ It should be noted that many compounds may have non-systematic or semi-systematic names (some of which are not accepted by IUPAC for several reasons, for example because they are ambiguous) and IUPAC rules allow for more than one systematic name in many cases. IUPAC is working towards identification of single names which are to be preferred for regulatory purposes ([Preferred IUPAC Names](http://www.iupac.org/), or PINs). *Note:* In this document, the symbol ‘=’ is used to split names that happen to be too long for the column format, unless there is a convenient hyphen already present in the name.

The boundaries between ‘organic’ and ‘inorganic’ compounds are blurred. The nomenclature types described in this document are applicable to compounds, molecules and ions that do not contain carbon, but also to many structures that do contain carbon (Section 2), notably those containing elements of Groups 1 – 12. Most boron-containing compounds are treated using a special nomenclature.⁸

1 STOICHIOMETRIC OR COMPOSITIONAL NAMES

A **stoichiometric** or **compositional** name provides information only on the composition of an ion, molecule, or compound, and may be related to either the empirical or molecular formula for that entity. It does not provide any structural information.

For **homoatomic entities**, where only one element is present, the name is formed (Table 1) by combining the element name with the appropriate **multiplicative prefix** (Table 2). Ions are named by adding charge numbers in parentheses, e.g. (1+), (3+), (2–), and for (most) homoatomic anion names ‘ide’ is added in place of the ‘en’, ‘ese’, ‘ic’, ‘ine’, ‘ium’, ‘ogen’, ‘on’, ‘orus’, ‘um’, ‘ur’, ‘y’ or ‘ygen’ endings of element names.⁹ Exceptions include Zn and Group 18 elements ending in ‘on’, where the ‘ide’ ending is added to the element names. For some elements (e.g. Fe, Ag, Au) a Latin stem is used before the ‘ide’ ending (cf. Section 2.3).⁹ Certain ions may have acceptable traditional names (used without charge numbers).

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¹ Freely available at: (a) <http://www.iupac.org/publications/pac/>;

(b) <http://www.chem.qmul.ac.uk/iupac/>.

² K.-H. Hellwich, R. M. Hartshorn, A. Yerin, T. Damhus, A. T. Hutton, Brief Guide to the Nomenclature of Organic Chemistry, *Pure Appl. Chem.*, in preparation.

³ R. C. Hiorns, R. J. Boucher, R. Duhlev, K.-H. Hellwich, P. Hodge, A. D. Jenkins, R. G. Jones, J. Kahovec, G. Moad, C. K. Ober, D. W. Smith, R. F. T. Stepto, J.-P. Vairon, J. Vohlidal, *Pure Appl. Chem.* 84(10), 2167–2169 (2012).

⁴ *Principles of Chemical Nomenclature – A Guide to IUPAC Recommendations, 2011 Edition*, G. J. Leigh (Ed.), Royal Society of Chemistry, Cambridge, U.K., ISBN 978-1-84973-007-5.

⁵ *Nomenclature of Inorganic Chemistry – IUPAC Recommendations 2005*, N. G. Connelly, T. Damhus, R. M. Hartshorn, A. T. Hutton (Eds.), Royal Society of Chemistry, Cambridge, U.K., ISBN 0-85404-438-8.

⁶ *Nomenclature of Organic Chemistry – IUPAC Recommendations and Preferred Names 2013*, H. A. Favre, W. H. Powell (Eds.), Royal Society of Chemistry, Cambridge, U.K., ISBN 978-0-85404-182-4.

⁷ *Compendium of Polymer Terminology and Nomenclature – IUPAC Recommendations 2008*, R. G. Jones, J. Kahovec, R. Stepto, E. S. Wilks, M. Hess, T. Kitayama, W. V. Metanowski (Eds.), Royal Society of Chemistry, Cambridge, U.K., ISBN 978-0-85404-491-7.

Table 1: Examples of homoatomic entities

Formula	Name	Formula	Name
O ₂	dioxygen	Cl [–]	chloride(1–) or chloride
S ₈	octasulfur	I ₃ [–]	triiodide(1–)
Na ⁺	sodium(1+)	O ₂ ^{2–}	dioxide(2–) or peroxide
Fe ³⁺	iron(3+)	N ₃ [–]	trinitride(1–) or azide

Table 2: Multiplicative prefixes for simple and complicated entities

No.	Simple	Complicated	No.	Simple	Complicated
2	di	bis	8	octa	octakis
3	tri	tris	9	nona	nonakis
4	tetra	tetrakis	10	deca	decakis
5	penta	pentakis	11	undeca	undecakis
6	hexa	hexakis	12	dodeca	dodecakis
7	hepta	heptakis	20	icosa	icosakis

Binary compounds (those containing atoms of two elements) are named stoichiometrically by combining the element names and treating, by convention, the element reached first when following the arrow in the element sequence (Figure 1) as if it were an anion. Thus the name of this formally ‘electronegative’ element is given an ‘ide’ ending and is placed after the name of the formally ‘electropositive’ element followed by a space (Table 3).

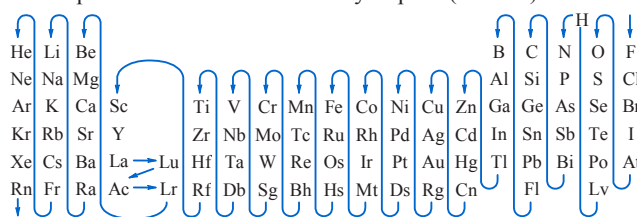


Figure 1: Element sequence

Table 3: Examples of binary compounds

Formula	Name	Formula	Name
GaAs	gallium arsenide	FeCl ₂	iron dichloride or iron(II) chloride
CO ₂	carbon dioxide	FeCl ₃	iron trichloride or iron(III) chloride
CaF ₂	calcium difluoride or calcium fluoride	H ₂ O ₂	dihydrogen dioxide or hydrogen peroxide

Again, multiplicative prefixes (Table 2) are applied as needed, and certain acceptable alternative names¹⁰ may be used. Stoichiometry may be implied in some cases by the use of oxidation numbers, but is often omitted for common cases, such as in calcium fluoride.

Heteropolyatomic entities in general can be named similarly using compositional nomenclature, but often either substitutive¹¹ or additive nomenclature (Section 2) is used. In the latter case information is also provided about the way atoms are connected. For example, POCl₃ (or PCl₃O, compositional name phosphorus trichloride oxide) is given an additive name in Table 10.

Certain ions have traditional short names, which are commonly used and are still acceptable (e.g., ammonium, NH₄⁺; hydroxide, OH[–]; nitrite, NO₂[–]; phosphate, PO₄^{3–}; diphosphate, P₂O₇^{4–}).

Inorganic compounds in general can be combinations of cations, anions and neutral entities. By convention, the name of a compound is made up of the names of its component entities: cations before anions and neutral components last (see examples in Table 4).

The number of each entity present has to be specified in order to reflect the composition of the compound. For this purpose

Table 4: Use of multiplicative prefixes in compositional names

Formula	Name
Ca ₃ (PO ₄) ₂	tricalcium bis(phosphate)
Ca ₂ P ₂ O ₇	dicalcium diphosphate
BaO ₂	barium(2+) dioxide(2–) or barium peroxide
MgSO ₄ ·7H ₂ O	magnesium sulfate heptahydrate
CdSO ₄ ·6NH ₃	cadmium sulfate—ammonia (1/6)
AlK(SO ₄) ₂ ·12H ₂ O	aluminium potassium bis(sulfate)—water (1/12) or aluminium potassium bis(sulfate) dodecahydrate
Al ₂ (SO ₄) ₃ ·K ₂ SO ₄ ·24H ₂ O	dialuminium tris(sulfate)—dipotassium sulfate—water (1/1/24)

⁸ Reference 4, Chapter 10.

⁹ Reference 5, Table IX.

¹⁰ Reference 4, Table P10.

¹¹ Reference 5, Chapter IR-6.



multiplicative prefixes (Table 2) are added to the name of each entity. The prefixes are ‘di’, ‘tri’, ‘tetra’, *etc.*, for use with names for simple entities, or ‘bis()’, ‘tris()’, ‘tetrakis()’, *etc.*, for names for most entities which themselves contain multiplicative prefixes or locants. Care must also be taken in situations when use of a simple multiplicative prefix may be misinterpreted, *e.g.*, tris(iodide) must be used for 3I^- rather than triiodide (which is used for I_3^-), and bis(phosphate) rather than diphosphate (which is used for $\text{P}_2\text{O}_7^{4-}$). Examples are shown in Table 4. There is no elision of vowels (*e.g.*, tetraqua, pentaoxide), except in the special case of monoxide.

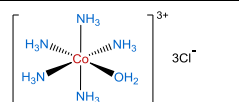
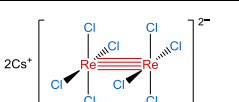
Names of neutral components are separated by ‘em’ dashes without spaces. Inorganic compounds may themselves be components in (formal) **addition compounds** (last four examples in Table 4). The ratios of component compounds can be indicated, in general, using a stoichiometric descriptor in parentheses after the name (see the last three examples in Table 4). In the special case of hydrates, multiplicative prefixes can be used with the term ‘hydrate’.

2 COMPLEXES AND ADDITIVE NOMENCLATURE

2.1 Overall approach

Additive nomenclature was developed in order to describe the structures of coordination entities, or complexes, but this method is readily extended to other molecular entities as well. Mononuclear complexes are considered to consist of a central atom, often a metal ion, which is bonded to surrounding small molecules or ions, which are referred to as ligands. The names of complexes are constructed (Table 5) by adding the names of the ligands *before* those of the central atoms, using appropriate multiplicative prefixes. Formulae are constructed by adding the symbols or abbreviations of the ligands *after* the symbols of the central atoms (Section 2.7).

Table 5: Producing names for complexes: simple ligands

Structure to be named		
Central atom(s)	cobalt(III)	2 × rhenium
Identify and name ligands	ammonia → ammine water → aqua	chloride → chlorido
Assemble name	pentaammineaqua= cobalt(III) chloride	caesium bis(tetrachlorido= rhenate)(Re—Re)(2-)

2.2 Central atom(s) and ligands

The first step is to identify the central atom(s) and thereby also the ligands. By convention, the electrons involved in bonding between the central atom and a ligand are usually treated as belonging to the ligand (and this will determine how it is named).

Each ligand is named as a separate entity, using appropriate nomenclature⁴ – usually substitutive nomenclature for organic ligands^{2,4,6} and additive nomenclature for inorganic ligands. A small number of common molecules and ions are given **special names** when present in complexes. For example, a water ligand is represented in the full name by the term ‘aqua’. An ammonia ligand is represented by ‘ammine’, while carbon monoxide bound to the central atom through the carbon atom is represented by the term ‘carbonyl’ and nitrogen monoxide bound through nitrogen is represented by ‘nitrosyl’. Names of **anionic ligands** that end in ‘ide’, ‘ate’, or ‘ite’ are modified within the full additive name for the complex to end in ‘ido’, ‘ato’, or ‘ito’, respectively. Note that the ‘ido’ ending is now used for halide and oxide ligands as well. By convention, a single coordinated hydrogen atom is always considered anionic and it is represented in the name by the term ‘hydrido’, whereas coordinated dihydrogen is usually treated as a neutral two-electron donor entity.

2.3 Assembling additive names

Once the ligands have been named, the name can be assembled. This is done by listing the ligand names in alphabetical order before the name of the central atom(s), *without* regard to ligand charge.

If there is more than one ligand of a particular kind bound to a central atom in the same way, the number of such identical ligands is indicated using the appropriate multiplicative prefix for simple or complicated ligands (Table 2), not changing the already established alphabetical order of ligands. The nesting order of enclosing marks,

for use in names where more than one set of enclosing marks is required, is: (), [()], {[()]}, {(())}, *etc.*

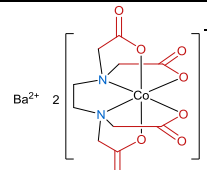
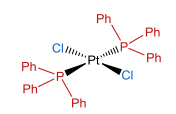
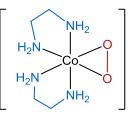
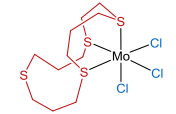
Any **metal-metal bonds** are indicated by placing the central atom symbols in parentheses, in italics and connected by an ‘em’ dash, after the name of the complex (without spaces). The **charge number** of the complex or the **oxidation number** of the central atom is appended to the name of the complex. For **anions** that are named additively, the name of the central atom is given the ‘ate’ ending in a similar way to the ‘ide’ endings of homoatomic anions (Section 1). In some cases, by tradition, the Latin stem is used for the ‘ate’ names, such as in ferrate (for iron), cuprate (for copper), argentate (for silver), stannate (for tin), aurate (for gold), and plumbate (for lead).¹² Finally, the rules of compositional nomenclature (Section 1) are used to combine the additive names of ionic or neutral coordination entities with the names of any other entities that are part of the compound.

2.4 Specifying connectivity

Some ligands can bind to a central atom through different atoms under different circumstances. Specifying just which ligating (coordinating) atoms are bound in any given complex can be achieved by adding **κ-terms** to the name of the ligand. The κ-term comprises the Greek letter κ followed by the italicised element symbol of the ligating atom. For more complicated ligands the κ-term is often placed within the ligand name following the group to which the κ-term refers. Multiple identical links to a central atom can be indicated by addition of the appropriate numeral as a superscript between the κ and element symbols (see Table 6). These possibilities are discussed in more detail in the Red Book.¹³ If the ligating atoms of a ligand are contiguous (*i.e.*, directly bonded to one another), then an **η-term** is used instead, for example, for many organometallic compounds (Section 2.6) and the peroxido complex in Table 6.

A κ-term is required for ligands where more than one coordination mode is possible. Typical cases are thiocyanate, which can be bound through either the sulfur atom (thiocyanato-κS) or the nitrogen atom (thiocyanato-κN), and nitrite, which can be bound through either the nitrogen atom (M–NO₂, nitrito-κN), or an oxygen atom (M–ONO, nitrito-κO). The names pentaammine(nitrito-κN)cobalt(2+) and pentaammine(nitrito-κO)cobalt(2+) are used for

Table 6: Producing names for complexes: complicated ligands

Structure to be named		
Central atom	cobalt(III) → cobaltate(III)	platinum(II)
Identify and name ligands	2,2',2'',2'''-(ethane-1,2-diyl=dinitrilo)tetraacetate → 2,2',2'',2'''-(ethane-1,2-diyl=dinitrilo)tetraacetato	chloride → chlorido triphenylphosphane
Specify ligating atoms	2,2',2'',2'''-(ethane-1,2-diyl=dinitrilo-κ ² N)tetraacetato-κ ⁴ O	<i>not required for chloride</i> triphenylphosphane-κ ^P
Assemble name	barium [2,2',2'',2'''-(ethane-1,2-diyl)dinitrilo-κ ² N]tetraacetato-κ ⁴ O]cobaltate(III)	dichloridobis(triphenyl=phosphane-κ^P)platinum(II)
Structure to be named		
Central atom	cobalt(III)	molybdenum(III)
Identify and name ligands	ethane-1,2-diamine peroxide → peroxido	chloride → chlorido 1,4,8,12-tetrathiacyclopentadecane
Specify ligating atoms	ethane-1,2-diamine-κ ² N η ² -peroxido	<i>not required for chloride</i> 1,4,8,12-tetrathiacyclopentadecane-κ ³ S ¹ ,S ⁴ ,S ⁸
Assemble name	bis(ethane-1,2-diamine-κ²N)= (η²-peroxido)cobalt(III)	trichlorido(1,4,8,12-tetrathiacyclopentadecane-κ³S¹,S⁴,S⁸)molybdenum(III)

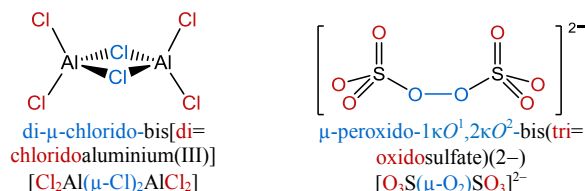
¹² Reference 5, Table X.

