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Comment from the President



By the time that you read this, you will no doubt have received your annual subscription notice for membership of the Institute. At the recent NZIC Council meeting, it was decided not to raise membership subscriptions this year. Membership of the Institute therefore represents excellent value for money, especially for students, who can also apply to their Branch for travel grants to attend conferences.

One way in which you can assist the Institute is to publish your research in either *Chemistry – An Asian Journal* or *Physical Chemistry Chemical Physics (PCCP)*. NZIC is now one of thirteen partner societies that together comprise the Asian Chemical Editorial Society (ACES), which publishes *Chemistry – An Asian Journal*. The journal covers all aspects of chemistry from biochemistry through organic and inorganic chemistry to physical chemistry, including interdisciplinary topics. *Physical Chemistry Chemical Physics (PCCP)* is owned and run by sixteen chemical societies (including NZIC), is published by the Royal Society of Chemistry and covers the fields of physical chemistry, chemical physics and biophysical chemistry. As partners and owners of these journals, the NZIC receives a royalty every time the journal publishes an article by a New Zealand based researcher so I strongly encourage members to consider these journals when it comes to publishing their work.

For our student members, I would also like to highlight the Reaxys Australasia Chemistry Challenge. This chemistry challenge is opened to all Bachelor of Science (BSc) and

Master of Science (MSc) students who are currently studying in universities in Australia and New Zealand, majoring either in chemistry or in related programmes such as chemical engineering or pharmacology. There are excellent cash and travel prizes to be won and further details can be found on the official webpage <http://asia.elsevier.com/AustralasiaChemistryChallenge>

Finally, Council and the new editorial team are putting some thought into the future direction of *Chemistry in New Zealand* so a survey is being conducted on Institute members' opinions of the current format and content of the Journal. A print version of the survey appears elsewhere in this issue and a web-based/email-based version will soon be available. It is your journal and your Institute so please take the opportunity to fill in the short survey and share your thoughts.

Michèle Prinsep
NZIC President



From the Editor



In the last issue I mentioned that I would like to encourage feedback on the format and content of *Chemistry in New Zealand*. This is being taken a step further in the form of a short reader survey which you will find on page 95 of this issue. It has been designed to be as quick and easy to complete as possible while still being comprehensive enough to enable responses to be used to direct the future of our publication. The survey will be made available to NZIC members online and via email shortly after this issue of the journal has been published. Alternatively, you are welcome to complete the printed version and return a paper copy by post. I would really encourage you to participate as this is the only way we can find out what you really think about the journal. Results will be made available in a future issue.

Staying on the theme of reader feedback and involvement, I am keen to promote discussion and debate of journal articles

and submission of unsolicited material. If you feel compelled to contact an author after reading an item, please also consider sending any correspondence to me so that it can be published as a Letter to the Editor. If you have an idea for a piece that you think would interest members, please get in touch - you do not have to wait to be asked by your branch editor to contribute! And although scientific articles published in *Chemistry in New Zealand* are not peer-reviewed, they can still be included in formal assessments of research outputs, for example in PBRF portfolios. It is also a useful way for students to gain experience in writing and publishing papers.

Several updates have recently been made to the NZIC website which are relevant to *Chemistry in New Zealand*. These include the publication schedule, deadlines for copy, author guidelines and branch news for the current quarter. Articles appear on the site six months after publication. Many thanks to our webmaster, Tim Allison, for this. If you have not visited the website recently, you might like to take a look at it (<http://nzic.org.nz>) and perhaps even provide some feedback on that too!

Catherine Nicholson

New Zealand Institute of Chemistry

supporting chemical sciences

April News

AUCKLAND

The Auckland Branch held its AGM in November 2013 and planned several activities for the year ahead including two events centered on postgraduate students. Associate Professor **Gordon Miskelly** has taken over the role of the Branch Chair from Dr **Viji Sarojini**.

The Auckland Branch sponsored three student prizes at the very successful 12th International Conference on Frontiers on Polymers and Advanced Materials (ICFPAM) which was organised by Professors **Jadranka Travas-Sejdic** and **Paul Kilmartin** at Auckland in December 2013.



NZIC student prize winners at the 12th ICFPAM with Viji Sarojini

School of Chemical Sciences, University of Auckland

Awards, promotions and appointments



Professor Kevin Smith

Professor **Kevin Smith** took over the Head of School of Chemical Sciences in January. Professor Smith did his undergraduate education at the University of Dublin, Trinity College and postgraduate education at Yale. Before joining SCS, he was Professor of Physics, Chemistry and Materials Science at Boston University. His research interests revolve around the electronic structure of complex materials using synchrotron radiation-excited photon and electron spectroscopies. Professor Smith was the founding Academic Director of

the Center for Excellence in Teaching at Boston University, recipient of the Boston University Prize for Excellence in teaching and was named as the 2001 Massachusetts Professor of the Year by the Carnegie Foundation for the Advancement of Teaching. He was also the Academic Director of BU's Trustee Scholar's Program and the chair of BU's Natural Sciences Curriculum Committee.

The School is proud to have three of its excellent academics promoted to the rank of Professor in 2014. Our new Professors are **James Wright**, **Jadranka Travas-Sejdic** and **Paul Kilmartin**.

Congratulations to **Mike Wadsworth** who has been successfully nominated for the Emerging Leaders 2014 programme.

Science redevelopment: new teaching labs and research facilities

The major science redevelopment plan is progressing fast and will provide state of the art research and teaching facilities for the Faculty of Science. One of the initial projects in this plan was refurbishment of chemistry undergraduate teaching laboratories, which successfully completed one full year of operation providing advanced laboratory teaching experience for our students. The state of the art labs were also handy to temporarily house the research laboratories during summer holidays while their labs were being worked on.

The School of Chemical Sciences at the University of Auckland has opened its new mass spectrometry facility. It is equipped with a range of complementary mass spectrometers such as ESI-qToF, ICP-MS and GC-MS. Furthermore, different sample introduction systems are available ranging from laser ablation and capillary electrophoresis to liquid chromatography.

The School's newly acquired Bruker



Professors Wright, Travas-Sejdic and Kilmartin

AVANCE III HD 500 MHz NMR spectrometer will be available for both solid-state and solution-state NMR experiments.

The combined X-ray facilities of the Schools of Chemical Sciences and Environment have a new PANalytical – Empyrean powder diffractometer and a new PANalytical Axios WDXRF spectrometer. The powder diffractometer is equipped with a high vacuum/high temperature setup as well as a capillary setup for small samples.

International symposium on minerals and dairy products

Associate Professor *Yacine Hemar* organised the successful 2nd International Symposium on Minerals and Dairy Products (26-27 February, 2014) in partnership with the Science and Technology of Milk and Eggs research unit of the National Institute of Agricultural Research (INRA at Rennes, France) and the Institute of Food, Nutrition, and Human Health at Massey University. This international symposium brought together the latest scientific and industrial developments in the area of milk minerals and mineral-fortified dairy products.

The New Zealand Institute of Advanced Study, Massey University, Auckland

Sciences at the Albany Campus have seen a large increase in student numbers with a significant first year enrolment for the new chemistry major. A new lecturer position in organic chemistry is to be advertised. It is anticipated that we have a full chemistry section in place by 2016 with a new science building ready on the West Precinct of the Albany Campus.

The Theoretical Chemistry and Physics Research Centre published its annual report (see <http://ctcp.massey.ac.nz>). 2013 was a particularly successful year with over 40 papers published in top international journals such as *Physical Review Letters*, *Angewandte Chemie* or *Nature Chemistry*. The research centre has now moved into the new Bob Tindall Building on the Oteha Rohe side. The CTCP Computer Cluster will be

upgraded in steps starting in 2014 totalling more than \$NZ 1 million to support the large computational community at the Albany Campus. The machine can be used free of charge (!) by all Massey staff.

Elke Pahl received the Massey University Women Award for her outstanding contributions to the Monte-Carlo simulation of melting processes. The group of *Peter Schwerdtfeger* landed a title page in the January issue of the ACS journal "Journal of Chemical Information and Modeling" on Goldberg-Coxeter Transforms of Fullerenes. Peter attended the ACS spring meeting in Dallas to report on new progress in superheavy element chemistry. He is also organising a conference in Cadiz (Spain) on "Cluster and Solid-State Chemistry and Physics" (July 2014) and on "Relativistic Effects in Heavy Elements" in Smolenice, Slovakia (September 2014).

CANTERBURY

The NZIC Canterbury Branch AGM was held on Thursday 13th February. Retiring committee members *Paul Kruger*, *Francine Smith*, *Jayne Gulbransen* and *Rossana Archer* were thanked for their years of hard work. Sarah Masters was welcomed to the committee and the following people elected or re-elected to various posts: *Michael Edmonds* (NZIC Branch Chair, Council Delegate, Chemical Education Group Representative), *Darren Saunders* (ESR, Co-Treasurer, Branch Editor), *Sandra Atkinson* (UC, Secretary (joint), Student Representative), *Emma Livingston* (UC, Secretary (joint), Student Representative), *Andy Pratt* (UC, Events Publicity/Coordinator), *Jan Wikaira* (UC, Student Liaison Representative), *Graham Townsend* (UC), *Sarah Masters* (UC).

University of Canterbury

Awards

The Department of Chemistry extended congratulations to three chemists closely associated with it. *Professor Vickie McKee* of Loughborough University, UK, has recently completed a Velux Fellowship in Odense with *Christine McKenzie* and

Raewyn Town. *Professor Mark Turnbull*, Clark University, Worcester, MA, has been appointed to the Carl J. and Anna (Kranz) Carlson Chair of Chemistry at Clark and *Professor Ray Butcher*, Howard University, Washington, D.C., published his 1000th paper in 2013.

Prof Butcher, co-editor of *Acta Crystallographica E* and recipient of two Fulbright scholarships, has published 1006 articles since 1975. His most prolific production has been in the years since 2007, a period when he produced between 60-100 articles per year. Butcher, a native of New Zealand, began his career in 1974 at the University of Virginia as a chemistry instructor where he was awarded the Sigma Xi Visitors medal for Outstanding Research. A year later, Butcher joined Howard as an associate professor in the Department of Chemistry.

When Butcher was first awarded the Fulbright International Scholarship in 1989, he used the opportunity to establish relationships with local scientists. When he was once again awarded a Fulbright-Nehar scholarship in 2009 to teach in India, he formed even more professional relationships. These relationships with local scientists have proved to be fruitful, allowing him to co-author more than 500 publications with Indian scientists. Earlier in 2013 Butcher returned from India where he worked as a visiting professor at the Indian Institute of Technology.