¹³ Reference 5, Section IR-9.2.4.

each of the isomeric nitrito complex cations. More examples of constructing names using κ -terms to specify the connectivity of ligands are shown in Table 6. A κ -term may also be used to indicate to which central atom a ligand is bound if there is more than one central atom (Section 2.5).

2.5 Bridging ligands

Bridging ligands are those bound to more than one central atom. They are differentiated in names by the addition of the prefix ‘ μ ’ (Greek mu), with the prefix and the name of the bridging ligand being separated from each other, and from the rest of the name, by hyphens. This is sufficient if the ligand is monoatomic, but if the ligand is more complicated it may be necessary to specify which ligating atom of the ligand is attached to which central atom. This is certainly the case if the ligating atoms are of different kinds, and κ -terms can be used for this purpose.



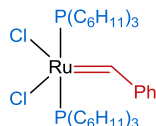
2.6 Organometallic compounds

Organometallic compounds contain at least one bond between a metal atom and a carbon atom. They are named as coordination compounds, using the additive nomenclature system (see above).

The name for an organic ligand **binding through one carbon atom** may be derived either by treating the ligand as an anion or as a neutral substituent group. The compound [Ti(CH₂CH₂CH₃)Cl₃] is thus named as **trichlorido(propan-1-ido)titanium** or as **trichlorido(propyl)titanium**. Similarly, ‘methanido’ or ‘methyl’ may be used for the ligand –CH₃.

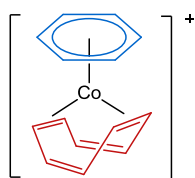
When an organic ligand forms **two or three metal-carbon single bonds** (to one or more metal centres), the ligand may be treated as a di- or tri-anion, with the endings ‘diido’ or ‘triido’ being used, with no removal of the terminal ‘e’ of the name of the parent hydrocarbon. Again, names derived by regarding such ligands as substituent groups and using the suffixes ‘diyl’ and ‘triyl’ are still commonly encountered. Thus, the bidentate ligand –CH₂CH₂CH₂– would be named propane-1,3-diido (or propane-1,3-diyl) when chelating a metal centre, and μ -propane-1,3-diido (or μ -propane-1,3-diyl) when bridging two metal atoms.

Organometallic compounds containing a **metal-carbon multiple bond** are given substituent prefix names derived from the parent hydrides which end with the suffix ‘ylidene’ for a metal-carbon double bond and with ‘ylidyne’ for a triple bond. These suffixes either replace the ending ‘ane’ of the parent hydride, or, more generally, are added to the name of the parent hydride with insertion of a locant and elision of the terminal ‘e’, if present. Thus, the entity CH₃CH₂CH= as a ligand is named propylidene and (CH₃)₂C= is called propan-2-ylidene. The ‘diido’/‘triido’ approach, outlined above, can also be used in this situation. The terms ‘carbene’ and ‘carbyne’ are not used in systematic nomenclature.

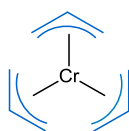


dichlorido(phenylmethylidene)bis(tricyclohexylphosphane- κ P)ruthenium,
dichlorido(phenylmethanediido)bis(tricyclohexylphosphane- κ P)ruthenium,
or (benzylidene)dichloridobis(tricyclohexylphosphane- κ P)ruthenium

The special nature of the bonding to metals of unsaturated hydrocarbons in a ‘side-on’ fashion *via* their π -electrons requires



(η^6 -benzene)[(1,2,5,6- η)-cycloocta-1,3,5,7-tetraene]cobalt(1+)

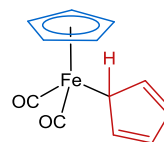


tris(η^3 -prop-2-en-1-ido)chromium,
tris(η^3 -prop-2-en-1-yl)chromium,
or tris(η^3 -allyl)chromium

the **eta (η) convention**. In this ‘hapto’ nomenclature, the number of *contiguous* atoms in the ligand coordinated to the metal (the hapticity of the ligand) is indicated by a right superscript on the eta symbol, e.g., η^3 (‘eta three’ or ‘trihapto’). The η -term is added as a prefix to the ligand name, or to that portion of the ligand name most appropriate to indicate the connectivity, with locants if necessary.

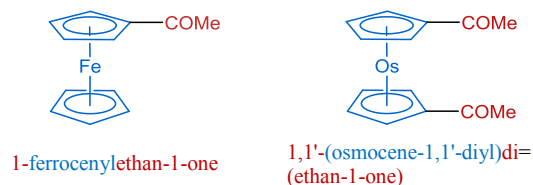
A list of many **π -bonding unsaturated ligands**, neutral and anionic, can be found in the Red Book.¹⁴

Note that the ubiquitous ligand η^5 -C₅H₅, strictly η^5 -cyclopenta-2,4-dien-1-ido, is also acceptably named η^5 -cyclopentadienido or η^5 -cyclopentadienyl. When cyclopenta-2,4-dien-1-ido coordinates through one carbon atom *via* a σ bond, a κ -term is added for explicit indication of that bonding. The symbol η^1 should not be used, as the eta convention applies only to the bonding of contiguous atoms in a ligand.



dicarbonyl(η^5 -cyclopentadienido)(cyclopenta-2,4-dien-1-ido- κ C¹)iron
or dicarbonyl(η^3 -cyclopentadienyl)(cyclopenta-2,4-dien-1-yl- κ C¹)iron

Discrete molecules containing two *parallel* η^5 -cyclopentadienido ligands in a ‘sandwich’ structure around a transition metal, as in bis(η^5 -cyclopentadienido)iron, [Fe(η^5 -C₅H₅)₂], are generically called **metallocenes** and may be given ‘ocene’ names, in this case ferrocene. These ‘ocene’ names may be used in the same way as parent hydride names are used in substitutive nomenclature, with substituent group names taking the forms ‘oceny’l’, ‘ocenediyl’l’, ‘ocenetriyl’l’ (with insertion of appropriate locants).



By convention, ‘organoelement’ compounds of the **main group elements** are named by substitutive nomenclature if derived from the elements of Groups 13–16, but by additive nomenclature if derived from the elements of Groups 1 and 2. In some cases compositional nomenclature is used if less structural information is to be conveyed. More detail is provided in the Red Book.¹⁵

2.7 Formulae of coordination compounds

Line formulae for coordination entities are constructed within square brackets to specify the composition of the entity. The overall process is shown in Table 7. The symbol for the central atom is

Table 7: Producing line formulae for complexes

Structure		
Central atom(s)	Co	2 × Re
Ligands	NH ₃ , OH ₂	Cl
Assemble formula	[Co(NH ₃) ₅ (OH ₂)]Cl ₃	Cs ₂ [Cl ₄ ReReCl ₄]
Structure		
Central atom(s)	Co	Pt
Abbreviate ligands	2,2',2'',2'''-(ethane-1,2-diyl)dinitrilotetraacetate → edta	Cl triphenylphosphane → PPh ₃
Assemble formula	Ba[Co(edta)] ₂	[PtCl ₂ (PPh ₃) ₂]

¹⁴ Reference 5, Table IR-10.4.

¹⁵ Reference 5, Section IR-10.3.

placed first and is then followed by the symbols or abbreviations for the ligands (in alphabetical order according to the way they are presented in the formula). Where possible the coordinating (ligating) atom should be placed nearer the central atom in order to provide more information about the structure of the complex. If possible, bridging ligands should be placed between central atom symbols for this same reason (see examples in Section 2.5). Generally ligand formulae and abbreviations are placed within enclosing marks (unless the ligand contains only one atom), remembering that square brackets are reserved to define the coordination sphere. Multiple ligands are indicated by a right subscript following the enclosing marks or ligand symbol.

2.8 Inorganic oxoacids and related compounds

Inorganic oxoacids, and the anions formed by removing the acidic hydrons (H^+) from them, have traditional names, many of which are well-known and can be found in many textbooks: sulfuric acid, sulfate; nitric acid, nitrate; nitrous acid, nitrite; phosphoric acid, phosphate; arsenic acid, arsenate; arsenous acid, arsenite; silicic acid, silicate; *etc.* These names are retained in IUPAC nomenclature, firstly because they almost invariably are the names used in practice, and secondly because they play a special role in organic nomenclature when names are needed for organic derivatives. However, all the oxoacids themselves and their derivatives may be viewed as coordination entities and named systematically using additive nomenclature (Table 8).¹⁶

Table 8: Examples of inorganic oxoacids and derivatives

Formula	Traditional or organic name	Additive name
H_2SO_4 or $[S(O)_2(OH)_2]$	sulfuric acid	dihydroxidodioxidosulfur
$(CH_3)_2SO_4$ or $[S(O)_2(OMe)_2]$	dimethyl sulfate	dimethoxidodioxidosulfur or dimethanolatodioxidosulfur
H_3PO_3 or $[P(H)(O)(OH)_2]$	phosphonic acid*	hydridodihydroxidooxido=phosphorus
$PhP(O)(OH)_2$	phenylphosphonic acid	dihydroxidooxido(phenyl)=phosphorus

*Note: The term 'phosphorous acid' has been used in the literature for both the species named phosphonic acid in Table 8 and that with the formula $P(OH)_3$, trihydroxidophosphorus. It is used in organic nomenclature in the latter sense.

The traditional oxoacid names may be modified according to established rules for naming derivatives formed by **functional replacement**¹⁶; thus 'thio' denotes replacement of =O by =S; prefixes 'fluoro', 'chloro', *etc.*, and infixes 'fluorid', 'chlorid', *etc.*, denote replacement of -OH by -F, -Cl, *etc.*; 'peroxy'/'peroxo' denote replacement of -O- by -OO-; and so forth (Table 9).

If all hydroxy groups in an oxoacid are replaced, the compound is no longer an acid and is not named as such, but will have a traditional **functional class name**¹⁶ as, *e.g.*, an acid halide or amide. Such compounds may again be systematically named using additive nomenclature (Table 10).

A special construction is used in **hydrogen names**, which allows the indication of hydrons bound to an anion without specifying exactly where. In such names, the word 'hydrogen' is placed at the front of the name with a multiplicative prefix (if applicable) and with no space between it and the rest of the name, which is placed in parentheses. For example, dihydrogen(diphosphate)(2-) denotes $H_2P_2O_7^{2-}$, a diphosphate ion to which two hydrons have been added, with the positions not known or at least not being specified. One may view the common names for partially dehydrated oxoacids, such as hydrogenphosphate, HPO_4^{2-} , and dihydrogenphosphate, $H_2PO_4^-$, as special cases of such hydrogen names. In these simplified names, the charge number and the

Table 9: Examples of derivatives of inorganic oxoacids and anions formed by functional replacement

Formula	Name indicating functional replacement	Additive name
H_3PS_4 or $[P(S)(SH)_3]$	tetrathiophosphoric acid or phosphorotetrathioic acid	tris(sulfanido)sulfido=phosphorus
H_2PFO_3 or $[PF(O)(OH)_2]$	fluorophosphoric acid or phosphorofluoric acid	fluoridodihydroxido=oxidophosphorus
$S_2O_3^{2-}$ or $[S(O)_2(S)]^{2-}$	thiosulfate or sulfurothioate	trioxidosulfido=sulfate(2-)
$[O_3S(\mu-O_2)SO_3]^{2-}$	peroxydisulfate	see Section 2.5

¹⁶ Reference 5, Chapter IR-8.

Table 10: Examples of functional class names and corresponding additive names

Formula	Functional class name	Additive name
PCl_3O	phosphoryl trichloride	trichloridooxido=phosphorus
SCl_2O_2	sulfuryl dichloride	dichloridodioxidosulfur
$S(NH_2)_2O_2$	sulfuric diamide	diamidodioxidosulfur

parentheses around the main part of the name are left out. Again, these particular anions may be named systematically by additive nomenclature. The word 'hydrogen' is placed *separately* in forming analogous names in organic nomenclature, for example, dodecyl hydrogen sulfate, $C_{12}H_{25}OS(O)_2OH$. This difference between the two systems has the consequence that the important carbon-containing ion HCO_3^- can be named equally correctly as 'hydrogen carbonate' and as 'hydrogencarbonate' (but not as bicarbonate).

3 STEREODESCRIPTORS

The approximate geometry around the central atom is described using a **polyhedral symbol** placed in front of the name. The symbol is made up of italicised letter codes for the geometry and a number that indicates the coordination number. Frequently used polyhedral symbols are *OC-6* (octahedral), *SP-4* (square-planar), *T-4* (tetrahedral), *SPY-5* (square-pyramidal), and *TBPY-5* (trigonal-bipyramidal). More complete lists are available.¹⁷

The relative positions of ligating groups around a central atom can be described using a **configuration index** that is determined in a particular way for each geometry,¹⁸ based on the Cahn-Ingold-Prelog priorities of the ligating groups,¹⁹ and it may change if the ligands change, even if the geometry remains the same. The absolute configuration can also be described. Generally configuration indices are used only if there is more than one possibility and a particular stereoisomer is to be identified. The full stereodescriptors for the particular square-planar platinum complexes shown below are (*SP-4-2*) and (*SP-4-1*), for the *cis* and *trans* isomers, respectively. Alternatively, a range of traditional stereodescriptors may be used in particular situations. Thus the isomers that are possible when a square-planar centre is coordinated by two ligating groups of one type and two of another are referred to as *cis*- (when the identical ligands are coordinated next to each other) or *trans*- (when they are coordinated opposite to each other).



cis-diamminechloridoplatinum(II) *trans*-diamminechloridoplatinum(II)

Octahedral centres with four ligands of one kind and two of another can also be referred to as *cis*- (when the two identical ligands are coordinated next to each other) or *trans*- (when they are coordinated opposite each other). Octahedral centres with three of each of two kinds of ligand can be described as *fac*- (facial), when the three ligands of a particular kind are located at the corners of a face of the octahedron, or *mer*- (meridional), when they are not.

4 SUMMARY

This document provides an outline of the essential nomenclature rules for producing names and formulae for inorganic compounds, coordination compounds, and organometallic compounds. The complementary document for nomenclature systems of [organic chemistry](#)² will also be useful to the reader.

Names and formulae have only served half their role when they are created and used to describe or identify compounds, for example, in publications. Achieving their full role requires that the reader of a name or formula is able to interpret it successfully, for example, to produce a structural diagram. The present document is also intended to assist in the interpretation of names and formulae.

Finally, we note that IUPAC has produced recommendations on the graphical representation of chemical structures and their stereochemical configurations.²⁰

¹⁷ Reference 4, Table P5; Reference 5, Tables IR-9.2 and IR-9.3.

¹⁸ Reference 5, Section IR-9.3.3.

¹⁹ R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385–415 and 511 (1966); V. Prelog, G. Helmchen, *Angew. Chem., Int. Ed. Engl.*, 21, 567–583 (1982).

²⁰ J. Brecher, K. N. Degtyarenko, H. Gottlieb, R. M. Hartshorn, G. P. Moss, P. Murray-Rust, J. Nyitrai, W. Powell, A. Smith, S. Stein, K. Taylor, W. Town, A. Williams, A. Yerin, *Pure Appl. Chem.*, 78(10), 1897–1970 (2006); J. Brecher, K. N. Degtyarenko, H. Gottlieb, R. M. Hartshorn, K.-H. Hellwich, J. Kahovec, G. P. Moss, A. McNaught, J. Nyitrai, W. Powell, A. Smith, K. Taylor, W. Town, A. Williams, A. Yerin, *Pure Appl. Chem.*, 80(2), 277–410 (2008).



Trends in technological use and social relevance of New Zealand's geothermal waters

Peter Hodder

Victoria Business School, Victoria University of Wellington and HodderBalog Social and Scientific Research, Wellington, New Zealand (email: peterh@hodderbalog.co.nz)

Keywords: *social history, electricity generation, chemical analysis, geothermal waters, ore deposits*

The thermal springs of the North Island of New Zealand were well known to Māori, and they were quick to capitalise on the springs' commercial potential once European tourists arrived. Prince Albert's visit in 1870 further popularised the Pink and White Terraces – and their silica-laden waters. However, it was the Government's appointment of a balneologist, Arthur Stanley Wohlmann in 1902,¹ that initiated the prospect of spa towns in New Zealand to mimic those of Europe.² Wohlmann travelled throughout New Zealand, compiling his data initially into three pamphlets relating to Te Aroha, Hanmer and Rotorua, and later combined into a single book.³ He was also responsible for the development of a 'Geyserland' at the 1906-1907 International Exhibition of Arts and Sciences, in Christchurch (Fig. 1), modelled on Rotorua. The exhibit included a mound of silica which was said to be a replica of Waikite Geyser in Rotorua, from which "vapour came in soft white clouds from the geyser-well and every now and then puia burst forth (regulated in some occult fashion behind the scenes by the guardian tohunga, Mr Turner from Whakarewarewa) and hurled its glittering columns of water and spray into the air with all the fuss and commotion of the 'the real thing'. The fact that the spray when it fell on one was cold in no way detracted from the general effectiveness of the imitation puia."⁴

Wohlmann made favourable comparison of the chemical compositions of the New Zealand waters with those of the famous spas of Europe:⁵ in a comparison with the Vichy waters of France, he noted that those at Te Aroha contained "a very much larger proportion of sodium-bicarbonate, and ranking as one of the strongest, probably the actual strongest, alkaline thermal waters of the world." This provided the impetus for an industry of 'taking the waters': for example, bathing in Rotorua, symbolised by the Tudor-inspired bath house. Wohlmann's statistics – summarised in Table 1 – indicated that most of those seeking treatment at Rotorua's spa suffered from rheumatic disorders, and the majority found the treatment efficacious.⁶

Despite variations in the composition of the waters used in Rotorua and their allocation to bathers with particular medical conditions (Table 2), Wohlmann appears to have been under no illusion that the effectiveness of treatment was attributable to the temperature of the water rather than its composition, commenting, "A few minutes immersion in one of the acid baths causes a bright scarlet hyperaemia of the skin ... I believe the hyperaemia to be an active arterial one and that it is this active hyperaemia which constitutes the essential value of these waters."

Although the Tudor-inspired Rotorua bath house is the



Fig. 1. Early promotion of a geothermal area as a tourist attraction: 'Geyserland' at the 1906-1907 exhibition in Christchurch.

Upper: A view of Wohlmann's exhibit, showing the 'silica' mound from which a 'geyser' erupted cold water. The hills beyond the manuka fence at rear of the photograph are not the Port Hills of Canterbury, but are representations of the hills around Rotorua, painted on a canvas. Photo: Cowan (1910).

Lower: Wohlmann hosting Sir Joseph and Lady Ward at his exhibit. Part of the mural of 'Rotorua' hills is clearly shown below the tops of the towers that flanked the entrance to the exhibition building. Photo: *The Weekly News*, 15 November 1906.

best known New Zealand spa, the Edwardian elegance of the Te Aroha spa and its grounds is the better remaining example of both built and landscape spa architecture. Its waters were also more suitable for drinking (Fig. 2A).⁷ Water from No. 15 spring (Fig. 2B) was recommended in the 1870s for drinking by those suffering from dyspepsia and was also claimed to "confine the bowels", while that from Spring No. 8 was said to "relax them".⁸ Although Spring No. 8 has a higher concentration of silica and carbonate species, is overall more highly mineralised than Spring No. 15, and has a lower temperature (Table 3), there is no obvious link between the chemical composition of these waters and their alleged difference in therapeutic benefits.

Rather more recent chemical analysis of the Te Aroha waters suggested that they contained significant amounts of arsenic and boron,⁹ and a sign was later erected advising against drinking them.¹⁰

Table 1. Diseases ‘treated’ by Wolmann at the Rotorua spa and the efficacy of treatment

Medical condition	Rheumatic	Diseases of the nervous system	Arthritis, bone disease etc.	Miscellaneous	Diseases of the skin	Disease of the digestive system
	44.4%	30%	12.5%	6.2%	3.9%	2.5%
Efficacy of treatment	Very much better	Much better	Better	Unchanged	Worse	Dead
	48.5%	19.9%	21.7%	9.4%	0.5%	0%

* From Wohlmann (1914), pp. 94-95.

Table 2. Composition of selected waters at Rotorua*

	Postmaster Spring	Old Priest Spring	New Priest Spring
	<i>Chemical composition †</i>		
Potassium chloride	2.00	0.94	2.68
Sodium chloride	8.89	7.03	15.10
Sodium sulfate	14.25	10.85	19.94
Aluminium sulfate	13.60	9.60	12.38
Iron sulfate	0.52	0.06	1.30
Calcium sulfate	6.25	6.46	4.85
Magnesium sulfate	1.91	1.68	0.60
Silica	15.11	12.10	22.82
Sulfuric acid	22.29	3.77	16.80
All dissolved species	86.81	52.49	96.47
CO ₂ and H ₂ S	Fairly abundant	Fairly abundant	Comparatively scant
Temperature	98 – 120 °F	98 – 120 °F	130 – 160 °F
Therapeutic use	Chronic arthritis, ‘lumbago’, sciatic perineuritis or neuralgia	Chlorosis, and anaemic, rheumatoid, rheumatic, and neurosthenic cases	Chronic dry eczema, psoriasis

* From Wohlmann (1914), pp. 80-81.

† Composition in grains per gallon (1 grain per UK gallon = 0.014 g L⁻¹)

Table 3. Comparison between the chemical compositions of Spring No. 8 and Spring No. 15 at Te Aroha*

<i>Cited by Wohlmann (1914)</i>									
Spring	NaCl	NaHCO ₃	Na ₂ SO ₄	KCl	Ca(HCO ₃) ₂	Mg(HCO ₃) ₂	SiO ₂	CO ₂	Ra
No. 8	59.1	648.0	39.2	10.0	8.9	2.5	8.0	55	0.0010
No. 15	59.5	657.4	40.1	11.0	6.8	2.5	7.0	37.4	0.0012
Δ †	-0.4	-9.0	-0.9	-1.0	+2.1	0	+1.0	+17.6	-0.00002
Δ %	-0.7%	-1.4%	-2.2%	10%	+24%	0%	13%	+32%	-20%
<i>Cited by Wells (2003)</i>									
Spring	NaCl	NaHCO ₃	Na ₂ SO ₄	KCl	CaCO ₃	MgCO ₃	SiO ₂	Total	T/°F
No. 8	66.14	451.97	32.91	1.96	7.47	4.21	8.60	573.26	109
No. 15	43.11	331.76	22.16	-	6.91	3.61	7.05	414.60	139
Δ †	+23.03	+120.2	+10.75		+0.56	+0.60	+1.55	158.66	-39
Δ %	+35%	+27%	+33%		+7.5%	+14%	+18%	+28%	-36%

* Concentrations of all species except radium in grains per gallon; radium in grammes x 10⁻¹² per cc.

† Δ is concentration in Spring No. 8 minus concentration in Spring No. 15; Δ% is that difference in concentration (Δ) relative to the concentration in Spring No. 8, and expressed as a percentage.

The initial emphasis on the alleged medical benefits of the geothermal waters faded as the twentieth century progressed, although immersion in the warmth of the waters continued to be considered to provide relief for rheumatism and similar disorders. In Rotorua, the 1930s saw the opening of the Ward Baths and the Blue Baths, the latter of which was clearly aimed at the leisure market. However, the balneological heritage of the Rotorua spa was not lightly abandoned: a poster advertising Rotorua as a resort shows a montage of illustrations of activities and facilities available at Rotorua (Fig. 3), which includes a view of the swimming baths as well as patients

undergoing massage therapy (being treated by Schnee multipolar electric bath and high frequency valve, and an Aix massage douche). In the same decade, a promotional campaign combined balneology and recreation, using as a slogan ‘Better health – a better holiday. Rotorua – Nature’s own’. As part of this campaign the New Zealand Railways Publicity Branch, in conjunction with the Rotorua Borough Council and the Government Tourist Bureau, published a poster featuring “two panels with yellow backgrounds showing man at left and woman at right, both waving cheerfully”, each panel labelled ‘Rotorua – Nature’s cure’.¹¹

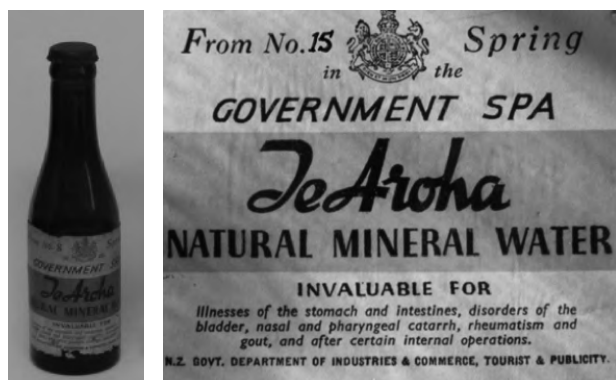


Fig. 2. Selling geothermal water on the basis of its chemistry. Left: Glass bottle containing water from Spring No. 8, Te Aroha thermal springs. This particular bottle dates from the 1930s. Photo: http://www.museums.co.nz/account/3026/object/804/Mineral_Water_Bottle. Right: Label of water bottled from Te Aroha's No. 15 spring. Photo: <http://www.nz museums.co.nz/account/3026/object/803/Label>.



Fig. 3. 'A montage of illustrations of activities and facilities available at Rotorua', with balneological therapy at the top and recreation at the bottom of the poster. Photo: Alexander Turnbull Library, Ref.: Eph-E-TOURISM-Rotorua-1932-01.

Some patrons made the most of the recreational opportunities the Ward Baths offered: "The opacity of the water, tinged asprin-grey by its minerals, facilitated approaches and the tentative touching of feet and the other bathers rarely noticed what was going on..."¹² The 'minerals' are principally clay minerals resulting from the reaction of silicates with the acidic geothermal water, these clay minerals and the silica content of the water contributing to its 'opacity'. More typically patrons of geothermal recreational facilities appear to prefer their warm waters to be slightly alkaline and of low turbidity,¹³ akin to the blue waters of the pools on the White Terrace, as painted by Charles Blomfield (Fig. 4).¹⁴

A decline in recreational swimming in geothermal resorts and thermal pools was perhaps hastened by the behaviour of some patrons, particularly at Rotorua's Ward Baths, and almost certainly by a few highly publicised fatal cases of amoebic meningitis attributed to diving into geothermal waters that had been in contact with soil



Fig. 4. The White Terrace, Charles Blomfield, oil on canvas, 1917.

containing the amoeba *Naegleria fowleri* "at places along the primeval course of the Waikato River between Taupo and Matamata".¹⁵ Some public awareness of this risk remains, for example, in 2013 a swimmer at Otumuheke swimming area in the Waikato River on the northern outskirts of Taupo commented:

"I loved this spot – only I didn't see ANY warning signs about preventing the incurable meningitis by swimming with my head above the water, and also found out about the risk after I spent the day splashing about and pseudo-snorkeling in the river just off the hot stream. I called the nurse who didn't seem too concerned, but there needs to be warnings about these risks... I doubt I'll get sick but the anxiety is enough to make the next seven days a drag..."¹⁶

The number of visits to the New Zealand Hot Pools website since its establishment in 2005 (Table 4)¹⁷ suggests that the popularity of commercial and non-commercial hot pools continues. However, some visitors' comments suggest that the hot springs serve social purposes in addition to simply recreational swimming, as indicated by the examples below.

"Go here every time we go to Rotorua. Never disappoints. Amazing when the full moon is up too! Hamburgers in the cafe are the best value for money we have eaten. Entry, a little pricey, but still worth it. Just get in there before the tourist groups arrive around 6pm onwards." (Polynesian Pools, November 2011).