Butcher earned his Bachelor of Science Degree, with honours, from the University of Canterbury, Christchurch, New Zealand and also earned his doctorate from the school.

Best poster prize

Lita Lee (Downard research group) won a best poster prize at the International Society of Electrochemistry Satellite Student Regional Symposium in Melbourne (25-26 November 2013).

UC chemistry student awarded internship at Douglas Pharmaceuticals.

James Butcher was awarded a summer internship at Douglas Pharma-

ceuticals based in Auckland. Douglas Pharmaceuticals was very impressed with James who received a stipend from Callaghan Innovation. He gained practical training and help in the evaluation of the performance of new products under development.

Winner of award for Best Student Talk at MacDiarmid Symposium

The MacDiarmid Institute Postgraduate Symposium is an annual meeting of MacDiarmid Institute Investigators and their post-docs and students. This year the meeting was held in Wellington and the theme was *Spreading the Word*: communicating your science both to your peers and to the public. **Jan-Yves Ruzicka** presented his work at the symposium and was honoured with an award for the best student talk. Jan-Yves states, "I now wish I'd applied to talk at previous symposia: not only is it good practice for presenting your work to the public, but it makes you stand out from the crowd. Attendees know who you are and what you do, and are much more likely to approach you and ask questions or even just introduce themselves."

RACI NZ representative

During the December meeting of the Inorganic Division of the Royal Australian Chemical Institute (RACI) at the University of Queensland, Professor Paul Kruger was elected to serve as the New Zealand representative on the committee of the Inorganic Division of the RACI.

MANAWATU

The Manawatu Branch hosted a student information evening in March following the success of a similar event last year. At the event, prizes for the highest achieving final-year undergraduate students were awarded to **Leonie Etheridge** from Massey University, and **Minen Su** from UCOL. Upcoming events for this year include a technician's information evening and an industry tour, the timing of which is yet to be confirmed.

Congratulations to **Luke Liu** who, as the Manawatu Branch representative, took out the student speaker competition at the NZIC 2013 conference in

December last year.

Landcare Research

Benny Theng and wife, Judy, have recently returned from an enjoyable and profitable 11 weeks visit to China by invitation from Dr Hongping He of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS). While there, Benny gave a series of lectures on the clay-polymer interaction but for most of the time he was helping postgraduate students write manuscripts for publication in international journals. Benny and Judy made a brief stopover in Yantai (Shandong province) to see Dr Guodong Yuan who left Landcare Research, Palmerston North, in July 2013 to take up a professorship at the Institute of Coastal Zone Research, CAS. They also had the opportunity to visit Huangshan (Yellow Mountain) in Anhui province, and admired the iconic scenery of granite peaks, deep gorges, cliffs, and clinging pine trees, depicted in many classical Chinese scroll paintings. Another memorable occasion was the 3-day trip to Xiamen, a port city in Fujian province from where Benny's great grandfather was presumed to have sailed to Java in the 1840s.

Massey University, Institute of Fundamental Sciences

Summer students who have completed their projects include **Nina Wan Ahmad Nizar** and **Joseph Corrigan** who were working with **Paul Plieger** on quino-quinoline derivatives for supramolecular applications, and beryllium binding respectively.

Paul Plieger and 3rd year PhD student **Nirosha De Silva** recently attended SANZMAG in Sydney. This was a joint Southampton-Australia-New Zealand workshop on molecular magnetism.

Shane Telfer attended the IC13 conference in Brisbane in December, where he gave a talk on Programmed Pore Architectures in MOFs.

Mark Waterland attended the 38th annual Condensed Matter and Materials Meeting on Waiheke Island in early February, and presented some preliminary results on graphene nanoribbons.

He also spent two weeks in Bangalore at the beginning of March funded by a New Zealand India Studies grant visiting the laboratory of Prof Siva Umaphathy, working with the Umaphathy group on pathohistological applications of Raman microscopy.

Mark Waterland and **Adrian Jull** have been hosting Palmerston North Boys High School teachers and students, conducting workshops on the new NCEA Level Achievement Standard 3.2 that introduces students to spectroscopic analysis of organic compounds.

Shaune Blackwell completed her PGDipSci in February working with **Mark Waterland** and **Jasna Rakonjac**, using self-assembling bacteriophages that bind gold nanoparticles to develop a nanostructured platform for SERS and other plasmonic applications. Shaune will be starting PhD studies later in 2014.

Recent talks at Massey University have included **Romarc Vincent** who talked about *Self-rheology of cell monolayers*, and **Shaune Blackwell**, who gave a presentation on results from her PGDipSci, titled *Creating a Surface Enhanced Raman Spectroscopy probe with a nanophage platform*.

OTAGO

University of Otago, Department of Chemistry

A large contingent of staff and students from the Department attended the IC'13 Inorganic Chemistry Conference in Brisbane during December 2013. In addition to keynote talks from **Sally Brooker**, **James Crowley** and **Nigel Lucas**, Crowley group PhD student **Jamie Lewis** spoke as a finalist for the Don Stranks Awards, which he went on to win. Also successful was **Tae Kim** (Lucas/Crowley groups) who received one of two student poster prizes.

Guy Jameson presented at SANZMAG-1, the 1st Southampton-Australia-New Zealand Workshop on Molecular Magnetism, held in Sydney between 17-28 February. Guy explained the basic theory of Mössbauer spectroscopy and provided



Previous and current Brooker's Bunch members, left to right: Paul Plieger (Massey), Sally Brooker (Otago), Jon Kitchen (Southampton), Reece Miller (Otago) and Jason Price (Australian Synchrotron), at the SANZMAG conference, Sydney, Australia, 17-20 February 2014.

some guidance on sample preparation. Jameson group PhD student *Casey Davies* published his first paper (Widger, Davies, *et al.* *J. Am. Chem. Soc.* **2014**, *136*, 2699–2702: *Dramatically Accelerated Selective Oxygen-Atom Transfer by a Non-heme Iron(IV)-Oxo Complex: Tuning of the First and Second Coordination Spheres*).

Also presenting at the SANZMAG meeting was Sally Brooker who gave an invited tutorial on spin crossover with thermal hysteresis. Her PhD student *Reece Miller* also gave an invited lecture, on predictable tuning of spin crossover temperature by ligand modification. It was an excellent meeting, made even more enjoyable for Sally by the reunion of a small number of previous research group members (see photo). Brooker's Bunch has recently expanded, with new PhD students *Santiago Rodriguez* (Barcelona) and *Ross Hogue* (Otago) who started on 1 February, and Honours student *Hannah Davidson* who started in mid-February.

Garon Smith, a Professor of Chemistry at The University of Montana in Massoula, has been visiting the Department since January, hosted by *Dave Warren*. Garon, under the guise of Garon the Wizard (G. Wiz), has been conducting outreach activities around New Zealand and during April-June is based at the University of Waikato.

Lars Stevens-Cullinane has completed a Plant & Food Research summer studentship under the supervision of *Bill Hawkins* and *Nigel Perry*. Lars synthesised analogs of the strigolactones, a recently discovered class of plant growth hormones with potential agrochemical applications. Active analogs were tested by plant biologists and biochemists at Plant & Food Research Mt Albert, in Auckland. Summer studentships are offered for research projects at Plant & Food Research centres all around New Zealand. The benefits include generous pay and a two day leadership training course in Auckland. In the summer of 2013-14, 45 students were employed, including another from University of Otago Chemistry: *Alistair Richardson* worked on tomato pigment analyses at Palmerston North.

WAIKATO

The Waikato Branch Committee for 2014 is as follows:

Chairperson: Michael Mucalo

Treasurer: Michael Mucalo

Secretary: Wendy Jackson

Council Delegate: Jo Lane

Chemistry Education Group Representative: Jo Lane

Student Representative: Maria Revell

Student Liaison Representative: Bill Henderson

Branch Editor: Michèle Prinsep

Committee Members: Megan

Grainger, John McDonald-Wharry, Raymond Onyekachi

University of Waikato

Emeritus Professor *Richard Field* from the University of Montana visited the university from February to mid-April to work alongside *Megan Grainger* in a continuation of work simulating the conversion of dihydroxyacetone to methylglyoxal in manuka honey. While at Waikato, Richard also delivered lectures in the Master's Physical Chemistry course.

Undergraduates *Nicholas* (Nick) *Kuan* and *Jain Abraham* have been working in the department over summer, assisting two doctoral students. Nick has been working with Megan Grainger on validating a new method for analysis of dihydroxyacetone in honey and comparing it to established methods and Jain has been working with *Maria Revell*, investigating dihydroxyacetone in manuka leaves and flowers.

Michael Mucalo will be going to ANSTO in Sydney as part of an AINSE-funded project involving NAA analysis of metal catalysts which is an integral part of his student *Jacob Jaime's* PhD project. Michael Mucalo acquired AINSE funding for this purpose last year and both will be collaborating with Dr John Bennett, Head of the Centre for Nuclear Applications in ANSTO, Lucas Heights.

Prajusha Velayudhan successfully completed her MSc with Michael Mucalo on a project investigating domestic pottery and ceramics from Victorian times to the present day. Prajusha currently works for Fonterra in the Waikato area. Over the summer, Michael supervised BSc(Hons) student *Richard Brunton* who continued Prajusha's research as part of a summer project, as well as graduate *Adrian Owens* who did some work on calcium phosphate and other inorganic chemistry.

Michael Mucalo's position of Chairperson of Chemistry concluded at the end of March 2014.

WELLINGTON

Two Callaghan research teams have been transferred to Victoria Univer-

sity. The carbohydrate chemistry team, led by Dr *Richard Furneaux*, has morphed into the Ferrier Research Institute, while the superconductivity and energy team, led by Dr Bob Buckley, is now the Robinson Research Institute. The new University institutes remain at their current Gracefield location and continue to offer the same services, delivering on existing contracts.

Prof *Roy Tasker* (Science and Health, University of Western Sydney) gave the first Branch lecture of 2014 on February 13. It followed his one day teachers' symposium at Victoria University. He spoke on *Research into Practice: visualizing the molecular world by combining simulations with animations in a sustained teaching approach* and explained how the difficulty in teaching chemistry could stem from students' difficulties in grasping the link between the molecular world and the symbolic representations taught in undergraduate courses.