"If you want to relieve yourself of stress then sitting back in this Waiotapu Stream is just the medicine. The further up towards the bridge you go, the hotter the water gets. This place is like hydrotherapy. Cleans the pores of your skin, and soothes aching muscles... Don't be shy about going in the lovely warm water in the nude, guys and girls! It really is a stress reliever especially going au natural, and you will make the passers-by happy too with some eye candy to look upon. They aren't perving, they are admiring your courage that you went in the raw, and admiring your human beauty, and will remember what they saw in the weeks that follow." (HotnCold, January 2013)

Table 4. Visitor numbers and ratings of hot springs and spas in Rotorua area*

Name	Character	Visitor ratings and reviews			No. of web-page visitors†
		Rating /10	No. of voters	No. of reviews	
Kerosene Creek	Natural spring	9.0	98	108	220,879
Polynesian Pools (Rotorua)‡	Commercial	7.3	24	30	111,058
Waikite	Commercial	9.5	64	73	110,737
The Bridge /HotnCold	Natural spring	8.4	36	40	91,279
Waitangi Soda Spring (Lake Rotoma)	Natural spring	7.6	44	74	84,507
Blue Baths (Rotorua)	Commercial	9.5	6	6	51,636
Maungataniwha	Natural spring	10.0	1	1	47,340
Te Rata Bay (Lake Tarawera)	Natural spring	7.9	10	12	42,916
Manupirua Thermal Springs (Lake Rotiti)	Natural spring	9.2	19	23	39,681
Waterfall Spout (Waiotapu)	Natural spring	8.1	14	16	38,393
Hell's Gate (Tikitere)	Commercial	6.2	6	7	25,611
Kuirau Park Footbaths (Rotorua)	Natural spring	7.0	6	6	21,698
Awakeri Hot Springs	Commercial	7.9	14	15	20,926
Wairua Stream (Lake Tarawera)	Natural spring	8.0	5	5	20,690
Rotoma Holiday Park	Commercial	9.9	3	5	20,749
Tumoana Point	Natural spring	4.0	1	1	20,044
Lake Rotowhero	Natural spring	4.5	2	3	16,121
Hinemoa's Pool (Mokoia Is)	Natural spring	4.0	2	3	15,131

* <http://www.nzhotpools.co.nz/>; downloaded 4 March 2015.

† Not all visitors to the web-pages will visit the facilities, but the number may be indicative of an interest in doing so.

‡ This facility is on the site of the Ward Baths.

"Carlton football club has been visiting this spot for the past 5-6 years on our annual football trip from Auckland. It is one of the highlights of our weekend. Would recommend it to anyone but keep your head out of the water as a couple of guys have been sick in the past. Locals are very friendly." (HotnCold, October 2005)

"Seriously the best end to the perfect day with the family. Use to come here 20 years ago after tramping with groups of friends – never had any trouble with the locals – sad to see some people have. Keep it clean, keep it green - God I seriously love my country - don't spoil it!!!!" (Kerosene Creek, February 2014)

"A special friend took me there late one night when there was a full moon. We were fortunate enough to be the only ones there and lit the bank up with candles. One of the most magical places I have ever been to...and I have travelled most of the world." (Kerosene Creek, 2006)

"Despite playing host to dozens of glamorous galas, gorgeous weddings and glorious corporate functions every year, we have never lost sight of the fact that swimming was what drew people to The Blue Baths back in 1933 when daring mixed bathing (a New Zealand first) adding to the excitement of socialising with family and friends at "the Blueys." (Blue Baths, undated)

Scientific and technological interest in geothermal waters has waxed and waned over the latter years of the nineteenth century and the first fifty years of the twentieth century (Fig. 5).

An empirical approach to determining how this interest in geothermal waters has changed over time is to consider the variation in the number of publications:¹⁸ there is a peak of research publications in the late 1800s, and

another flurry of research publications in the 1910s. The final peak in the graph is attributed to a growing interest in the possibility of using geothermal resources as an energy source just after World War Two. Further analysis of these data shows that although most publications were about the chemical composition of the geothermal waters or their geological setting, a small number were about health, tourism, or potential technological uses (Fig. 6).

If just these last three categories are considered, an interest in the late 1800s in tourism is supplemented by health interests in the early decades of the twentieth century, to be supplanted by prospects for using the heat from the water for purposes other than bathing (Fig. 7). Coupled with these trends has been the rise of professional science and engineering interest at the expense of amateur scientists, business-folk, photographers and others (Fig. 8).

The prospect of geothermal waters having an economic benefit beyond tourism that was foreshadowed by a few papers published prior to 1950, received a post-war stimulus by the suggestion that the deuterium content of the waters meant that they had potential use in nuclear power plants. A proposal to use the water in this way by the United Kingdom's Atomic Energy Commission came to nothing,¹⁹ but paved the way for the investigation of using the heat in geothermal waters as an energy source. The shortage of electricity in the North Island in the late 1940s gave impetus to such investigations.²⁰ A significant proportion of scientific papers on 'geothermal resources' for the period 1951-1969,²¹ are on topics related to exploration, e.g., various methods of geophysical and geochemical surveying, and exploitation, e.g., drilling wells, costs, and estimates of energy, as shown in Fig. 9.

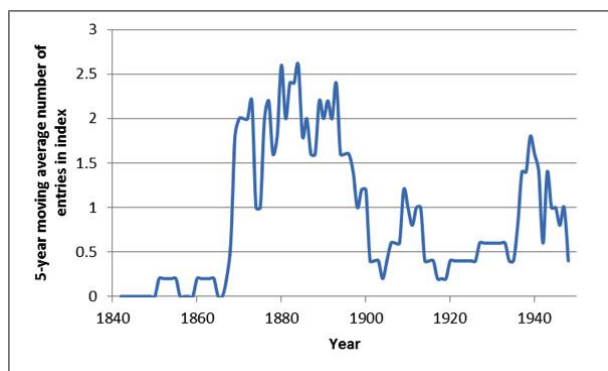


Fig. 5. Variation of five-year moving average of the number of entries about ‘thermal waters’ in an index to a bibliography of geological research covering the period from 1840-1950.

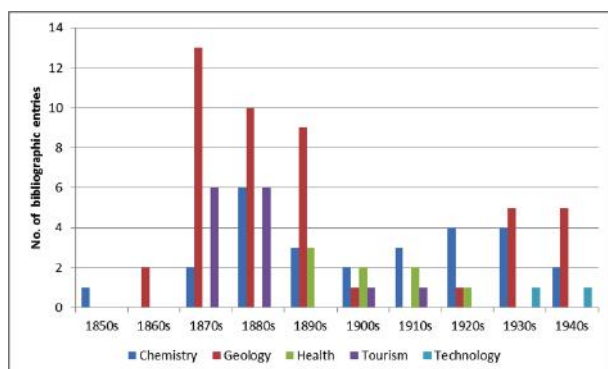


Fig. 6. Number of publications related to ‘thermal waters’, 1850s-1940s, by category.

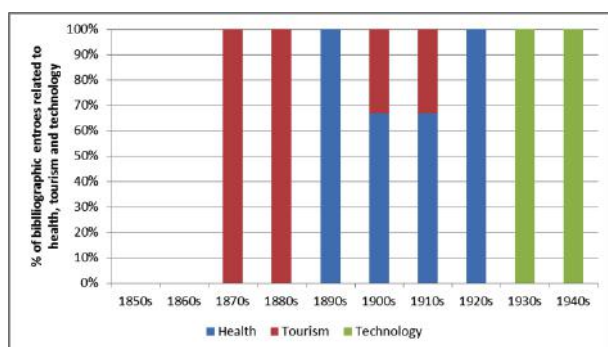


Fig. 7. Proportion of bibliographic entries related to health, tourism and technology, i.e., %health + %tourism + %technology = 100%, 1850s-1940s. (Note: ‘technology’ publications are about using the heat of the waters.)

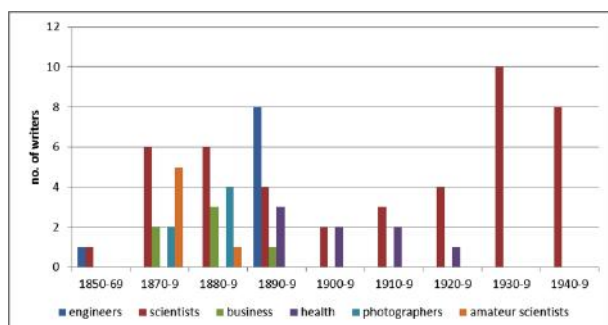


Fig. 8. Trends in occupations of writers about thermal springs, 1850s-1940s. Professional scientists have progressively dominated over other those occupations with interest in the waters.

Most of the scientific effort was concentrated at the Wairakei geothermal field, but the field at Broadlands (later to host the Ohaaki geothermal power station) and those at Kawerau, Ngawha, Orakeikorako and Waitapu

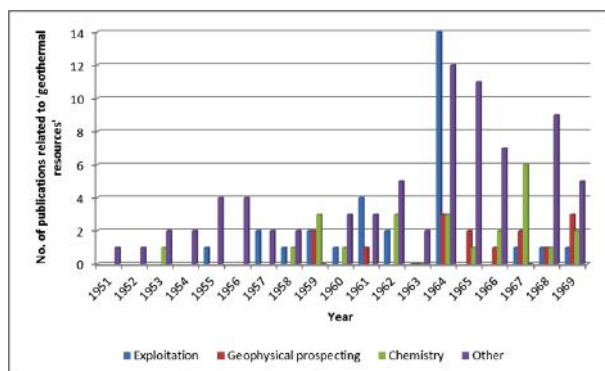


Fig. 9. Publications on geothermal resources, 1951-1969, by category.



Fig. 10. Left: S.H. Wilson - “a leading New Zealand geochemist”. Photo: *Geochemistry* 1977. Right: Early steam collection at Wairakei in about 1952, with Wilson (at left) and G.A. Patchett: an example of Ellis’ memory (reference 28) of “his ready ability to improvise field equipment; and his dedication to the task in hand”. Photo: Hughson and Ellis, Fig. 64.

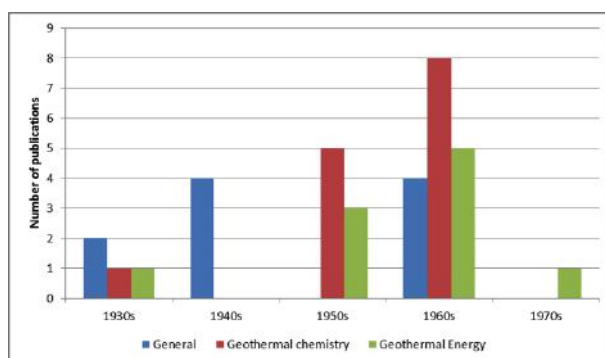


Fig. 11. Publications of S.H. Wilson, 1931-1970.

were also investigated. The 1951-1969 *Index* also lists papers on ‘thermal waters’, a term which implies the paper might be less about exploitation, although many of the papers are the same as those listed in ‘geothermal resources’. In a bibliography and index for the subsequent period 1970-1989,²² research into geothermal waters continues to be dominated by exploitative themes (Table 5).

Thus, from 1950 geothermal waters came to be technologically confined – not in bottles (as in Fig. 1), but in pipes and other equipment for electricity generation. The development of a power station at Wairakei, a location which was considered to be a ‘typical section’ of the thermal region stretching from Ruapehu to the Bay of Plenty,²³ using steam separated from the high pressure water from deep wells led to dramatic reductions in the periodicity and height of eruption of geysers in the area and significant changes in the temperature and compo-

Table 5. Exploitative, explorative and scientific publications related to 'geothermal' topics, 1970-1989

Theme of investigation	Index terms	No. of entries in index
Exploitative	Geothermal energy utilisation	24
	Geothermal field development	8
	Geothermal field exploitation	1
	Geothermal field management	1
	Geothermal field utilisation	1
	Geothermal power	3
	Geothermal power plants	6
	Geothermal utilisation	1
	Geothermal wells	17
Explorative, i.e., prospecting	Geothermal exploration	9
	Geothermal prospecting	17
Scientific	Geothermal processes	26
	Geothermal solutions	5
	Geothermal surveys	1
	Geothermal waters	4
	Geothermometers	3
	Geothermometry	4
	Geysers	5

Technology												
Science												
Medicine												
Energy												
Social												
Tourism												
Leisure												
Lifestyle												
	1870s	1880s	1890s	1900s	1910s	1920s	1930s	1940s	1950s	1960s	1970s	1980s

Fig. 12. Overall trends in technological use and social relevance of geothermal waters.

sition of the water.²⁴ The changes in composition were attributed to temperature-dependent chemical reactions between the water and the rocks in which it is confined: this led to the application of geothermometry as a measure of the heat content and then to assessment of the economic value of geothermal waters. Chemists played their part in this: some of them changing their interests from analysis of the water, perhaps seeking an association of water chemistry with health; to the water's chemical composition being a proxy for temperature and thereby the water's potential for geothermal power generation. The research outputs of S.H. Wilson, a leading geochemist to which a compilation of papers in the 1970s was dedicated (Fig. 10),^{25, 26} shows this trend clearly (Fig. 11).

Through the 1950s and 1960s, pipes confining the geothermal water spread across the landscape.²⁷ The 'mining' of geothermal waters as a feedstock for electricity generation is not sustainable, as the rate of natural recharge of the aquifers in which the resource is stored, even where supplemented by re-injection of water, is far slower than the rate of extraction. The decrease in geyser activity in Whakarewarewa in the 1980s, considered to be caused by excessive extraction of fluid from the geothermal field by hotels and domestic users in Rotorua is a

similar example of unsustainable practice.²⁸ Despite such examples, exploitation of the resource in geothermal power stations, albeit on a smaller scale than the initial projects at Wairakei and Ohaaki, continues. In late 2014, retiring Chief Executive of Mighty River Power, Doug Heffernan, noted:

"The geothermal renaissance that's occurred over the last decade is the No 1 thing that has made a dramatic difference to the energy footprint in New Zealand, and put it back on a track to a higher proportion of renewable energy. The second is the partnership model that was developed in working with Māori land trusts that has enabled them to participate in economic wealth creation in a way that hasn't occurred at any time in the past in the energy sector."²⁹

As well as his role with Mighty River Power, Heffernan was also a director of Tuaropaki Power Company and chairman of Rotokawa³⁰ and Nga Awa Joint Ventures. These roles were instrumental in the co-development with Maori of geothermal resources, the first of which was brokered at the time the Ohaaki power station on the Broadlands geothermal field was being developed.

A final twist in the saga has been the recognition of a

formal analogy between gold and silver deposits of the Coromandel with the mineral deposition regime of highly saline geothermal waters.³¹ The 1980s saw considerable activity among chemists to determine the nature of inorganic complexes of gold, silver and other metals with chloride ions and sulphur species which were stable at the high temperatures and pressures of the deep geothermal aquifers, but which would precipitate gold, silver, and base metal sulphides on cooling.³² However, this “collaborative work by the geologists and chemists of the New Zealand DSIR in investigating natural geothermal systems and experimenting on mineral solubilities” foundered: “budget cuts in the late 1980s severely decreased the work the group could take on. The nucleus of key scientists is now scattered around the world, and the programme of fundamental research that put New Zealand at the forefront of modern geochemistry is finished.”³³

Thus, over the past 150 years, geothermal waters have changed from being primarily a spectacle for tourists, to their being perceived as healthy to drink and bathe in, to being recreational venues, and to being sources of energy and potentially for economic minerals, as is shown schematically in Fig 12.