NZIC Tertiary Chemistry Teaching Symposium

The 6th annual Tertiary Chemistry Teaching symposium was held at Victoria University again this year and organized by Dr Suzanne Boniface. The invited speaker was *Roy Tasker* (Professor of Chemistry Education, University of Western Sydney), whose primary teaching responsibilities are in first year chemistry. His research interests are in *how* and *what* students learn using interactive multimedia resources. He has produced a suite of molecular-level animations in a collaborative *VisChem* project, and from research with students he then developed a best-practice strategy to use these animations to assist students to build their own mental models of the molecular world, and

understand chemistry in a deep way. Roy was an inspiring speaker and shared a number of resources that could make a difference to student learning in our chemistry courses. The symposium was attended by teachers of first-year courses from most NZ universities and there were a number of thought provoking and interesting presentations providing insight into student learning. There was some discussion about the future of a National Chemistry Quiz and it was decided to offer instead an alternative competition for senior chemistry students based around chemistry in their local community. A national crystal growing competition for school students will also be run to mark International Year of Crystallography.

Victoria University - SCPS

Drs *Bridget Stocker* and *Mattie Timmer* explained the basics of sugar (and sweetness!) on the *This Way Up* programme on Radio NZ National radio in late January. Mid-February saw the SCPS welcome *Brendon Monk* (Head of Science at Paraparaumu College) to his RSNZ sponsored sabbatical. He is working with *Rob Keyzers* and *Peter Northcote* until mid-year looking at the use of organic spectroscopy in drug discovery from New Zealand marine algae.

Masters student *Shyamal Prasad* (supervised by *Justin Hodgkiss*) won a 'best student talk' prize at the 12th International Conference on Frontiers of Polymers and Advanced Materials (ICFPAM-12). *Michelle Cook* has completed her MSc degree with 1st class honours under the direction of Prof *Jim Johnston* and *Hemi Cumming*, his PhD under the joint supervision of Drs *Joanne Harvey* and *Paul Teesdale-Spittle*.

Prof *Ken MacKenzie* was the guest speaker at the mid-February retirement symposium for Prof *Kiyoshi Okada* at the Tokyo Institute of Technology. The pair has had a productive collaboration over the past 18 years that has generated some 50 papers and two periods for Ken as Visiting Professor with his group.

Recent visitors to SCPS Chemistry have included the last in 2013, Dr *Mona Treguer* (University of Bordeaux) who met with colleagues and gave a seminar entitled *Synthesis of hybrid nanoparticles*. She pointed out that development of new nano-objects for realizing new properties or functions is one of the major challenges in nanosciences and nanotechnology. In this context, she outlined why hybrid nanosystems offer a wide range of new and unexplored possibilities. As the first 2014 visitor it was appropriate that the International Year of Crystallography be marked with a lecture from a crystallographer. This was ably done by Dr *Alison Edwards* (Bragg Institute, Australian Nuclear Science and Technology Organization) with her discourse *W(h)ither Crystallography?* She met staff on January 31 to outline the new neutron diffraction structure facility and then outlined in her lecture the great detail and correctness of results that can be obtained. Another visitor was Dr *Valeska Ting* (Chemical Engineering, University of Bath). She is a 2002 VUW graduate with a PhD from the Australian National University and the 2012 University of Bath's Prize Research Fellow in Smart Nanomaterials. Her research lies in the area of sustainable technologies and she gave a presentation entitled *A peek within the pores - development of nanoporous materials for applications in hydrogen storage*.

Communicate a phenomenon – engaging students in dialogue between science and arts

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Keywords: effective science communication, group work, graduate attributes, reflection

Abstract

Communication skills are vital for scientists and it is very important that we can convey the importance of our work to a non-specialist audience. The purpose of this project was to provide science students with experience in oral and written science communication, and to engage them in ways to express their science. This communication project was a collaborative effort between the Department of Chemistry, the School of Fine Arts and the Department of Art History and Theory at the University of Canterbury. The chemistry students developed ideas with the School of Fine Arts students to create pieces of art that communicated a scientific concept. The artworks were then presented in a public exhibition designed and curated by students from the Postgraduate Diploma in Art Curatorship and the Art History and Theory Honours programme, who also produced an exhibition catalogue. Science student assessment was based upon texts prepared for the exhibition catalogue and on the results of reflecting on what did and did not work during the communication phase of the task.

Introduction

Chemistry is all around us, in the objects we use, the food we eat and the medication we take. We are also surrounded by art and material culture, which simultaneously reflect and shape society and the way we live. Art, everyday objects, and elements of chemical science are explicitly linked in the practice of various artists. Take, for example, the sometimes controversial work of the 1995 Turner Prize winner Damien Hirst, who used platinum and diamond in his iconic skull sculpture of 2007, titled *For the Love of God*,¹ as well as representations of various drugs in his 1988 *Sinner* installation, part of the *Medicine Cabinets* series.² Other examples where chemistry constitutes the focus of visual art include various representations of the periodic table,³ and an initiative by the School of Chemistry at the University of Edinburgh to knit graphene as part of their tercentenary celebrations.⁴ Chemistry is linked intrinsically to the action of creating a painting or other type of artwork. The different chromophores in paint impart different colours, allowing contrasting hues to be used. Chemistry also has implications for the appearance, display, and preservation of art. Some pigments are not stable and colours therefore fade; other effects, such as patina on copper or bronze sculptures are also utilized. These effects all add to the character and meaning of artworks.

There are many literature examples where three-dimensional models and art are used as teaching tools in chem-

istry to convey scientific concepts in a non-standard manner.⁵ This tends to be more prevalent in the teaching of symmetry, as the subjects naturally overlap.⁶⁻⁹ The use of visual art has also been shown recently to be beneficial in the teaching of various chemical concepts, such as the effect of temperature on solution colour intensity, and the colour intensities in a saturated solution and a pigment hue.¹⁰

A paper in the early 1980s by Young¹¹ makes statements regarding the purpose of the fields of science and fine arts. Young states that “the purpose of science is to satisfy our curiosity about natural phenomena. The purpose of the fine arts is to communicate to others the joy (or other emotion) the artist feels”. Whilst this is of course subjective and limited, it raises the interesting question as to whether artists can successfully communicate information provided by scientists. This communication project sought to discover whether the combination of chemistry and art could be used to enhance and assess the verbal and written communication skills of a set of chemistry and biochemistry students.

Methods

The students were working to a very tight timeframe within this project (Table 1). Teamwork was a key component, as each link in the chain of events was dependent on the successful completion of the preceding task. Groups consisted of four or five science students and one art student.

Table 1 Timeframe for science communication project.

Week number	Activity ^a
Week 1	Briefing; Assignment of groups; Communication of preliminary ideas
Week 2	Independent ideas development within groups
Week 3	Artwork development within groups; Planning of exhibition concept and installation; Production of written explanations for scientific content
Week 4	Installation of exhibition; Gallery opening; Peer feedback; Staff feedback; Gallery floor talks by student curatorial team
Weeks 5-6	Exhibition open to the public
Week 7	Deinstallation of exhibition by student curatorial team

^a Staff were available at set times for consultation by groups or individuals regarding the project, ideas development and operational issues.

Student groups

The courses involved in this project were chemistry (CHEM212)/biochemistry (BCHM212) [84 students], graphic design (DESI201) [7 students], sculpture (SCUL201) [10 students], art history and theory (ARTH417) [4 students] and art curatorship (ARTC402) [3 students]. Prior to the initial face-to-face meeting, the CHEM/BCHM students were asked to form into groups of 5 (to make a total of 17 groups) and to think about what they would like to communicate. Some students did this successfully and others did not. At the initial face-to-face meeting the remaining CHEM/BCHM students were assigned into groups of 5 and then a DESI/SCUL student randomly assigned to each CHEM group. At this stage the ARTH/ARTC students were acting in an observational capacity, noting conversations and interactions within the groups in order to begin formulating the concept for the exhibition's installation and catalogue.

Roles and responsibilities of students in each group

The role of the CHEM/BCHM students was to communicate effectively a scientific phenomenon to a non-expert in their subject area with little assumed background knowledge of science. The students were then expected to work within their groups to generate text for curatorial wall labels/catalogue entries to be used in the final exhibition. These texts took two forms – one for a general audience, and one for an audience with a deeper knowledge of science and scientific language (in the latter case, students were advised to write for their peers). The groups were responsible for providing these texts by a deadline that would allow the ARTH/ARTC students to meet printing and other internal deadlines. Each student was also required to reflect individually upon their perception of science communication, both during and outside of this group task, and generate a list of “dos” and “don'ts” to inform others.

The role of the DESI/SCUL students was to be receptive to the information provided by the CHEM/BCHM students, and create a piece of artwork to represent visually the material or concept described. They had to work to a tight deadline to enable the ARTH/ARTC students to design and install the exhibition in time for the gallery opening. The DESI/SCUL students also had to liaise with the ARTH/ARTC students in order to ensure that the spatial requirements of their artworks, and the associated practical requirements of installing them, could be accommodated within the exhibition space and budget.

The ARTH/ARTC class initially acted in an observational capacity, to gauge the interactions within the groups in order to gather ideas relating to the staging of the exhibition. They then produced the exhibition by devising an appropriate conceptual framework for it, and planning the layout of the exhibits and catalogue materials in accordance with this. Crucially, they decided upon what the exhibition would be called, naming it *Communication is the key to every healthy relationship* as a light-hearted reference to managerial initiatives within institutions. They also received the informational texts from the CHEM/BCHM

students, and wrote an introductory essay describing the exhibition's concept, processes, and exhibits. The ARTH/ARTC students then used these various pieces of text as the basis of an exhibition catalogue, which was created in close collaboration with a fourth-year graphic design student (this student was also a representative of the committee for Ilam Campus Gallery's Student Series, under the umbrella of which *Communication is the key to every healthy relationship* fell). The ARTH/ARTC students were also working to tight deadlines, and were reliant on material and information being provided in a timely manner by the other two groups of students.

Outcomes

There were several different outcomes from the project, some tangible and some acquired. This discussion focuses on the outcomes for the CHEM/BCHM students, and how the project connects with the BSc graduate profile for the University of Canterbury.

The key BSc graduate attributes that this project targeted were:

- Demonstrate the development of skills for lifelong learning
- Demonstrate an ability to think independently
- Demonstrate in-depth knowledge of and skill in his or her majoring subject
- Effectively access and use information relevant to the subject
- Work collaboratively on tasks
- Communicate effectively both in written and spoken English

Overall, we felt that the project allowed the students to develop skills for lifelong learning. Whilst the exact meaning of this graduate profile stipulation is open to interpretation, our graduate students should be equipped with the skills they need to continue their professional development post-BSc. Thus, they need to learn how to learn, and how to deal with situations that are not always the norm within their specific subject area. This project was certainly a departure from their usual mode of learning (laboratory, lecture, tutorial or workshop) and pushed some students out of their “comfort zone”. Two possible responses were envisaged, either that the student would shut down and not engage, or that she or he would face the challenge head-on and try to better themselves. The majority of the students faced the challenge head-on, “went with the flow”, and engaged with and enjoyed the task. Some students obviously felt uncomfortable, and relied on others in their group to speak on their behalf. For many students this was a first exposure to this type of communication activity. With more regular exposure, their comfort levels should rise, and, with that, their confidence.

The process of communicating the scientific phenomenon responded to a number of the key attributes sought in BSc graduates. The groups had to work together collaboratively to ensure that a clear message was conveyed to the DESI/SCUL students. They also had to demonstrate

in-depth knowledge of their subject to accurately communicate the phenomenon, and be able to think around the chosen subject in order to convey information using accessible language and using appropriate formats. Again, for many this was a new situation, which they coped with admirably. It was interesting to observe group dynamics as the face-to-face task progressed, with leaders emerging and obvious team players also developing.

Having communicated the scientific phenomenon of their choosing to the DESI/SCUL students, the most tangible outcome was the creation of the artwork. This demonstrated how effectively the communication worked, and how the DESI/SCUL students responded to the brief, manifesting itself more broadly at the exhibition. Observation of attendees at the exhibition opening revealed that those with a science background were observing pieces of work and drawing conclusions as to what they represented prior to reading the information about the pieces. In general, most people were able to discern what each piece of art represented, thus demonstrating the effectiveness of both the original oral communications, and the fine art students' practical responses. Some of the pieces produced for the exhibition are shown in Figures 1 and 2.

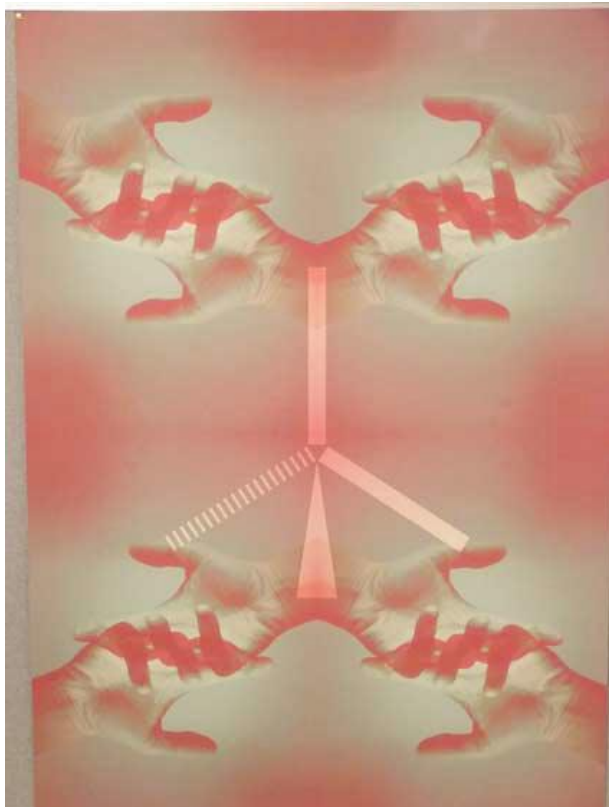


Fig. 1. Poster depicting chirality, created by a DESI201 student for the art exhibition

Assessment

The CHEM/BCHM students undertook several written tasks for assessment relating to this project, both in group settings and as individuals. The group work related to the generation of the accompanying texts for the artworks, which explained the various scientific phenomena represented. The groups were asked to write short descriptions of their chosen concepts for both general audiences and



Fig. 2. Sculptures depicting chirality, created by separate SCUL201 students for the art exhibition

for audiences with a deeper science background. The language used for each description was expected to be quite different to cater for the different levels of assumed background knowledge. Eventually these descriptions were used in the exhibition catalogue produced by the curatorial students. Attendees at the exhibition used both formats to aid their interpretation, understanding, and – hopefully – enjoyment of the pieces of art.

The CHEM/BCHM students were also individually assessed, undertaking personal reflections on what does and does not work in science communication through explanations. This was based both on previous experience, and on events during the group phase of the project. A word map was generated based on the responses, and is shown in Figure 3.

A description of the project was released to the media and posted on several popular news and events websites.¹²⁻¹⁵ The work was also discussed in oral presentations during the 2013 University of Canterbury Teaching Week,¹⁶ and at the 2013 New Zealand Institute of Chemistry Conference (Wellington, 1–5 December 2013).¹⁷

The quality of New Zealand-produced olive oil compared with imported product

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Keywords: olive oil, quality, volatiles, polyphenols, principle component analysis

Introduction

The purpose of this study was to compare the quality of commercially available New Zealand and foreign olive oils. This was done not only by employing the standard regulatory measures of quality, but by the application of a Gas Chromatograph-Mass Spectrometry (GC-MS) Head-Space Solid Phase Micro Extraction (HS-SPME) analysis for determining the concentration of key volatile compounds known to be markers of quality in olive oil. The results of the volatiles analysis along with total polyphenol concentrations then were used to ascertain if the quality of the New Zealand product was significantly different from that of the imported products. The study also examined whether the levels of these compounds could be employed as an indicator of olive oil origin.

The olive – an exceedingly brief history

The fruit of the evergreen olive tree *Olea europaea*, which originated from Asia Minor, has been cultivated for thousands of years in the Mediterranean area.¹ Olive oil has been produced from its fruit for at least 6000 years.² In ancient times, Crete was one of the earliest and largest centres of olive oil production. The olive was a highly beneficial crop for the Minoan civilisation, as olives could be grown on marginal agricultural land, opening up new areas to food production. From about 2000 B.C., the olive groves of Crete and elsewhere provided the Minoans and other Mediterranean peoples with fruit, oil for culinary purposes, lamp fuel, medicine, cosmetics, skin care and cleaning (later in soap), timber for roof construction and firewood for cooking and heating.³ Today, olives are cultivated around the world, with Spain, Italy, Egypt and Greece in descending order being the major producers for approximately 90% of world production in 2010. Countries such as Australia, South Africa, America, Argentina, Chile and New Zealand are producing increasing quantities. Total world production of this important commodity has more than doubled in the last 20 years to more than 3 million tonnes annually.⁴

Given the usefulness of the olive it should come as no surprise that this tree made an early appearance in New Zealand. We know the olive existed here prior to 1835 since Charles Darwin, following his visit to the Bay of Islands, mentioned in a letter that he had found olives planted in Waimate North. Between 1860 and 1880, two prominent early settlers, Logan Campbell and Sir George Grey, independently attempted to establish an olive industry, but these attempts failed after a few years and were abandoned. It was not until the mid-1980s that the New Zealand olive oil industry began to develop, when Israeli-born, FAO Horticultural Representative, Gidon Blumen-

feld retired to Marlborough and planted a grove, establishing a nursery of imported Barnea and other cultivars.⁵ Most groves in New Zealand are located on the East coast from Canterbury to Hastings and around Auckland, with Northland and Nelson also important production regions.

Olive oil – composition

The major components of olive oil are triglycerides accounting for more than 98% of olive oil by weight. Oleic acid (18:1 n-9) is the most abundant fatty acid with levels ranging from 56 to 84% of the total fatty acid content. It is the abundance of this monounsaturated fatty acid that sets olive oil apart from other vegetable oils. Olive oil also has high levels of the essential polyunsaturated fatty acid linoleic acid (18:2 n-6), with content ranging from 3 to 21%. Minor components account for approximately 2% of the total oil weight and include more than 230 compounds such as aliphatic and triterpenic alcohols, sterols, hydrocarbons, volatile compounds and antioxidants.²

Polyphenols

Olive oils contain at least 30 different polyphenols which, in addition to their claimed health benefits, contribute to the oils' bitterness and pungency.

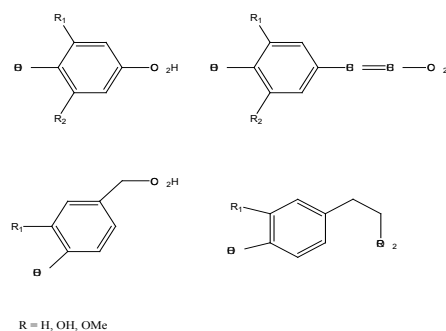


Fig. 1. Generic structural formulae for olive oil polyphenols

According to Martin-Pelaes *et al*⁶: “The Mediterranean diet and consumption of olive oil has been connected in several studies with longevity and a reduced risk of morbidity and mortality... The benefits of consuming olive oil have been known since antiquity and were traditionally attributed to its high content of oleic acid. However, it is now well established that these effects must also be attributed to the phenolic fraction of olive oil with its antioxidant, anti-inflammatory and anti-microbial activities. The mechanism of these effects are varied and probably interconnected. For some activities of olive oil phenolic compounds, the evidence is already strong enough to enable the legal use of health claims on foods.”

Oil extraction and quality

Olive oil is produced by grinding the olives and extracting the oil mechanically or chemically. Traditionally, olives were ground to a paste using large millstones. The paste was spread on fibre disks which were stacked and placed in a press. Pressure on the stack squeezed out the oil and water which was allowed to separate. However, most olive oil currently is produced using hammer mills or disc crushers followed by centrifugal extraction. The paste left after mechanical extraction may contain 5-10% of the total oil which can be removed by chemical extraction.

Olive oil quality/grades

From the first oil extracted from the centrifuge to the last portion bound to the paste, olive oil comes in various quality grades. The Codex Alimentarius Commission gives the classifications and criteria for each, as shown in Table 1.

The Quality of New Zealand Produced and Foreign Oils – A Comparison

Aroma and quality

Much work has been done investigating aroma-active compounds for evaluation of olive oil quality. Currently, this is determined by sensory evaluation via a “Panel Test”, developed by the International Olive Council.

While using well-trained panellists produces reproducible and reliable results, there remains the issues of a lack of stable, standardised reference oils and the large number of panellists required for statistically robust results.¹⁰ Volatile compounds in olive oil are mainly produced by oxidation of fatty acids. It is generally agreed that endogenous plant enzymes are responsible for the positive aroma perceptions, while chemical oxidation and exogenous enzymes, usually from microbial activity, are associated with sensory defects. Both the processing and storage of the fruit and the oil contribute to the flavour and overall quality of olive oil.

The aroma of olive oil is attributed to a mixture of aldehydes, alcohols, esters, hydrocarbons, ketones and furans. Levels of these volatile compounds are highest in virgin olive oils. The phenolic content is also known to have a significant impact on the stability and sensory characteristics of olive oil, in addition to claimed health benefits. Evaluation of the sensory quality of virgin olive oils involves determination of the following favourable and unfavourable sensory attributes via the taste panel.¹¹

Positive attributes

- (i) Fruity: characteristic of oil from healthy, fresh fruits either ripe or unripe.