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Employing new chemistry graduates - some thoughts from the field

Michael Gray

Chemsafety Ltd., PO Box 8141, Christchurch 8440 (email: mike@chemsafety.co.nz)

Keywords: *employment, graduates, industry, skills*

Introduction

Universities have a range of goals in mind when designing the syllabus for chemistry papers and degrees. These range from support training for students pursuing other degree majors, to providing fundamental knowledge and skills for those pursuing a BSc in chemistry and promoting higher academic knowledge in preparation for post-graduate study or research. However, a major consideration must surely be the preparation of students for a career in chemistry related industries beyond academia, with preparation of recruits in skills that will see them find work in the wider community.

Chemsafety is a science consultancy company which recruits and employs fresh chemistry graduates for a career in science interacting with the wider world. Established in 1992, Chemsafety is Christchurch-based and provides services nationwide in occupational hygiene (occupational chemical hazard assessment, exposure monitoring, noise surveys, and providing remedial advice), hazardous substances (HSNO: storage and use advice, training and certification), and asbestos consultancy (building surveys, exposure monitoring, and management advice).

We have employed 19 chemistry graduates over the last 20 years, 12 of whom remain working for the company. All but two were employed as fresh graduates into their first science position. Not all walked straight into a science role. Some spent considerable time painting houses, driving forklifts or working in retail before finding employment in their chosen career. So, what are we looking for when we recruit, and what can universities do to help promote their students into such chemistry-based work?

Firstly, for us, recruits need the knowledge held within a base degree in chemistry, and thereafter the 'X' factor counts. The 'X' factor is a natural intelligence and way of looking at the world, where someone faced with a large and complex situation can simplify it in their mind so that it can be measured and managed. They are confident but not overly so, will not be easily swayed but will not be dogmatic and will be willing to change their opinion if new evidence dictates it. They need to communicate well both in written and oral form (and convey technical matters in an easy to comprehend manner) and mix in well with both our staff and our clients.

A higher degree is nice if we can get it, but only as a secondary consideration to the above. In general we have observed that people with higher degrees have unrealistic expectations around salary and the type of work they desire. We are reluctant to seriously consider someone whose primary interest is research as we do not do pure research, and we do not wish to be used as a temporary 'holding position' job until something else comes along. Are students planning a PhD counselled on their life plan? A higher degree may not necessarily be beneficial to obtaining employment in their chosen career, and may in fact be detrimental. Should they be made aware of the potential downside of their planned postgraduate degree when looking for a job in industry?

Fresh graduates, regardless of their level of degree, do not make us money. They need to be trained first. This requires our experienced staff to be drawn away from their core work. The new recruit will generally require several months training before finally starting to generate a sustainable income for the company. Graduates are not

aware that they are initially a cost to the company when assessing their salary expectations. A new recruit would typically require a \$15,000 investment by the company before they start to 'earn their keep', and will take at least six months to reach break-even.

So what university training would be helpful to our company and to a new recruit? Report writing practice is a must. Fresh graduates are generally abysmal at this. There is an essay-averse streak in many science students, but being able to write comprehensible 'complete' pieces of work is an essential skill.

Practice at calculations comes next. Graduates struggle converting weights and measures into meaningful units for concentration calculations. Then converting, say mg/m³ in air to ppm is a further challenge. The key here is meaningful – does the result you have just determined make sense given the situation you have encountered?

Finally, there appears to be a strong emphasis on academic study, and little on practical skills or on the chemistry used in day to day industry. There is interesting science in the conversion of, say, limestone to quick and hydrated limes, and to cement. This includes thermodynamics, heat of hydration, and the balancing of chemical equations. Likewise, organic synthesis of industrial chemicals could add an interesting structure to the organic syllabus. Could these practical aspects be taught without diminishing from the academic curriculum or adding to course

time? Killing two birds with one stone, so to speak.

In summary, before beginning a chemistry major, should universities provide students with counselling on career opportunities in their chosen areas of interest and then on the best degree for that work? This might include advice on the likelihood of succeeding in being recruited into that field. A chemistry degree gives great training in academic chemistry, but does it prepare the graduate for recruitment into the wider community beyond the university? Is there coordination between high school career counsellors and university departments? Should departmental staff take an active interest in the career and recruitment of their students and make this a priority, or should their only concern be with providing an academic understanding of chemical principles? Is career planning a once-a-year tick box endeavour, or built into the whole curriculum to some extent or other?

Interestingly, not so long ago we approached three universities asking for them to make their graduating class of chemists aware that we were recruiting chemistry consultant trainees. One placed our vacancy in their departmental newsletter, and not long thereafter had placed one of their graduates on the first step of what is likely a long career in science. After several fruitless phone calls we gave up on the other two universities. This lack of concern for students' wellbeing beyond the classroom is disappointing.

Joan Muriel (Mattingley) Cameron, Hon. FNZIC (1926-2015)



Joan Muriel Mattingley was born in Wellington in 1926. She attended Ngaio School and Wellington Girls College, where she played the violin in the school orchestra. Joan commenced a BSc at Victoria University College in 1943 while working as laboratory assistant to Dr Marion Cunningham at Karitane Food Products Ltd. in Melrose, and graduated BSc in

Zoology in 1948. She later returned to university, completing an MSc in Zoology in 1970 and a PhD in Biological Chemistry in 1977 under the direction of Professor James Duncan.

Apart from two years during the 1950s at the Lister Institute in London, most of Joan's working life was spent

as a clinical chemist in the laboratory of Wellington Public Hospital where she became the Senior Scientific Officer. She was active in our Institute taking on Chairwoman of the Wellington Branch over the 1963-1964 period and then from 1965-1976 was editor of the Institute's Journal. This latter 12 year tenure is the longest of all our editors.

Joan was active in the Federation of Graduate Women, being President in 1980 and 1981 and then Vice-President of the Wellington Branch in 1982. In 1982 she convened a Study Group on Women in Science concerned with advancing science education for girls and career opportunities for women in the scientific workforce. The Federation granted her a Harriet Jenkins Award in 1983 to assist in the writing of her biography (under her married name) of the late Dr Brian Shorland. Joan accepted the Presidency of the NZ Association of Scientists from 1987 to 1989 having been on the Council for several years. In that role she was outspoken about the restructuring of science.

In 1974 Joan married Charles Cameron who predeceased her in 1997. She became a member of the Institute in 1958, a Fellow in 1974 and later attained the highest honour, namely that of Hon. Fellow.

Brian Halton & Neil Curtis

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.

Heinrich Caro (1834-1910)

Brian Halton

School of Chemical & Physical Sciences, Victoria University, PO Box 600, Wellington 6140
(email: brian.halton@vuw.ac.nz)



Caro, adapted from BASF AG

Heinrich Caro was born in the town of Posen in Prussia (now Poznan, Poland) on February 14, 1834, son of Simon and Amelia (née Schitzer) Caro. His parents were of Jewish descent, his father's family having emigrated from Portugal to the town of Glogau in Silesia. His mother came from a jeweller family who had moved from Amsterdam to Wroclaw (Breslau) in Silesia. After moving to Posen, Heinrich's father and grandfather established a grain merchant company. Of Heinrich's five siblings only his two-year elder brother Julius survived. Shortly after Heinrich started school the family moved to Berlin via Breslau, his mother's home town, in the hope of a better education and life for their family.¹

Once in Berlin, Heinrich attended the Kölnische Regalgymnasium for 10 years from the autumn of 1842. His youth in Berlin was centred on music, adventure and drama. His mother, who had much interest in opera, engendered in him a significant interest in music and had the boy learn German folk tunes and listen to military bands.² He was part of an informal drama circle, after one of whom (Anna Peters nicknamed *rosenfingerrigne Eos*) he subsequently named his dye eosin (eos Gk; goddess of the dawn). He became artistically oriented and was labelled as a dreamer by a colleague in his BASF days. The fourteen year old Caro saw first-hand the revolution of 1848 that sought liberal reforms; his home was in a building that also housed the much disliked state censor and mayor of Berlin. The street battles and their aftermath impacted significantly on him. According to Travis² the impact of these events allowed Caro to retreat into a dream world of his own and play out the adventures of his boyhood heroes.

The Regalgymnasium had a chemical laboratory and the young Caro became fascinated with the experimental work as he saw the subject offering much advantage to all branches of the trades. Prior to graduating, he was performing experiments at home that he had done in the lab and others he obtained from textbooks. From there he moved for trade training at the Royal Commercial Institute becoming a colourist in cotton dyeing and printing, and taking chemistry lessons at the University



Origin of the Flag of Germany: Cheering revolutionaries in Berlin, on March 19, 1848 (see: http://en.wikipedia.org/wiki/Revolutions_of_1848_in_the_German_states)

of Berlin. In doing so he likely had some training and input from the Berlin textile manufacturer Benjamin Lieberman, the largest calico-manufacturer in Germany and father of chemist Carl Liebermann with whom he subsequently collaborated. As an outstanding student graduating in 1855, Caro gained a position as colourist with calico printer Troost in Mülheim an der Ruhr, where natural dyes and secret recipes were still in use.



Troostsche Textilfabrik, Mülheim an der Ruhr (Ralf Huels, Wikimedia Commons)

Before the mid-1850s, all dyes were obtained from natural products and the experts in their application and improvement were textile colourists. Their job was to analyse the (mainly) vegetable-based extracts, e.g. the blue from indigo and the red from the madder plant root, and

improve dye fastness. This required the application of then known chemistry involving simple chemical analyses of the carbon-containing vegetable products and of certain metal compounds, the mordants that fixed the dye to the fabric. These often led to distinct colours.

This was the era into which Caro entered the textile industry. He soon demonstrated the power of scientific solutions to certain production problems and was sent to England in 1857 to learn the up-to-date dyeing techniques including advances in the use of steam. This was the year after William Perkin's discovery of mauve from aniline. Caro gained the needed information on the developments in England where he spent some time with the firm of Roberts, Dale & Co. in Manchester; he had met John Dale in Germany whilst a student.³ On return to Mülheim and Troost he was required to undertake military service and on discharge in 1858 Caro joined the new calico printing company, Louisenhaler Actiengesellschaft in Mülheim, but he stayed there for less than a year. He was ambitious and restless, and felt he could make a name for himself more easily in England than in his home country.

Back in England, Caro soon gained a permanent position with Roberts, Dale & Co. at their Cornbrook Mill at Hulme in Manchester and he stayed there until 1866. He was given the responsibility for quality control and for providing calico printing clients with the recipes for natural colours that included the madder extract, alizarin. At that time, South Lancashire was increasingly becoming the centre of British chemical industry. Large scale coal-tar production came to the fore from about 1859 and the development of synthetic dye manufacture gave a new aspect to chemical industry closer to academic chemistry (even pharmacy) than the then more traditional manufacture of acids and alkalis.⁴ By the spring of 1859, mauve (mauveine) manufactured by Perkin & Sons in London was at the forefront of fashion. It was this that led to the coal-tar hydrocarbons benzene and naphthalene being nitrated and reduced to amines that were, in turn, treated with a vast range of reducing agents in the hope of providing new synthetic colourants in what is now recognised as the aniline dye industry. It was this environment that saw Caro back in Manchester where he became a key figure in the development of 19th century synthetic dyestuffs.⁴ Roberts, Dale & Co. decided to become a significant player in this market and used to the full its German employees Caro, Martius and Leonhardt, and consultants Carl Schorlemmer (Owens College, Manchester) and Peter Griess (Allsopp's Brewery, Burton on Trent).

Working in his own time, Caro undertook a series of experimental studies with aniline in the hope that something practical might ensue. Inspired by Perkin,⁴ Caro subjected aniline to a variety of oxidising agents and found that copper sulfate and sodium chloride provided Perkin's mauve more efficiently than the potassium permanganate used by him. Together with John Dale the process was patented in May 1860, subsequently to go into production with Caro made a partner in the firm to work the patent. He was always careful to ensure that his mauve was suitable to his consumers and over the en-

suuing years improved versions were available from both Roberts, Dale & Co. and Perkin & Sons. The Manchester dye provided Perkin with his sole competitor of significance and it was so successful there that Heinrich Caro adapted and mechanised the equipment for the manufacture of nitrobenzene and aniline to allow the company to expand. His understanding of the needs of the calico printer and his after-sales service in his work for Dale, Roberts & Co. was to the extent that he was given charge of marketing their full range of products including the mauve, and it was left to him to set the selling price of their dyes in Europe. As we will see below, this contrasts with his reputation at BASF.

It is worthy of mention that it was only in 1858 that Kekulé and Couper had advanced the concept of tetravalent carbon and that Kekulé's historic six-membered ring structure of benzene did not appear until 1865. Thus, it is not surprising that the nature of the Perkin mauve (mauveine) was not settled until the 20th century, in fact only in 1994 when the presence of four phenazinium salts [3-amino-2-methyl-5-aryl-7-(*p*-tolyl)amino derivatives; mauvine A, B, B2 and C] were identified (Chart 1).⁵ The presence of the *o*- and *p*-toluidine moieties in mauvine stem from the impurities present in the aniline of the late 1850s and 1860s and they are critical to the synthesis. The proportion of the components in mauvine depended upon the quantities of the impurities, but mauvine A (from aniline:*o*-toluidine:*p*-toluidine in a ratio of 2:1:1) always dominated; now, a total of 12 components have been identified.⁶

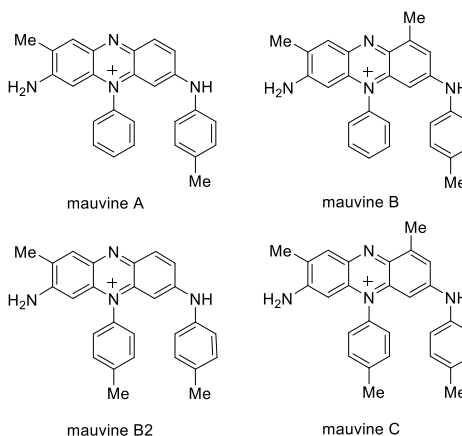
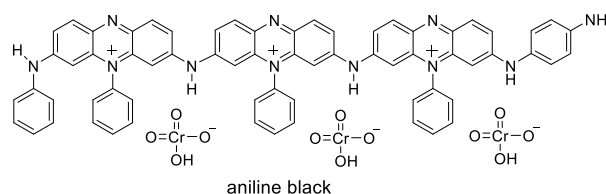


Chart 1. The structures of mauvine present in the Perkin and Caro products; the dye was commonly the acetate salt.

The Caro mauve process was not entirely straightforward as it left a black residue.² However, this residue provided a first-rate fast black (aniline black) for calico printers from ca. 1862. John Lightfoot of Accrington had first provided this compound but his method employed the use of aniline and copper salts directly in the printing process. The effect of the copper was slowly to corrode the steel rollers of the printing machines in England, but the



procedure worked well with the wooden rollers used in continental Europe. The Caro product had no such undesirable effect as the dye had been independently produced and it gave the company significant advantage.