Table 1. Codex Alimentarius standards for olive oils and olive pomace oils^{7,8}

Grade ^a	FFA (%) as oleic acid ^b	Peroxide value (mEq/kg) ^c	Abs @ 270 nm ^d	ΔK^e	Median defect (odour and taste) ^f
Extra virgin olive oil	≤0.8	≤20	≤0.22	≤0.01	Me=0 (fruity Me>0)
Virgin olive oil	≤2.0	≤20	≤0.25	≤0.01	0<Me≤2.5 (fruity Me >0)
Ordinary virgin olive oil	≤3.3	≤20	≤0.3	≤0.01	2.5<Me≤6.0
Refined olive oil	≤0.3	≤5	≤1.10	≤0.16	N/A
Olive oil (refined and virgin blend)	≤1.0	≤15	≤0.90	≤0.15	N/A
Refined olive oil pomace	≤0.3	≤5	≤2.00	≤0.20	N/A
Olive-pomace oil	≤1.0	≤5	≤1.70	≤0.18	N/A

^a Virgin oils must be produced by physical means, e.g. crushing, washing, decanting, centrifuging and filtering. Heat and chemicals are not permitted. Refined oils may be caustically refined, bleached and deodorised.

^b Free Fatty Acid (FFA) is a crude indicator of the quality of the fruit and handling procedures prior to milling. It is a measurement of hydrolytic breakdown of the fatty acid chains from triglycerides into diglycerides and monoglycerides, liberating free fatty acids

^c Peroxide value is a crude indicator of the amount of primary oxidation that has occurred to form peroxide compounds within the oil. A high value indicates that the olives or paste was likely handled improperly, the oil could be defective, and the oil might not keep well. A rancid taste may become noticeable between 30 and 40 mEq/kg.

^d Absorbance at 270 nm is a more delicate indicator of oxidation, especially in oils that have been heated in the refining process. It measures the quantity of certain oxidized compounds that absorb at wavelengths of 232 and 270 nanometers (nm) in the ultraviolet spectrum.

^e Delta (Δ) K detects the use of colour removing substances and the presence of refined or pomace oil by measuring the difference between absorbance at 270 nm and the absorption difference between 266 nm and 274 nm.

^f Taste Panel determination of quality. The volatile compounds formed during the processing of olive fruit contribute a combined sensation of smell and taste. Evaluation of the sensory quality of virgin olive oils involves perception of both favourable and unfavourable sensory attributes. Aroma and taste are very complex and cannot currently be determined in the laboratory. The tongue can also detect texture differences difficult to measure analytically. The first and primary objective in sensory evaluation of olive oil is to determine if oils contain one or more of the defects that commonly occur in oils from improper fruit storage, handling, pest infestation, oil storage, or processing.⁹

- (ii) Bitter: primary taste produced by quinine, caffeine and other alkaloids.
- (iii) Pungent: the biting tactile sensation characteristic of oils produced at the start of the crop year, primarily from unripe olives.

Negative attributes

- (i) Fusty: characteristic of oil produced from fruit stored for long periods before extraction undergoing anaerobic fermentation.
- (ii) Musty-humid: a characteristic of oils from fruit infested with large numbers of fungi and yeast.
- (iii) Muddy sediment: a characteristic of oil that has been left in contact with sediment for a long time.
- (iv) Winey-vinegary: flavour due to fermentation of olives forming acetic acid, ethyl acetate and ethanol.
- (v) Metallic: occurs in oils with prolonged contact with metallic surfaces.
- (vi) Rancid: flavour of oils that have undergone oxidation.

Table 2 lists some of the key volatile compounds responsible for the positive and negative attributes of olive oils as determined by the taste panel.

Table 2. Key volatile compounds linked to positive and negative attributes investigated in this study. Volatiles considered undesirable in excess contributing to negative attributes are in bold italic^{10,12}

Volatile	Odour/taste	Volatile	Odour/taste
ethanol	fermented/musty	<i>cis-2-hexenyl acetate</i>	end product of linolenic acid oxidation
penten-3-one	green	<i>trans-2-hexenyl acetate</i>	end product of linolenic acid oxidation
<i>ethyl butyrate</i>	sweet, fruity, cheesy	hexanol	fruity, banana
<i>ethyl-2-methyl butanoate</i>	fruity	2-nonanone	musty
<i>ethyl-3-methyl butanoate</i>	fruity	<i>cis-3-hexenol</i>	leafy
<i>hexenal</i>	green	nonanal	fatty, waxy, pungent
<i>isoamyl acetate</i>	pear, banana	<i>trans-2-hexenol</i>	grassy, green
2-heptanone	sweet, fruity	<i>trans-2-nonenal</i>	paper-like, fatty
<i>trans-2-hexenal</i>	green, astringent	ethyl salicylate	medicinal
<i>3-methyl butanol</i>	woody, whiskey, malty	<i>t,t-2,4-decadienal</i>	deep-fried
<i>2-phenyl ethanol</i>	sweet, winey, musty		

Table 3. Mean results for free fatty acid content, peroxide value, polyphenols and total volatile compounds of samples purchased locally

Grade	FFA (%) Mean (range)	Peroxide (mEq/kg) Mean (range)	Total volatiles (mg/kg) mean (maximum)	Polyphenols (mg/kg) as gallic acid mean \pm s.d.
Olive oil (n=7)	0.145 (0.069-0.273)	6.6 (5.6-9.0)	1.5 (2.3)	40 \pm 7
Extra light (n=5)	0.067 (0.042-0.130)	4.3 (0-7.5)	0.4 (0.7)	31 \pm 5
Extra virgin New Zealand (n=19)	0.178 (0.072-0.371)	12.7 (6.8-20.9)	23.5 (42.0)	295 \pm 133 ^a
Extra virgin imported (n=20)	0.372 (0.174-0.742)	12.2 (7.5-23.2)	21.3 (42.1)	188 \pm 53 ^a

^a Mean polyphenol levels in New Zealand products were higher than imported products, although the difference, given the wide range of levels found, could not be regarded as statistically different in the accepted sense, i.e. $p \leq 0.05$. The difference between these means only becomes "significant" at $p=0.2$ but given the very small sample set, this difference is tantalising indicating that the polyphenol levels of a larger olive oil sample set could be worth investigating.

Samples

A total of 51 olive oil samples were purchased in Christchurch from various supermarkets and other outlets or submitted by olive growers "ready for sale". Of these, 39 were "extra virgin" oils and 12 were classed as "olive oil" or refined "extra light olive oil". Of the 39 extra virgin oils, 19 were produced in New Zealand. The remaining 20 imported oils were Italian (9), Spanish (5), Australian (4), Greek (1) and Palestinian (1).

All samples had their levels of free fatty acids, peroxide, absorbance at 270 nm and ΔK determined to ensure the label claim on each product was accurate. Results for free fatty acids and peroxide are summarised in Table 3. Two Italian oils were found to have a high absorption at 270 nm and low polyphenol levels which could indicate possible refining or mixing with refined oil. The results of all other samples conformed to the label claim.

Polyphenol analysis

The total polyphenol content of olive oils in this study was determined using an adaption of the method of Gawel & Rogers 2006.¹³ Briefly, weighed portions of olive oil were dissolved in hexane and extracted with aqueous methanol. The extract was diluted with water and an aliquot was treated with Folin-Ciocalteu reagent and saturated Na_2CO_3 . The absorbance at 725nm was measured after 1

Table 4. Levels of key volatile compounds in New Zealand and imported extra virgin olive oils. Volatiles generally considered undesirable in excess are in bold italic.

Volatile	New Zealand mg/kg (s.d.) n=19	Imported mg/kg (s.d.) n=20
<i>ethyl butyrate</i>	0.003 (0.006)	0.098 (0.071)
<i>ethyl-2-methyl butanoate</i>	0.002 (0.002)	0.019 (0.020)
<i>ethyl-3-methyl butanoate</i>	0.000 (0.000)	0.005 (0.005)
<i>hexenal</i>	1.532 (0.633)	2.011 (0.868)
<i>isoamylalcohol</i>	0.009 (0.007)	0.042 (0.026)
<i>trans-2-hexenal</i>	11.111 (6.160)	5.238 (2.986)
<i>3-methyl butanol</i>	3.931 (3.375)	1.311 (1.102)
<i>cis-3-hexenol</i>	1.388 (1.064)	1.722 (0.842)
<i>trans-2-nonenal</i>	0.122 (0.061)	0.279 (0.165)
<i>t,t-2,4-decadienal</i>	0.193 (0.153)	1.490 (1.887)
<i>2-phenylethanol</i>	0.196 (0.110)	0.282 (0.150)
<i>cis-2-hexenylacetate</i>	0.856 (0.786)	2.260 (0.858)
<i>trans-2-hexenylacetate</i>	0.610 (0.609)	1.660 (0.789)

hour. Total polyphenols were quantitated by comparison with a standard curve made up of gallic acid in concentrations of 5, 10, 25, 50 and 100 mg/L.

The refining process to which the non-virgin oils are subjected clearly reduced the FFA and peroxide values, but stripped virtually all those volatiles examined from the oil and almost completely eliminated the polyphenols.

Determination of key volatiles

The key volatile compounds of extra virgin olive oils investigated in this study were quantitated using an adaption of the method of Vichi *et al*¹⁴. Briefly, one gram portions of olive oil were weighed into head space vials, 4-pentan-2-ol was added as an internal standard and the vial sealed. Volatiles were absorbed onto a divinylbenzene-carboxen-polydimethylsiloxane SPME fibre. Separation of volatiles was performed on a GC-MS equipped with a Supelco-wax-10, 30 m x 0.25 mm I.D., 0.25 µm film thickness capillary column. Standard curves were prepared by spiking genuine olive oil with key volatiles in concentrations of 0.1, 0.25, 0.5, 1.0, 1.5, 2.5 and 5.0 mg/kg. Oil blanks were also included and the endogenous volatiles subtracted from the spiked levels. Results are shown in Table 4. Not all compounds of interest could be quantitated in part due to the great difference in relative concentration between some of the volatiles, e.g. ethanol, which could be present at high levels compared with the other volatiles resulting in a detector overload. These volatiles have been excluded from Table 4.