By the end of 1862 both Perkin & Sons and Roberts, Dale & Co. had converted mauve into other colours and in late January 1864 Dale and Caro patented their after-treatment of magenta, mauve, and other aniline colours with acidic acrolein (propenal; $\text{CH}_2=\text{CH}-\text{CHO}$) that provided purple, blue, greens and other colours. These widened the range available and began to reduce the popularity of mauve.⁷

A.W. von Hofmann at the Royal College of Chemistry in London, and F-E. Verguin in Lyon, independently showed that (impure) aniline could give a new red dye, sometimes known as aniline red (fuchsine in France, rosaniline or magenta in England).^{3,4} It became the most sought after colour after mauve. In his synthesis, Hofmann used carbon tetrachloride while Verguin, who patented the process, used stannic chloride. Subsequently, Henry Medlock, a former Hofmann student, patented an improved process using arsenic acid as the oxidising agent. Although Caro could prepare the new dye using lead nitrate, it was of no better quality than that from the less expensive arsenic route. Once again, however, the manufacturing process was substantially improved at Roberts, Dale & Co. thanks to another Caro contact and subsequent employee, August Leonhardt. His Manchester procedure was so successful that Leonhardt was even able to promote it after his return to Germany in 1867.

Another new aniline dye of significance was aniline blue, discovered in France by Charles Girard George de Laire in 1860.^{3,4} It was obtained only by having an excess of aniline in the mixture that gave aniline red, was patented and became popular. Today it is recognised as being comprised of water blue, methyl blue or of a mixture of the two compounds (Chart 2). Although Caro and the company were interested in the blue dye, patents kept them

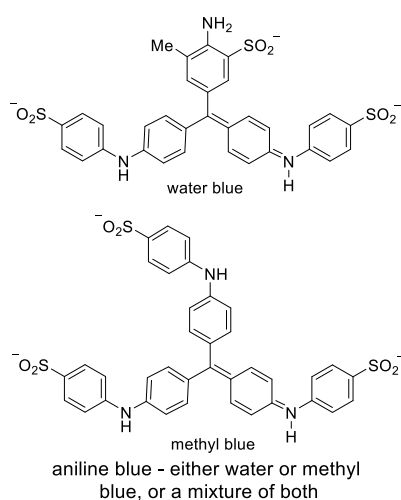
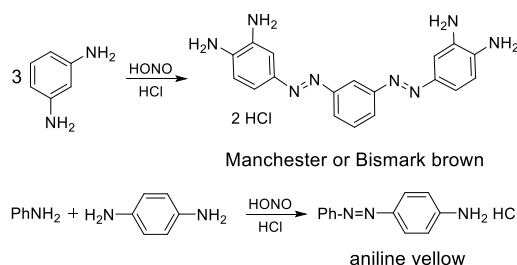


Chart 2

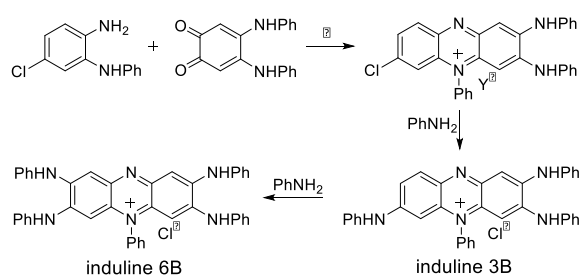
out of manufacture. Nonetheless, the Roberts, Dale & Co. consultant Carl Schorlemmer (Owens College) showed that the use of inorganic acid in the Girard de Laire process was inferior to the use of benzoic acid in a newer process devised by Wanklyn and Eisenlohr. Caro and Wanklyn published their results in the area,⁸

subsequently shown to have incorrect formulation, but published a few weeks before Hofmann's ground breaking paper on the composition of aniline blue as a triphenylated derivative.⁹ This latter paper showed the blue dye to carry 18 carbons and 12 hydrogen atoms more than the red dye and this was easily explained by the presence of three additional benzenoid rings. It was this work that opened the way for interaction between the industrial and academic chemists, though it was Caro and his subsequent move that really laid the foundation for technology transfer as we would now call it. The triphenyl dyes studied by Hofmann had also aroused Caro's attention and it was the study of these that led to his subsequent academic-industry career.

Carl Martius joined Roberts, Dale & Co. in 1863 from Hofmann's London laboratory and soon had a new brown dye available that was named Manchester brown (or phenyl brown) in Britain, but Bismark or Martius brown in Germany.³ It came from the reaction of *m*-diaminobenzene with nitrous acid and shortly thereafter aniline yellow was provided from *p*-diaminobenzene and aniline (Scheme 1). It was from the consultancy work of Peter Griess, done in his own time while working at the Allsopp's Brewery,³ that the wherewithal for the reaction of an aromatic amine with nitrous acid came. The now well-known diazotisation process that provided so many industrial dyes originates from the 1858 publication by Griess.¹⁰ Although their compositions were unknown, Manchester brown and aniline yellow were patented in 1863. That year Caro obtained the blue colour induline from reaction of aminoazobenzene with aniline and its hydrochloride at high temperature. It was a long-lived product and one of his major discoveries, again emanating from the exploratory work of Griess. The actual structure of the product is dependent upon the temperature and time period of the reaction and now several indulines are known; the most common are the 6B and 3B varieties as shown by Kehrman's authentic syntheses (Scheme 2).¹¹



Scheme 1



Scheme 2

It was Caro's training as a colourist in the printing industry that enabled him to fully appreciate the technical

challenges of dye application, and through this he facilitated the smooth transition from natural to artificial colourants. The various investigations and inventions on aniline and its derivatives carried the hallmarks of a new high-technology industry in the making. By the mid-1860s mauve had been displaced by the newer aniline dyes. However, mauve saw extensive use in wallpaper and paper printing and, through Caro's efforts, in the printing of postage stamps, probably its last commercial application.¹²

Caro developed respiratory problems during his time in Manchester and given this, and the better prospects that had become available in his home country, he resigned his position and returned to Germany in late 1866. But this was not before he married. He first met his future wife Edith Sarah Eaton in 1862 when she was twenty years old. They married on October 31, 1866, at Saint Saviour's Church in Chorlton-on-Metlock, south of Manchester city. The couple had a honeymoon on the Isle of Wight before leaving England for a brief sojourn in Berlin before settling in Heidelberg, where Heinrich worked in Bunsen's laboratory. They had three sons and four daughters.

During his time in Manchester Caro maintained contact with his German contemporaries and extended his circle of contacts so that while working in Bunsen's laboratory he was able to develop further his entrepreneurial skills. He became a consultant to the company Badische Anilin-und Sodafabrik formed in April 1865 by Friedrich Engelhorn, a trained goldsmith who became an entrepreneur in the gas lighting industry establishing a company in Mannheim. Engelhorn saw potential use in his major waste product, coal-tar, as a dye precursor. His initial objective was to have a factory sited on the Mannheim side of the Rhine but attempts to purchase a site fell through and so he set up BASF on the opposite side of the river in Ludwigshafen. Almost immediately he began to construct housing for his workers as the town became the fastest growing in Germany. The coal-tar dyes that the company manufactured were aniline red and its derivatives. However, they disappointed, being neither colour-fast nor lightfast and these factors (amongst others) led to Heinrich Caro's consultancy work.¹³

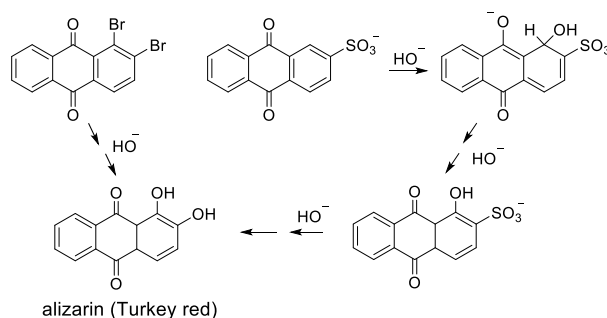


BASF, Ludwigshafen, 1866 (courtesy BASF AG)

By 1868 it was clear that the traditional natural dyes could no longer supply the growing demands of the textile industry and the need for intensive chemical research by BASF became obvious. Thus it was that Engelhorn, the Head of BASF, appointed Heinrich Caro as BASF's technical director and head of the test laboratory in 1868. His

laboratory at that time was in Mannheim until the building was sold and the facility moved to a lab just inside the main gate of the Ludwigshafen site. Caro became the company's first Research Director in the mid-1870s. His initial work was when the company was seeking to commercialise the production of synthetic alizarin (Turkey Red, Scheme 3), which with indigo was the most important dyestuff. That year, Carl Graebe and Carl (Theodore) Liebermann, each studying for his habilitation, had shown that alizarin could be degraded to anthracene and the following year they announced its synthesis from anthracene. It was the first laboratory preparation of a natural dye.¹⁴ Although they patented their process, Graebe and Liebermann sold their rights to BASF because the cost of the bromine needed to give the essential dibromoanthraquinone for the synthesis (Scheme 3) was too high for commercialisation.

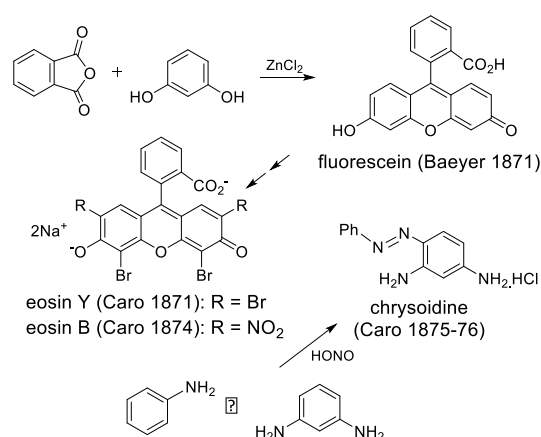
Caro's first job at BASF was to find a cost effective modification of the synthesis and this he did by sulfonating anthraquinone and then treating the resultant acid with base as shown in Scheme 3. The trio then patented the process for BASF,¹⁵ filing just one day before Perkin filed his patent for essentially the same process. Caro negotiated settlement, the outcome of which was a Perkin-BASF cartel that divided the international market for this important dye; Perkin had the UK and BASF Europe and the US. Commercialisation of the alizarin process was not easy and Carl Glaser, who had been taken on from Kekulé's Bonn laboratory following his habilitation in 1868, assisted Caro in obtaining a useful process. The difficulties revolved around the purification of the starting materials, but through their efforts synthetic alizarin was the first major success of the BASF Company. Glaser continued to be associated with Caro for most of the time the pair were with BASF (see below). The alizarin process has importance because its inventors and investigators gave tremendous support to the benzene-ring theory from their extensive studies. This led to the now traditional structural formulae for naphthalene and anthracene. The very early adoption of the benzene-ring theory by German chemists, particularly those involved in solving industrial problems, initiated the long period of competitive advantage held by the German dye and chemical industry.



Scheme 3

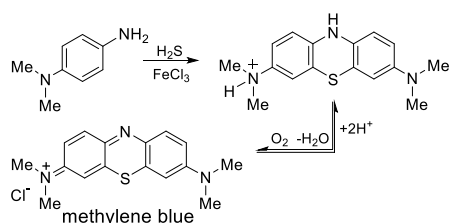
Following the alizarin work, Caro soon developed a fluorescent dye that he named *eosin*. Its origin came from synthetic work by Adolph von Baeyer in Munich that gave fluorescein in 1871. Caro took the Baeyer compound and brominated it to give his new eosin dye the same year

- a tetrabrominated fluorescein (Scheme 4). Some three years later he had modified his process and produced a dinitrodibromo analogue and these are now recognised as eosin Y (yellowish) and eosin B (bluish), respectively (Scheme 4). The following year (1874) saw the discovery of chrysoidine, an orange azo dye (Scheme 4). Although there seems to be some debate on whether it was Caro alone or in collaboration with Otto Witt (working at the Star Chemical Works in Brentford, Middlesex) who made the discovery, it was Witt who commercialised the dye although he did not patent it because the structure was not known. It proved to be the product of simple diazo coupling of aniline to *m*-diaminobenzene following the Griess studies and it marked an era in the azo dye industry (Scheme 4).



Scheme 4

Caro's next success came in 1876 and marks what has to be his major contribution to chemistry, namely the discovery of methylene blue [2,7-bis(dimethylamino)phenothiaz-5-ium chloride; Scheme 5]. It comes as dark green crystals or crystalline powder that has a bronze-like lustre but its solutions in water or alcohol have a deep blue colour. It was prepared by Caro from oxidation of 4-amiodimethylaniline with ferric chloride in the presence of hydrogen sulfide dissolved in hydrochloric acid. It was patented¹⁶ by him for BASF in 1876 and was the first dye from coal-tar patented in Germany. Apart from this, methylene blue has been described as the first fully synthetic drug used in medicine¹⁶ and was pioneered for treatment of malaria. It continued to be used in WWII, where it was not well liked by soldiers who stated: *Even at the loo, we see, we pee, navy blue*. Of note is that the production of blue urine was used to monitor the compliance of psychiatric patients with medication regimes. Antimalarial use of the blue dye has recently been revived but led to interest from as early as the 1890s to the present day in the drug's antidepressant and other psychotropic effects. It became the lead compound in research that led to the discovery of chlorpromazine, a



Scheme 5

dopamine antagonist of the typical anti-psychotic class of drugs used to treat schizophrenia.

The year of 1877 saw Caro develop Fast red A, which was followed by malachite green and rosolic acid (Chart 3). That year he not only co-founded the *Association for the interests of the German chemical industry* (now the German Chemical Industries Association) but he also gained his first honorary doctorate (The University of Munich). By this time he had become friendly with Adolph Baeyer in Munich and both of them began collaborating in the search for a suitable industrial synthesis of the natural dye indigo that Baeyer had prepared in 1870. It is work that was never successful but lasted for many years.

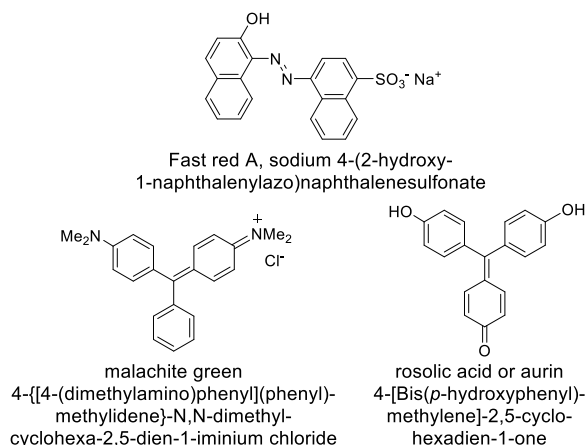
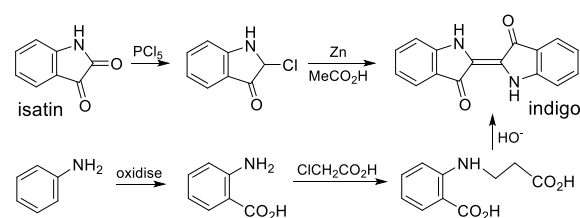


Chart 3

Baeyer recognised the potential of synthetic dyes and from 1865 he searched for a laboratory synthesis of natural indigo. It was extracted from tropical plants in the *indigofera* genus cultivated extensively in India; demand for it was high. Baeyer's success followed his establishment of the structure in 1870 and involved treating isatin as depicted in Scheme 6. However, isatin was too expensive a starting material for commercial synthesis and Caro came to an agreement with Baeyer to collaboratively seek an appropriate industrial process. BASF purchased Baeyer's indigo patent for a substantial sum but nothing that could be used industrially was ever found, despite a further synthesis by Baeyer. The breakthrough came in 1890 when Karl Heumann in Zurich found a way of making indigo from aniline (Scheme 6). A lucky accident at BASF involving a broken thermometer then revealed that mercury was a catalyst for a key part of the synthesis and the German company started production of synthetic indigo in 1897. Johannes Pflieger then discovered a better route to synthetic indigo that involved converting aniline into *N*-phenylglycine, which on fusion with NaNH₂ yielded glyoxyl that oxidises in air to indigo; this was used by BASF's competitor, Hoechst. The dye for blue jeans remains in high demand and is legendary.

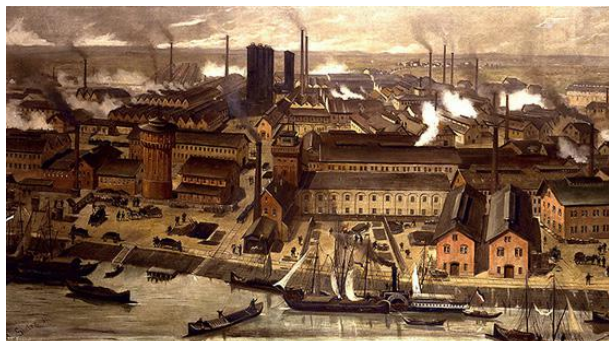


Scheme 6



Indigo cakes by David Stroe (http://en.wikipedia.org/wiki/Indigo_dye#/media/File:Indigo_cake.jpg)

By 1880 Heinrich Caro had become BASF's expert in patent issues and dealt with all such applications. He went on to become a leading spokesman for the German chemical industry, helping to develop patent law to protect chemical inventions. In 1884 he advanced to the BASF Board of Executive Directors. His personal nuances working for BASF have been



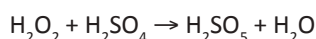
Belching smokestacks at the BASF works in 1881 (courtesy BASF AG)

provided by Carl Glaser and described in some detail by Anthony Travis.² To this author it is clear that Caro and Glaser had very different personalities and their working together for many years must have exacerbated matters between them. Glaser was the (perhaps) typical industrialist who worked regular hours seeing his goal as evolving industrial scale procedures for the company. In contrast, Caro appears to have evolved into an academic seeking new chemicals as well as his famed routes to valuable end products. He was an expert in the laboratory regularly singing when at work, but he became irregular in his work hours and this frustrated the systematic Glaser. Nonetheless, it was Caro who provided BASF in its early years with products and procedures that positioned the organisation as a major player in dyestuffs. It was he whose laboratory became recognised as the first industrial research facility. He had 22 chemists pass through his lab and was responsible for some 22 dye patents, another 8 from other related labs, and an additional 19 company patents that he was involved with. When Caro left BASF there were some 18 small laboratories on the Ludwigshafen site in addition to the newly opened Central Research Laboratory.

Glaser lays much of Caro's success to the persuasion that Englehorn was able to exert on his chief chemist until the latter's departure from the company in 1885. The acclaim that Caro gained has to have substance and, to this author, it seems that Caro's great strength was to see a valuable chemical and then modify the discoverer's synthesis of it to provide a commercially viable process. With the exception of methylene blue and Caro's acid (see below) most of his successes came from such effort, probably with much of his work carried out in his home laboratory in Mannheim. There is little doubt that Caro was responsible for more of Germany's successes in the dye industry than any other individual. Heinrich Caro left BASF at the end of 1889, not long after the Central Research Laboratory that he had designed opened; it became a formal business unit. Heinrich Caro transferred to the BASF Supervisory Board for the rest of his life.

Caro's contribution to the 1890 Kekulé 25th benzene anniversary did not appear until 1891 and was his history of the dye industry over its formative years. This work, now regarded as an epic,¹⁸ provides the most complete coverage of the era. It does this by Caro creating an imaginary dyestuffs manufacturer and describing in detail the operations and developments involved.

The manufacture of alizarin (Scheme 3) by BASF following Caro's initial work for the company required sulfonation of anthraquinone to provide the essential sulfonic acid. Because of this, BASF needed ever increasing volumes of fuming sulfuric acid (oleum). The key suppliers were the vitriol distilleries in Bohemia, who produced the sulfuric acid but they could not keep pace with the rising demand; oleum became scarce and expensive. Although BASF set up sulfuric acid production as early as 1866, it was Rudolf Knietsch, one of BASF's chemists (1884-1906) who developed an economical alternative process in 1888. His sulfuric acid contact process, initially using platinum on asbestos, made BASF the largest sulfuric acid producer in the world at that time. Thus, Heinrich Caro was more than aware of these needs and he experimented with sulfuric acid. However, it was not until 1898 that he published his work on the use of persulfates in the oxidation of anilines and reported on peroxy-sulfuric acid (H₂SO₅).¹⁹ This has become known as Caro's acid and comes from admixture of equimolar quantities of hydrogen peroxide and sulfuric acid:



One of Heinrich Caro's last industrial exploits was the successful production of pure hydrogen. Carl von Linde, the founder of the now multinational industrial gases and engineering company (1879) sought the collaboration of Adolf Frank and Heinrich Caro to find a way to produce pure hydrogen from water gas. The outcome was the 1909 Linde-Frank-Caro method whereby carbon dioxide and hydrogen are removed from water gas by condensation. Invented in 1909 by Adolf Frank, it was developed with Linde and Caro to become the most important method for hydrogen production. It involved water gas being compressed to 20 bar and pumped into a reactor where a water column removed most of the carbon diox-

ide and sulfur. Tubes with caustic soda then removed the remaining carbon dioxide, sulfur, and water from the gas stream. The gas then enters a chamber where it is cooled to $-190\text{ }^{\circ}\text{C}$, thus condensing most of the gas to liquid. The remaining gas is pumped to the next vessel where the nitrogen is liquefied by cooling to $-205\text{ }^{\circ}\text{C}$, leaving hydrogen gas as the end product.

Heinrich Caro was also dedicated to the betterment of science workers and he co-founded the Association of German Engineers in 1856, was a member of the Society of Chemical Industry, and the Society of German Chemists (now the Deutsche Chemisches Gesellschaft) and its chairman from 1898 to 1900. He received honorary doctorates from Munich (1877), Heidelberg, TH Darmstadt and, at the Perkin 25th celebration of mauvine, Leeds (1906). His daughter Amalie put his works in trust as a Special Collection with the Deutsches Museum in Munich (The Caro Nachlass).

There can be no doubt that Heinrich Caro was responsible for more of Germany's successes in the dye industry than any other individual. He died while on holiday visiting Dresden after being in Berlin and he is buried in Mannheim. Being first in the introduction of so many new dyes and cultivating close and fruitful contacts with academic chemists, Heinrich Caro attained almost a mythical status after his death.



Caro's grave in Mannheim (modified from Phaeton1 in Wikimedia Commons)

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Dates of Note

October

21 Georg Ernst Stahl, the German physician and chemist who developed the phlogiston theory of combustion and related biological processes such as respiration, fermentation, and decay, was born in 1660. In 1895, **Carl Linde** reported the production of liquid air for refrigeration and other purposes largely by machinery.

23 Gilbert Newton Lewis, known for his contributions to valence, the covalent bond, and the acids and bases named after him, was born in 1875. It is also the day that **Felix Bloch**, the Swiss-born American physicist who shared (with Purcell) the Nobel Prize for Physics in 1952 for developing nuclear magnetic resonance (NMR), was born in 1905.

25 Edward Robinson Squibb, the American chemist and pharmaceutical manufacturer who improved the purity and reliability of drugs in the mid-19th century, died in 1900.

28 Richard E. Smalley, who shared the 1996 Nobel Prize for Chemistry (with Curl and Kroto) for their joint 1985 discovery of C₆₀, died this day 10 years ago. Today is the 60th birthday of **Bill Gates**, who co-founded Microsoft.

30 Gerhard Domagk, the German bacteriologist and pathologist awarded the 1939 Nobel Prize for Physiology or Medicine for his discovery of the antibacterial effects of Prontosil {4-[(2,4-diaminophenyl)azo]benzenesulfonamide}, the first sulfonamide drugs, was born in 1895. **Gustav Hertz**, the German quantum physicist who (with Franck) received the 1925 Nobel Prize for Physics for their experiment which confirmed that energy can be absorbed by an atom only in definite amounts in accord with the Bohr atomic model, died in 1975.

31 This day marks the birth of three of chemistry's *greats*:

Adolf von Baeyer (1835) was the German research chemist who synthesised indigo (1880), formulated its structure (1883), and was awarded the 1905 Nobel Prize for Chemistry in recognition of his services in the advancement of organic chemistry and the chemical industry.

Sir **William Jackson Pope** (1870) was the English chemist who broadened understanding of stereoisomerism by producing an optically active compound that contained a chiral nitrogen atom (in 1899), but no chiral carbon proving that the Van't Hoff theory applied to atoms other than carbon.

John A. Pople (1925), the British mathematician and chemist who (with Kohn) received the 1998 Nobel Prize in Chemistry for his work on computational methodology to study the quantum mechanics of molecules, their properties, and how they act together in chemical reactions.

It is also the day 100 years ago that English chemist, Sir **Humphrey Davy** patented the miner's safety lamp.

November

1 Carl Alsberg, the American agricultural chemist and authority on the biochemistry of foods, second chief of the Bureau of Chemistry (the FDA from 1927) and the first editor of the *Journal of the Association of Official Agricultural Chemists*, died in 1940, 75 years ago.

2 In 1955, Americans **Carlton Schwerdt** and **Frederick L. Schaffer** crystallised the *polio virus*, the first animal virus so obtained.

3 On this day in 1845, **Michael Faraday** discovered diamagnetism.

5 Edward Lawrie Tatum, the American biochemist who helped create the field of molecular genetics, died in 1975.

8 In 1895, **Wilhelm Röntgen** discovered X-rays during an experiment at Würzburg University.

14 On this day in 1985 the discovery of a fullerene was published in *Nature*. Americans **Robert F. Curl, Jr.**, **Richard E. Smalley**, and **Harold W. Kroto** discovered the first fullerene, C₆₀, in 11 days of research at Rice University in September that year.

17 Nicolas Lémeray, the French chemist and pharmacist who prepared a comprehensive dictionary of pharmaceuticals (*Pharmacopée universelle*:1697; *Traité des drogues simples*: 1698), gave popular lectures on chemistry, and had his textbook, *Cours de chimie* (Paris, 1675) run to 31 editions by 1756, was born in 1645. **August Möbius**, famed for the strip named after him, was born in 1790. Sir **George Thomas Beilby**, the Scot who developed the process of manufacturing potassium by passing ammonia over a mixture of heated charcoal and potassium carbonate in 1890, was born in 1850. **William Merriam Burton**, the American chemist who devised the first thermal cracking process that more than doubled the proportion of gasoline yield from crude oil using high heat and high pressure, was born 150 years ago (1865).

18 George B. Kistiakowsky, the Russian chemist who immigrated to the US in 1926, taught chemistry at Princeton and then Harvard University (1930-71), served as special assistant to President Eisenhower for science and technology (1959-61), and as head of the explosives division of the Los Alamos Laboratory during WWII (1944-46), was born in 1900. In 1970, this was the day that Nobel laureate **Linus Pauling** stated that large doses of Vitamin C could ward off the common cold.

19 Rudolf Fittig, the German organic chemist famous for his extensive work synthesising organic compounds

in the late 19th century, died in 1910.

- 20 Francis William Aston**, the British chemist and physicist who was awarded the 1922 Nobel Prize for Chemistry for developing the mass spectrometer, died in 1945.
- 21 Georgius Agricola**, the German mineralogist and scholar known as *the father of mineralogy* and among the first to found a natural science on observation independent of the theories of the ancients, died this day in 1555. Sir **Chandrasekhara Venkata Raman**, the Indian physicist after whom Raman scattering is named, died in 1970.
- 25 Andrew Carnegie**, the Scottish-born American steel industrialist and humanitarian, was born in 1835. This was the day in 1975 that the first US patent for a *whole-body X-ray scanner* was issued to Robert S. Ledley that revolutionised medical diagnosis.
- 26 Thomas Andrews**, the Irish chemist and physicist who demonstrated the continuity of the gaseous and liquid states, died this day in 1885.
- 27** In 1895, **Alfred Nobel** had his will to establish the prizes drawn up in Paris and then deposited in a bank in Stockholm.
- 30 Henry Taube**, the Canadian-born American chemist and 1983 Nobel laureate for his extensive research into the properties and redox reactions of dissolved inorganic substances, was born this day 100 years ago and died on November 16, 10 years ago. **Nils Gabriel Sefström**, the Swedish chemist who discovered the element vanadium (Va; named after a Norse goddess), died in 1845.

December

- 1 Martin Rodbell**, the American biochemist awarded (with Gilman) the 1994 Nobel Prize for Physiology or Medicine for discovering G-proteins (natural signal transducers) that help cells in the body communicate with each other in the 1960s, was born in 1925.
- 2** This day in 1895, **James Dewar** exhibited his new apparatus for the production of liquid air at the Royal Institution. Sir **William de Wiveleslie Abney**, the English astronomer and chemist who investigated colour photography and colour vision, was the first to take infrared photographs and study the solar infrared spectrum, died in 1920. **Maria Telkes**, the Hungarian-American physical chemist who pioneered the application of solar energy to water distillation and home heating, died in 1995; she was born on December 12, 1900.
- 3 Richard Kuhn**, the Austrian biochemist awarded the 1938 Nobel Prize for Chemistry for work on carotenoids and vitamins, was born in 1900. In 1910, neon lighting, developed by French physicist **Georges Claude**, made its public debut at the Paris Motor Show.
- 5 Clair Cameron Patterson**, the US geochemist who, in 1953, made the first precise measurement of the Earth's age at 4.55 billion years, died in 1995.
- 6 Rudolf Fittig**, who died on November 19 (see above), was born in 1835. Sir **George Porter**, the English chemist awarded the 1967 Nobel Prize for Chemistry (with Norrish and Eigen), for studies of extremely fast chemical reactions using flash-photolysis, was born this day in 1920.
- 7 Walter Noddack**, the German chemist who discovered rhenium (Rh), in collaboration with his wife Ida Tacke, died in 1960.
- 8** Sir **Thomas Edward Thorpe**, the English chemist whose work included the supervision of research into the presence of arsenic in beer and how to make pottery glazes without lead, moved from the Royal College of Science, London (which became Imperial College) to become director of the government laboratories (1894-1909), was born in 1845. Sir **Christopher Kelk Ingold**, the English chemist known for his groundbreaking work in the 1920s and 1930s on reaction mechanisms, electronic structure and the introduction into mainstream chemistry of concepts such as nucleophile, electrophile, inductive and resonance effects as well as descriptors S_N1 , S_N2 , E1, and E2, died in 1970. He also was a co-author of the Cahn-Ingold-Prelog rules.
- 9 Lafayette Benedict Mendel**, the American biochemist whose discoveries concerning the value of vitamins and proteins helped establish modern concepts of nutrition, died in 1935.
- 11 Charles Frederick Cross**, the English chemist who, with Bevan and Beadle, discovered that cellulose could be produced by the dissolution of cellulose xanthate in dilute sodium hydroxide, was born in 1855.
- 12 William Henry**, the English physician and chemist who in 1803 proposed what is known as Henry's law, was born in 1774.
- 13 John Pell**, the English mathematician who introduced the division sign (the obelus, \div) into England, died in 1685. **Johann Wolfgang Döbereiner**, the German chemist who recognised the chemical triads as consecutive members of the groups of the periodic table, e.g. lithium, sodium, and potassium; calcium, strontium, and barium; chlorine, bromine, and iodine, was born in 1780.
- 13 Charles Alfred Coulson**, the British theoretical chemist known for applying molecular orbital theory to chemical bonding, the electronic structures of molecules and the concept of partial valence, was born in 1910. **Fritz Pregl**, the Austrian chemist awarded the 1923 Nobel Prize for Chemistry for developing the microanalysis of organic compounds, died in 1930. **Victor Grignard**, the French chemist and co-recipient (with Sabatier) of the 1912 Chemistry Nobel Prize for his Grignard reaction, died in 1935, 80 years ago.