Multivariate analysis

One of the aims of this investigation was to determine if the concentration of key volatiles in olive oils could be used to authenticate an olive oil as being of New Zealand origin. Dr Beverley Horn (ESR, Christchurch) undertook an exploratory multivariate analysis of the key volatile levels in 38 of the extra virgin oils (one sample was rejected as the results of the volatiles analysis were considered low and dubious). Principle component analysis (PCA) was conducted using scaled and centred measurements

using the R statistical package.¹⁵ The first two principle components provided the best differentiation between olive oils from New Zealand, Australia and other countries as illustrated in Fig. 2.

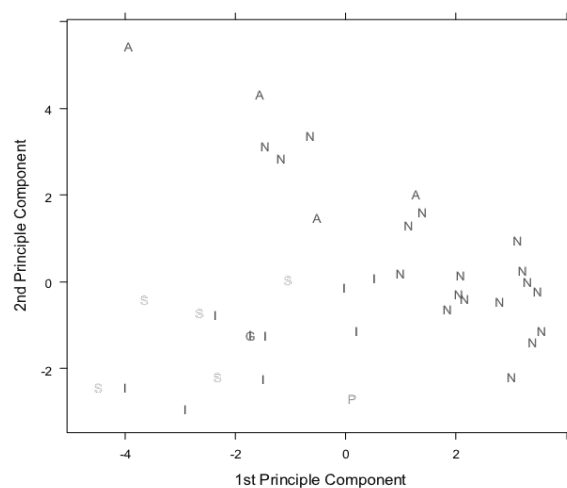


Fig. 2. Principle component analysis of olive oil volatiles with reference to country of origin. “A” = Australia, “G” = Greece, “I” = Italy, “N” = New Zealand and “P” = Palestine.

Classification trees using binary recursive partitioning of the untransformed data from the tree package suggested oils of New Zealand origin could be separated from other oils on the basis of their isoamyl alcohol concentration, with most New Zealand oils containing < 0.0225 mg/kg. Dr Horn noted in reference to the results, “Both the principle component analysis and the classification tree approach indicate that segregation of extra virgin olive oils according to origin based on volatiles analysis is feasible. Allocations are not completely accurate, but from this small data set, the results are encouraging.”

Discussion

While it must be remembered that the number of samples in this study is very small, the differences between New Zealand and imported olive oils in regards to total

polyphenol and positive/negative volatile concentrations appear to tell a consistent story. While resistant to auto-oxidation, olive oil does undergo degradation with time. Polyphenol levels decrease, while undesirable volatiles increase, such as *trans*-2-hexenyl acetate, one of the final products of the linolenic acid oxidation pathway in olive oil. The New Zealand oils in this survey appear to contain lower levels of some undesirable volatiles than the imported product, although the differences may not be statistically significant in all instances given the wide range of concentrations found for some compounds. The slightly higher level of polyphenols in New Zealand product combined with lower levels of undesirable volatiles may simply indicate that the New Zealand olive oils are often fresher than imported oils that may have been in storage for longer periods or spent more time being shipped than the local product.

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The role of sialic acid synthases in sialic acid biosynthesis

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Introduction

The sialic acids comprise a diverse family of nine-carbon keto-sugars, the majority of which are structural derivatives of neuraminic acid (Fig. 1). Neuraminic acid has an amino moiety at the C-5 position, and carboxylate at C-2 which confers negative charge at physiological pH. Whereas unsubstituted neuraminic acid is not known to exist in nature, over 40 substituted variations (classified as sialic acids) have now been described.¹ Common modifications to the core neuraminic acid framework include *O*-acetylation and esterification of the hydroxyl moieties, namely at positions C-7, C-8 and C-9 (Fig. 1).² Multiple substitutions at these positions allow further diversification of sialic acid structure. Other modifications include glycolation (*N*-glycolylneuraminic acid) and deamination (2-keto-3-deoxy-*D*-glycero-*D*-galacto-nononic acid) of the C-5 amino group. *N*-acetylneuraminic acid (NeuNAc), *N*-acetylated at position C-5, is the most prevalent sialic acid in nature and is often synonymous with the term sialic acid.¹

NeuNAc forms the terminal residue of cell surface glycoconjugates in mammals and therefore is critically involved in cellular recognition, signalling and cell adhesion processes.¹ Sialic acids are largely absent in plants and prokaryotes, however, several species of pathogenic bacteria incorporate sialic acid residues into their own cell wall glycoconjugates, allowing them to mimic the physiology of mammalian cells and evade detection by their mammalian host's immune system.³

Additionally, sialic acids expressed on mammalian cell surfaces facilitate the recognition and binding of certain viruses to the host cells prior to internalisation.⁴ For this reason, structural analogues of sialic acids have applications as anti-viral therapeutics, including the frontline influenza drugs Zanamavir (Relenza™) and Oseltamivir (Tamiflu®). The role of sialic acids in human disease emphasises the importance of understanding how they are biosynthesised, and how they function within biological systems.

The biosynthetic pathways of only a small number of these sugar molecules have been described. These include NeuNAc⁵, 2-keto-3-deoxy-*D*-glycero-*D*-galacto-nononic acid (KDN)⁶, and the sialic acid-like compounds; 5,7-diacetamido-3,5,7,9-tetra-deoxy-*L*-glycero-*L*-manno-nulosonic acid (pseudaminic acid)⁷ and 5,7-diacetamido-3,5,7,9-tetra-deoxy-*D*-glycero-*D*-galacto-nulosonic acid (legionaminic acid).⁸

The structural variation of these sialic acids allows them to fulfil different roles within living systems. NeuNAc and structurally similar KDN are components of both vertebral and bacterial cell surface glycoconjugates, mediating signalling and recognition processes.⁶ Conversely,

pseudaminic and legionaminic acid are apparently unique to bacteria and microorganisms, forming components of cell surface lipopolysaccharides, and other glycoconjugates.^{8,9} Additionally, pseudaminic acid has been shown to be critical for the proper development of flagella in certain gram-negative bacteria.⁷

The biosynthetic pathways of the aforementioned sialic acids involve the aldol-like condensation of phosphoenolpyruvate (PEP) with respective sialic acid precursors, a reaction catalysed by an evolutionarily related family of enzymes known collectively as the sialic acid synthases.¹⁰ A final step in the biosynthesis of all sialic acids is the activation of these molecules for incorporation into cell surface glycoconjugates. Condensation with cytidine triphosphate (CTP) yields the activated sialic acid, cytidine monophosphate-sialic acid (CMP-sialic acid), which acts as the glycosyl donor and can be transferred to the growing terminus of carbohydrate structures.¹¹ This activation step is catalysed by a family of enzymes known as the CMP-sialic acid synthetases, which are reviewed elsewhere.¹² This review provides a summary of the current understanding of sialic acid biosynthesis, with an emphasis on the structure and function of the enzyme that catalyses the central aldol-like condensation reaction of NeuNAc biosynthesis: NeuNAc synthase.

The pathways of sialic acid biosynthesis

NeuNAc biosynthesis

It was not until the 1960s that the first enzymes involved in sialic acid biosynthesis were identified. Comb and Roseman¹³ initially discovered an enzyme from mammalian tissue which could catalyse the cleavage of NeuNAc to pyruvic acid and *N*-acetylmannosamine (ManNAc). The reverse reaction of this 'NeuNAc lyase' enzyme was thought to be a potential biosynthetic source of NeuNAc. Further investigation uncovered an independent enzyme that almost exclusively catalysed the forward condensation reaction of PEP and *N*-acyl mannosamine 6-phosphate.¹⁴ The enzyme was tentatively named *N*-acyl neuraminic acid synthetase but was renamed shortly after to *N*-acetylneuraminic acid synthetase upon the discovery of its preference for acetylated mannosamine-6-phosphate (ManNAc-6-P) as a substrate.¹⁵ This enzyme is now known to be the primary facilitator of NeuNAc synthesis in mammalian systems. In the same year, an additional two steps of the mammalian NeuNAc biosynthesis pathway were described, the initial phosphorylation of ManNAc to ManNAc-6-P, and the subsequent dephosphorylation of NeuNAc-9-P.¹⁵ The first description of a NeuNAc biosynthetic enzyme from a bacterial source was reported in 1962.¹⁶ An enzyme isolated from *Neisseria meningitidis* was shown to be capable of catalysing the condensation of ManNAc and PEP to produce NeuNAc directly.

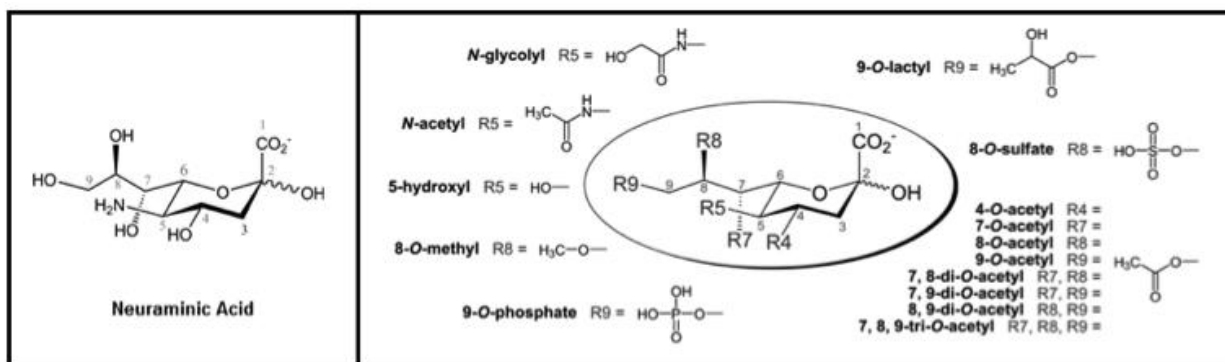


Fig. 1. Left: Unsubstituted neuraminic acid. Right: The family of naturally occurring sialic acids. Displayed in the centre is the sialic acid template architecture. Figure modified from Schauer (2004).²