- 15 Sir **Ernest Marsden**, the British-born New Zealand nuclear physicist who worked under Rutherford investigating atomic structure and became a founder father of the sciences in this country, died in 1970.
- 18 Sir **Henry Enfield Roscoe**, the English chemist who founded the Manchester school of chemistry and led chemical education in England for many years after he became professor of chemistry at Owens College in 1857, died this day 100 years ago.
- 19 **Alois Alzheimer**, the German psychiatrist who recognised the disease named after him, died 100 years ago.
- 20 **Jaroslav Heyrovský**, the Czech chemist who received the 1959 Nobel Prize for Chemistry for his discovery and development of the polarographic methods of analysis, was born 125 years ago (1890).
- 21 **Thomas Graham**, the Scottish chemist and father of colloid chemistry who studied the diffusion of gases and in 1833 proposed Graham's Law, was born this day in 1805.
- 26 **Ernst Felix Hoppe-Seyler**, the German physician and pioneer of physiological chemistry (biochemistry) from studies of the chemicals of blood and urine using the then new technique of absorption spectroscopy, prepared haemoglobin in crystalline form and clarified its role in red blood cells, was born in 1825.
- 27 Ether was first used as an anaesthetic in childbirth in 1845.
- 29 **Charles Goodyear**, the American inventor who baked rubber mixed with sulfur and discovered the vulcanisation process, was born in 1800.
- 31 The game of *Monopoly* was patented in 1935.
- 7 **John Ernest Walker**, the Britton who won a share of the Nobel Prize for Chemistry in 1997 for his pioneering work on how the enzyme ATP synthase catalyses formation of ATP, has his 75th birthday today.
- 9 This day in 1816 saw Sir **Humphry Davy's** safety lamp used in a coal mine for the first time.
- 10 **Sune K. Bergstrom**, the a Swedish biochemist who shared the 1982 Nobel Prize for Physiology or Medicine, (with Samuelsson and Vane) for the isolation, identification, and analysis of prostaglandins and related biologically active substances, was born 100 years ago today.
- 11 **Albert Hofmann**, the Swiss pharmacologist who discovered LSD, was born in 1906. In 1911 the forerunner of the present **Max Planck Society**, the **Kaiser Wilhelm Society for the Advancement of Science** was founded in Berlin. In 1939, the element francium (Fr) was discovered.
- 12 **Antonio de Ulloa**, the Spanish scientist and naval officer who discovered the element platinum (Pt), was born in 1716, 300 years ago. **Ruth R. Benerito**, the American chemical pioneer of wash-and-wear fabrics and holder of over 50 patents, was born 100 years ago today. **William Hewlett**, who co-founded the Hewlett-Packard Company, died in 2001.
- 15 **Henry Livingstone Sulman**, the British metallurgist and one of the originators of the froth flotation process for concentrating ores prior to the extraction of metal, was born in 1861.
- 16 **Charles Thurstan Holland**, the English radiologist who pioneered the clinical use of X-rays in the UK, died in 1941. **Nicolas Leblanc**, the French surgeon and chemist who developed a process for making soda ash (Na_2CO_3) from salt, died in 1806.

January

- 1 In 1896, German scientist, **Wilhelm Röntgen** announced his discovery of X-rays and in 1916 blood that had been stored and cooled was used for the first time in a transfusion.
- 4 **Benjamin Rush**, the American physician best known as a signer of the Declaration of Independence was a prominent US physician and the first professor of medical chemistry in the US; he was born in 1746. **Erwin Schrödinger**, the Austrian theoretical physicist best known for the equation named after him, died in 1961.
- 5 **Harold C. Urey**, the American awarded the Nobel Prize for Chemistry in 1934 for his discovery of deuterium, died in 1981.
- 6 **Étienne-François Geoffroy**, the French chemist and first to recognise the relative fixed affinities of reagents for one another, died in 1731. It was the day in 1851 that the rotation of the earth was proved experimentally by **Leon Foucault**.
- 17 **Robert Hare**, the American chemist who devised the first oxy-hydrogen blow torch, was born in 1781. **Richard Lower**, the English physician and physiologist who was the first to transfuse blood (from one dog to the veins of another) in 1665, died in 1691.
- 18 **Hans Goldschmidt**, the German chemist who invented the thermite (aluminothermic) process, was born in 1861.
- 21 Magnesium was first produced commercially in the US 75 years ago (1941) by the Dow electrolytic process.
- 23 **Karl Karlovich Klaus** (Claus) the Russian chemist and biologist who discovered ruthenium (Ru) in 1844, was born in 1796. **Otto Diels**, the German organic chemist who was awarded (with Alder) the Nobel Prize for Chemistry in 1950 for the cycloaddition reaction named after them, was born in 1876. In 1911, **Marie Curie's** nomination to the French Academy of Sciences was voted down by the Academy's all-male membership despite having already won one Nobel Prize.

Trying to find certainty in an uncertain world

Katherine Hebditch, Harriet Sandstad

Baldwins Intellectual Property, PO Box 5999, Wellesley St, Auckland
(email: katherine.hebditch@baldwins.com)

Innovators working in patentable areas of technology, like chemistry, often face uncertainty about the scope of other people's patent rights – whether there is “freedom to operate” or FTO. FTO is the ability to carry out your activities without infringing other people's rights, particularly patent rights. It can be achieved in different ways, for example through an agreement with the rights holder, by making sure your activities avoid infringement, or by successfully challenging the patent rights.

There is a particularly high degree of uncertainty when a patent application has been published but is not yet granted. Once a patent application is published, monetary damages for infringement can in some cases be calculated back to the publication date. However, the scope of the eventually-granted patent claims may, in some cases, be different to those that were published in the patent application. So, even if a patent is not granted yet you could be liable for damages for infringement when it does grant. In this case, the activities that will actually constitute infringement may be unclear.

What is clear is that it can be difficult to make business decisions in the face of this uncertainty!

This article looks at some of the options for challenging a patent application under the new New Zealand Patents Act 2013 before it grants, with a focus on those options which could be used to gain more certainty during examination. There are options for challenging a granted patent application, which will be the subject of an upcoming Patent Proze article. It is usually preferable to use pre-grant proceedings if possible because (among other things) you cannot be sued for infringement until the patent grants.

Requesting examination - of someone else's application

The new Patents Act 2013 requires applicants to request examination of their application (under the previous Patents Act 1953 examination was automatic). The new Act allows the Intellectual Property Office of New Zealand (IPONZ) to direct an applicant to request examination, and also gives third parties the ability to ask IPONZ to make the direction. If an applicant does not comply with a direction, the application will be abandoned.

In effect, therefore, you can ask IPONZ to direct examination of someone else's application if you want to know what the granted claims will be sooner rather than later. It is also possible the applicant will not want to continue with the application, and may abandon it rather than request examination – thus removing the potential FTO issue altogether.

However, the downside of this option is that the pat-

ent claims may be granted sooner rather than later. This means that if you infringe the granted claims the patentee would be able to take infringement action against you sooner.

Asserting your views during examination

Under the 2013 Act you can file “third party assertions” on the novelty and inventiveness of a published patent application that is being examined by IPONZ.

Ideally, the patent examiner would find all relevant information that would help him or her decide whether an invention is novel and inventive, and therefore whether a patent should be granted. However, this is not always the case. It may be that scientists actively working in the field of the invention have better knowledge of whether something is new and whether it is a significant advance over what is already known.

Anyone can file third party assertions consisting of written submissions providing the reasons that the invention is not novel or inventive, together with copies of any relevant documents demonstrating this. The examiner considers this information as part of the normal examination process. Third party submissions can be an attractive option if you are aware of information in the public arena that is relevant to the claimed invention.

Like any challenge proceeding, filing third party assertions has both pros and cons. On the “pro” side, it is cost-effective compared to other challenge procedures and any information brought to the attention of the applicant in New Zealand may have to be disclosed to other patent offices around the world. For example, in the United States there is a duty to disclose any relevant information to the patent office. This could influence the overseas examiner's opinion on the patentability of the invention.

On the “con” side, third party assertions are restricted to submissions on novelty and inventive step. Other procedures (discussed below) include additional ways to challenge a patent application which, depending on the circumstances, may be more relevant. Furthermore, the third party making the assertions is not involved in the process beyond filing the submissions. In contrast, the patent applicant will be able to have a dialogue with the examiner to argue why the assertions in the submissions are not relevant.

The patent applicant will also have the opportunity to amend the claims of the application to overcome the issue(s) raised in the assertion. Ideally, these amendments would achieve the practical result you are looking for, i.e. that your activities would no longer infringe and you would have FTO. However, there is a chance that the applicant would be able to amend the patent claims to overcome the issue(s) and still capture your activities.

Re-examination: worth another go?

Once IPONZ is satisfied the claims meet patentability requirements, the application is “accepted”. Acceptance is published and third parties can challenge the accepted application through opposition proceedings (discussed below) or by requesting that the application is re-examined. You can also request re-examination of a granted patent application.

Re-examination is based on written submissions. It has some similarities to filing third party assertions, and therefore has similar benefits and risks. However, with re-examination the challenger can rely on extra grounds to lack of novelty and inventive step. For example, you could request re-examination on the basis that the patent application is not clear or complete enough for the invention to be performed. IPONZ only re-examines patent applications if the examiner believes the issues raised by the challenger have merit. It is important to be careful when deciding to use re-examination to challenge a patent application or granted patent because doing so may prevent access to other challenge procedures. This could be a significant business risk.

The procedural rules for re-examination, including the fact that the party requesting re-examination is not involved in the process beyond filing its initial submissions, mean that the re-examination process is loaded in favour of the applicant. Re-examination may be appealing because it is relatively low cost. However, the risks associated with it mean it is best suited to very clear cases.

Opposing grant

In addition to challenging a potentially problematic accepted patent application by requesting re-examination,

you can also file an “opposition” against its grant. The outcome of oppositions is decided by IPONZ. In most cases, an opposition is likely to be considerably more costly than re-examination. However, as the challenger you have the advantage of the broader grounds available and are also involved throughout the opposition. This means you get a chance to present a counter-argument to any arguments the patent applicant makes, and also have the option to appear at an oral hearing.

During opposition the patent applicant will have the opportunity to amend the claims to overcome any issues raised. As part of these proceedings the parties will often come to an agreement on acceptable amendments so that the challenger gains FTO while the applicant/patentee retains some rights, or alternatively the parties may come to an agreement allowing the challenger to enter or stay in the market.

Consideration of competitor’s rights and your FTO is a challenge that many innovators have to address. Amicable agreements (and even productive joint ventures) are often the best outcomes. However, being aware of the options to challenge patent rights and their likelihood of success is an important part of a complex equation.

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

katherine.hebditch@baldwins.com or harriet.sandstad@baldwins.com



Katherine Hebditch of Baldwins Intellectual Property in Auckland specialises in chemistry and biotechnology patents. Katherine obtained her PhD in organic chemistry from the University of Manchester in the UK in 2004. She is currently working towards registration as a patent attorney. Harriet Sandstad of Baldwins Intellectual Property in Auckland specialises in patents; her main practice areas are biotechnology, agricultural technologies, and animal and human health. Prior to joining the firm in her current role Harriet completed her Masters degree as an intern in Baldwins’ specialist biotechnology patents team. Harriet’s research focussed on intellectual property strategy in early stage biotech companies. Harriet is currently working towards registration as a patent attorney.



Dr Alistair Campbell

The Lincoln University community, including the vast network of international alumni, will be saddened by the death of retired Associate Professor of Soil Science Dr Alistair Campbell, who died in Christchurch on Saturday 3 October 2015.

Dr Campbell was on the staff at Lincoln University for 44 years, 1959-2003, and on retirement was the longest-ever serving staff member.

Soil mineralogy and chemistry were his academic areas but his service to Lincoln University extended far beyond the classroom and laboratory. In sport he was long associated with the Soccer XI as player and club official. In staff welfare and relations with management he was a respected tertiary teachers' union representative and advocate. In campus cultural life he is well remembered for helping to organise and MC International Night for many years and his involvement with capping concerts.

Alistair was legendary for his international network of friends and contacts and he gave superlative service to Lincoln University maintaining overseas links, particularly in South East Asia and among former Colombo Plan students. For this work he was awarded a Lincoln University 125th Anniversary Medal. His generous help and sup-

port for students in general, especially in extra tutoring of chemistry, carried out in his own time, free of charge, was another facet of his dedication to the life of the University.

Beyond the University, Alistair was fully involved with the community of Lincoln township, where he lived. This included editing the Community Newsletter, service on the local historical society and above all serving on the Lincoln Community Committee.

In all of this work Alistair was loyally helped and supported by his wife Pat, herself a PhD graduate and Lincoln staff member of 31 years standing. They were a close team, involved fully in the academic and community life of Lincoln University and beyond it Lincoln township. The University's sympathy goes out to Pat at this sad time.

Alistair came to Lincoln University from Dunedin where he had his secondary education at King's High School (1949-1953) and graduated MSc from Otago University. He completed a PhD in Soil Science under Professor TW Walker in 1975 while a member of Lincoln's Soil Science staff. He retired in 2003 as an Associate Professor.

John Hay

Interim Vice-Chancellor, Lincoln University

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