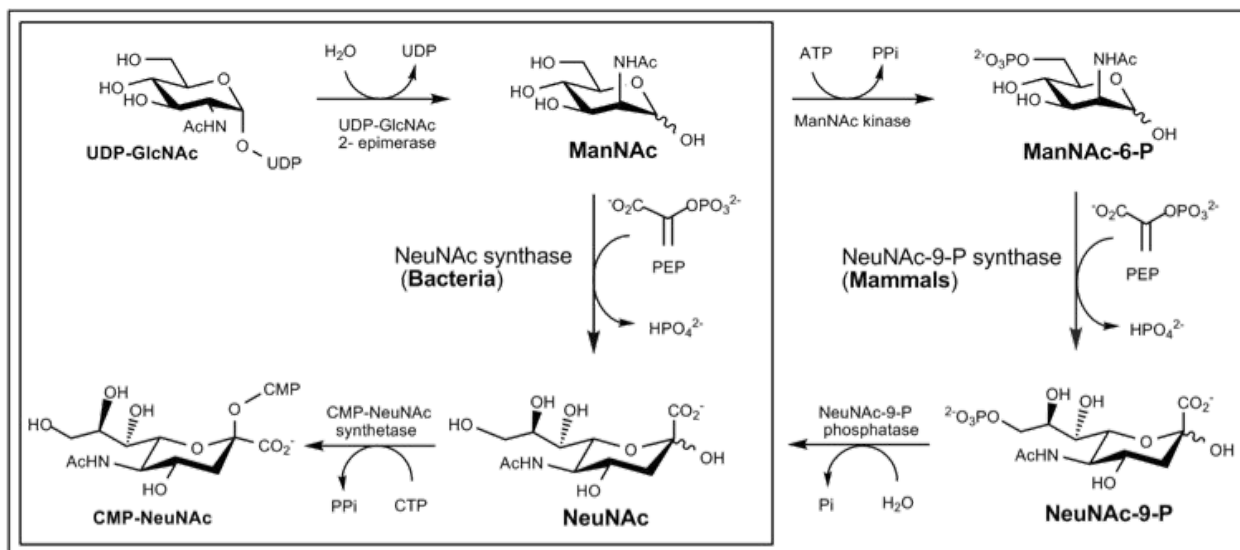


Fig. 2. The pathways of bacterial and mammalian NeuNAc biosynthesis. In bacterial systems (inner box), ManNAc condenses with PEP to give NeuNAc directly. The mammalian pathway (outer box) involves an additional two steps; phosphorylation of ManNAc to ManNAc-6-P, which then condenses with PEP to give NeuNAc-9-P, and then dephosphorylation of NeuNAc-9-P to NeuNAc. In both systems, a final step activates NeuNAc via condensation with cytidine triphosphate (CTP).

This early work provided the basis for the understanding of NeuNAc biosynthesis that we have today.

The initial epimerisation and hydrolysis of uridine diphosphate (UDP)-*N*-acetylglucosamine (UDP-GlcNAc), catalysed by UDP-GlcNAc 2-epimerase, provides the substrate ManNAc for both the bacterial and mammalian biosynthetic pathways of NeuNAc (Fig. 2).¹⁷ The bacterial pathway utilises this substrate directly in an aldol-like condensation reaction with PEP, which is catalysed by the enzyme NeuNAc synthase. The mammalian pathway involves an extra step in which ManNAc is phosphorylated via ManNAc kinase activity to ManNAc-6-P.¹⁵ This is the substrate for mammalian NeuNAc-9-P synthase which catalyses the aldol-like condensation of PEP with ManNAc-6-P yielding NeuNAc-9-P which can be subsequently dephosphorylated to form NeuNAc (Fig. 2).¹⁵ A final step in both bacterial and mammalian systems generates activated NeuNAc via conjugation to cytidine monophosphate, ready for incorporation into cell surface glycoconjugates.³

KDN biosynthesis

Almost 40 years following elucidation of the NeuNAc biosynthetic pathway, biosynthesis of a second sialic acid, KDN (2-keto-3-deoxy-D-glycero-D-galacto-nonon-

ic acid), was described. Angata *et al*⁶ demonstrated that purified soluble fractions from trout testis were able to catalyse the formation of KDN, from adenosine triphosphate (ATP), PEP and mannose-6-phosphate (Man-6-P). The suggested biosynthetic pathway is a three step process which begins with the ATP-dependent phosphorylation of mannose to yield Man-6-P, catalysed by the enzyme hexokinase (Fig. 3). Man-6-P then undergoes condensation with PEP to produce KDN-9-P and free phosphate. This central step is catalysed by KDN-9-phosphate synthase of the sialic acid synthase family.

Interestingly, human NeuNAc-9-P synthase is also capable of utilising Man-6-P as a viable substrate and thus exhibits secondary KDN-9-P synthase activity.¹⁸ KDN-9-P phosphatase then catalyses the dephosphorylation of KDN-9-P to give KDN as the product.⁶ Glycoconjugates containing KDN are often over-expressed in ovarian cancer cells, and postulated to contribute to the metastatic potential of these cells.¹⁹ A detailed review of KDN biosynthesis is available elsewhere.²⁰

Pseudaminic acid biosynthesis

More recently the pathway for the bacterial sialic acid, pseudaminic acid (5,7-diacetamido-3,5,7,9 tetrahydroxy-L-glycero-L-manno-nonulosonic acid), has been described

(Fig. 3).⁷ This sialic acid is required for flagella development and therefore motility in certain gram-negative bacteria such as the gastrointestinal pathogens *Helicobacter pylori* and *Campylobacter jejuni*.⁹ The pathway proceeds in the same way as both NeuNAc and KDN synthesis as previously described. Condensation of the pseudaminic acid precursor 2,4-diacetamido-2,4,6-trideoxy-L-altrose with PEP is catalysed by pseudaminic acid synthase (PseI), a sialic acid synthase initially isolated from *C. jejuni*.⁹ As for NeuNAc and KDN, pseudaminic acid is

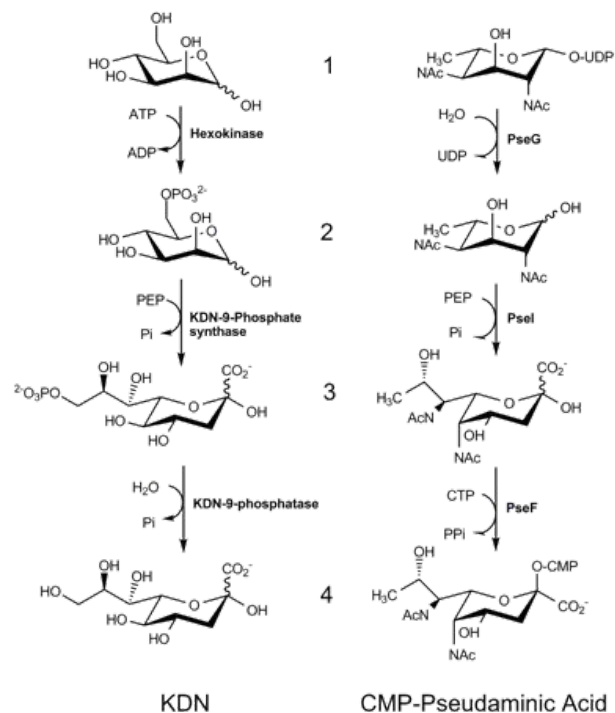


Fig. 3. The biosynthetic pathways of KDN and pseudaminic acid. **Left:** KDN (4) is synthesised via a three step process from mannose (1). A final step (not shown) conjugates KDN to CTP, forming CMP-KDN. **Right:** CMP-pseudaminic acid (4) synthesis proceeds via hydrolysis of UDP-2,4-diacetamido-2,4,6-trideoxy- β -L-altropyranose (1) derived from UDP-*N*-acetylglucosamine, releasing UDP and forming 2,4-diacetamido-2,4,6-trideoxy- β -L-altropyranose (2). Pseudaminic acid synthase (PseI) catalyses the condensation of PEP and 2,4-diacetamido-2,4,6-trideoxy- β -L-altropyranose to give pseudaminic acid (3) as the product.

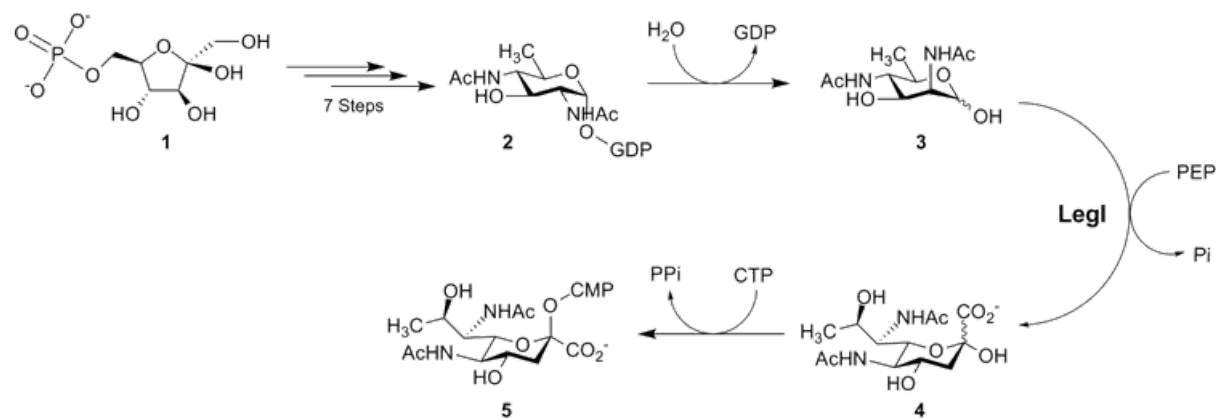


Fig. 4. The biosynthetic pathway of legionaminic acid in *C. jejuni*. Biosynthesis of legionaminic acid begins with the glycolytic intermediate fructose 6-phosphate (1). Hydrolysis of the pathway intermediate GDP-2,4-diacetamido-2,4,6-trideoxy- α -D-glucopyranose (2) yields 2,4-diacetamido-2,4,6-trideoxy-D-mannopyranose (3). Legionaminic acid synthase (LegI) catalyses the condensation of this metabolite with PEP to form legionaminic acid (4). In the final step, CMP-legionaminic acid synthetase conjugates cytidine-triphosphate to legionaminic acid, liberating pyrophosphate and CMP-legionaminic acid (5).

also activated for sialyltransferase activity via condensation with cytidine triphosphate. CMP-pseudaminic acid can then be exported to the cell surface for sialylation of flagellin, the major glycoprotein component of flagella.²¹

Legionaminic acid biosynthesis

Another sialic acid associated with the virulence of bacteria, notably *Legionella pneumophila* and *Campylobacter coli*, is legionaminic acid (5,7-diacetamido-3,5,7,9 tetra-deoxy-D-glycero-D-galacto-nonulosonic acid). These pathogenic bacteria are common causative agents of the acute respiratory infection known as legionnaires disease.²² The complete biosynthetic pathway of this sialic acid from *C. jejuni* was reported in 2009 by Schoenhofen *et al.*,⁸ and was shown to proceed via unique guanidine diphosphate (GDP)-linked intermediates, differing from the previously described sialic acid biosynthetic pathways which utilise UDP-linked intermediates. The legionaminic acid biosynthetic pathway is considerably longer than that of other sialic acids, and begins with the conversion of the glycolytic intermediate fructose 6-phosphate to glucosamine 6-phosphate. Seven subsequent reactions yield the sugar substrate 2,4-diacetamido-2,4,6-trideoxy-D-mannopyranose, which undergoes condensation with PEP to form legionaminic acid, a reaction catalysed by the sialic acid synthase denoted LegI (Fig. 4).⁸

N-Acetyl Neuraminic Acid (NeuNAc) Synthase

The enzymes responsible for catalysis of the central aldol-like condensation of PEP with sialic acid precursor sugars are collectively referred to as the sialic acid synthases. The most well understood of these enzymes is NeuNAc synthase, which catalyses the condensation of PEP with ManNAc (or ManNAc-6-P in mammalian cells), generating NeuNAc, the most abundant sialic acid in nature.

NmeNeuNAcS Structure

The first solved crystallographic structure of a sialic acid synthase was that of NeuNAc synthase from *N. meningitidis* (*NmeNeuNAcS*).²³ While several structures of *NmeNeuNAcS* are now available, no complete sialic acid synthase structure from any other species has been pub-

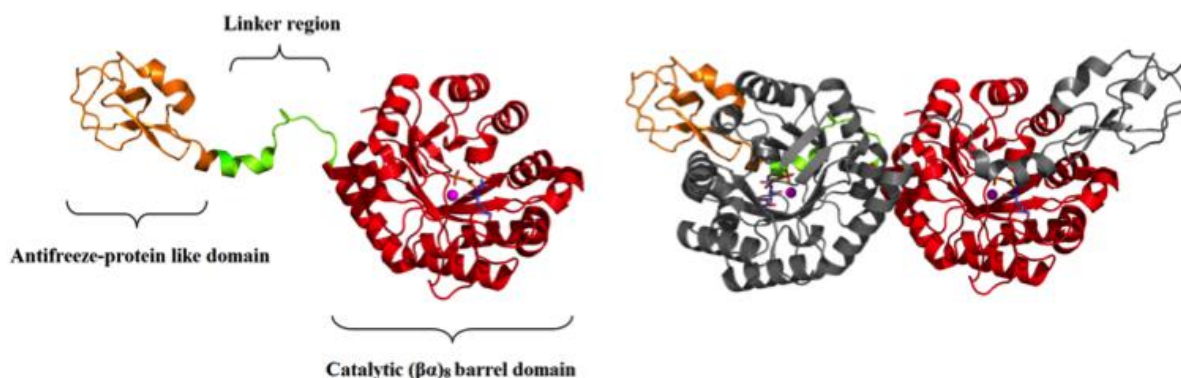


Fig. 5. Crystal structure of NeuNAc synthase from *N. meningitidis* in complex with *N*-acetylmannosaminitol, PEP and Mn^{2+} . The NeuNAc synthase monomer (left) consists of an N-terminal $(\beta\alpha)_8$ barrel domain (red) and a much smaller C-terminal AFP domain (orange). Note the presence of the substrate analogue rManNAc (blue), PEP (orange) and Mn^{2+} (magenta sphere) bound in the $(\beta\alpha)_8$ barrel active site. NeuNAc synthase from *N. meningitidis* forms a domain-swapped homo-dimer (right) in which the AFP-like domain of one monomer interacts with the $(\beta\alpha)_8$ barrel domain of the second monomer. Protein Data Bank (PDB) entry: 1XUZ.

lished to date. The initial crystal structure of *Nme*NeuNAcS revealed a unique domain-swapped homo-dimer (Fig. 5), with each monomer consisting of an N-terminal $(\beta\alpha)_8$ catalytic barrel domain and a C-terminal antifreeze protein-like (AFP) domain connected via an extended linker.²³ The presence of the AFP-like domain had been previously identified by a structural homology search against type III antifreeze proteins and was hypothesised to play a role in binding the sugar substrate ManNAc.²⁴

Light scattering experiments show *Nme*NeuNAcS exists primarily as a native dimer in solution, consistent with the asymmetric unit of the crystal structure.²³ Upon dimer assembly, the AFP-like domain of one monomer interacts with the $(\beta\alpha)_8$ barrel domain of the adjacent monomer, capping the active site and forming the domain swapped homo-dimer arrangement which has since been shown to be critical for catalysis.²⁵

This initial *Nme*NeuNAcS structure was obtained from crystals soaked with an excess of PEP and the substrate analogue *N*-acetylmannosaminitol (rManNAc). As can be seen in Fig. 5, the bound location of these molecules identifies the active site of NeuNAc synthase at the C-terminal end of the $(\beta\alpha)_8$ barrel domain, as is typical for enzymes of the $(\beta\alpha)_8$ barrel fold.²⁶ An interesting structural point to note is that the AFP-like domain from the adjacent monomer effectively seals the active site from bulk solvent, and contributes residues involved in substrate recognition.^{23,25}

The active site of *Nme*NeuNAcS is defined largely by residues from β -strands 2 and 4 at the C-terminal of the $(\beta\alpha)_8$ barrel, however the linker and AFP-like domain also contribute residues to the active site. NeuNAc synthases from various bacterial species are known to be highly dependent on the presence of divalent metal ions.^{10,27} A single manganese ion is present within the active site of the *Nme*NeuNAcS structure, and is coordinated with octahedral geometry by the imidazole moieties of histidine (His)-215 and His-236, O2P of PEP, O-1 of rManNAc and two water molecules (Fig. 6). The C-1 hydroxyl group of the substrate analogue rManNAc is replaced by an aldehyde in the native substrate ManNAc. O-1 (rManNAc) coordination of the metal suggests that the native substrate aldehyde may similarly coordinate the metal thus allowing activation of the carbonyl centre for nucleophilic attack by PEP.²³

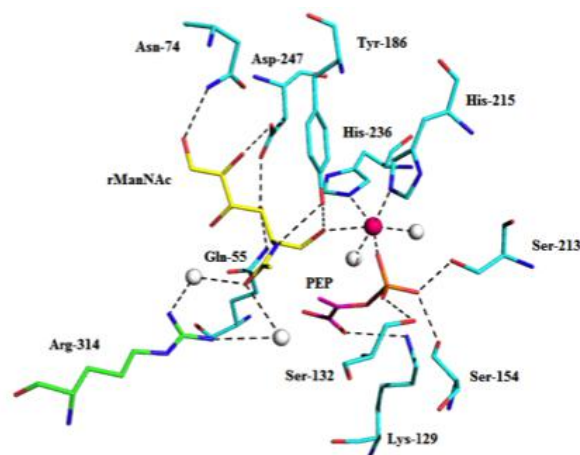


Fig. 6. The active site of NeuNAc synthase from *N. meningitidis*. The active site manganese ion (magenta sphere) has an octahedral coordination sphere, in which His-215, His-236, O2P of PEP (orange) and water (white spheres) fill the equatorial positions. An additional water molecule and O-1 from rManNAc (yellow) occupy the axial Mn^{2+} coordination sites. Multiple active site residues (cyan) form hydrogen bonds and/or salt bridges with the substrate molecules, stabilising catalytic orientations within the active site. Arg-314 (green/blue) from the AFP-like domain of the adjacent monomer extends into the active site and interacts with the *N*-acetyl group of rManNAc via active site water molecules. PDB entry: 1XUZ.

The substrate analogue rManNAc forms interactions with the highly conserved active site residues Asp-247, Gln-55 and Tyr-186 of *Nme*NeuNAcS. Interestingly, Arg-314 from the AFP-like domain of the adjacent monomer extends into the active site and forms hydrogen bonding interactions with the *N*-acetyl group of rManNAc via active site water molecules.^{23,28} Deletion of this highly conserved residue renders *Nme*NeuNAcS catalytically inert.²⁵ PEP also makes a number of interactions within the active site. The phosphate group of PEP forms hydrogen bonds with three conserved serine residues (Ser-132, Ser-154 and Ser-213) and the asparagine (Asn) residue Asn-184, while the PEP carboxylate is shown to form electrostatic interactions with two nearby lysine residues (Lys-129 and Lys-53).

As previously stated, only the full structure of *Nme*NeuNAcS has been solved, however the small AFP-like do-

main of the human sialic acid synthase NeuNAc-9-PS has been structurally characterised in solution by NMR.²⁸ This structure shows overall similarity to the bacterial AFP-like domain from *NmeNeuNAcS* with a backbone root-mean-square deviation (RMSD) value of 0.90 Å relative to residues 7-66 from the solved human domain (Fig. 7). Interestingly, the human AFP-like domain lacks the conserved residue Arg-314 that enters the active site in the bacterial enzyme (Fig. 7). Instead, conserved nearby lysine residues may facilitate the required electrostatic recognition and stabilisation of the mammalian substrate.^{28,29} Evolutionary analysis of the AFP-like domain of human NeuNAc-9-PS and type III antifreeze proteins from both bacteria and vertebrates suggests that the sialic acid synthase domain may be the evolutionary precursor to type III antifreeze proteins in vertebrates.²⁸ An antifreeze function of the ancestral sialic acid synthase domain may have evolved in response to changes in environmental temperature.²⁸

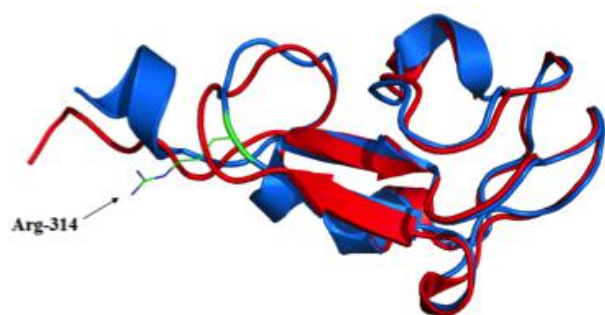


Fig. 7. Alignment of antifreeze protein-like domains from *NmeNeuNAcS* (blue) and human NeuNAc-9-PS (red). PDB entries: 1XUZ and 1WVO.

Mechanism of the sialic acid synthase catalysed reaction

Preliminary mechanistic studies on NeuNAc synthase from *C. jejuni* using deuterated substrates demonstrated that the enzyme catalysed aldol-like condensation reaction is stereospecific for nucleophilic attack of the *si* face of PEP with the *si* face of the aldehydic (open-chain) form of ManNAc.¹⁰ Subsequent labelling studies with *NmeNeuNAcS* showed that isotopically labelled ¹⁸O (bridging C-2 and P) from PEP is released as free phosphate through the course of the catalytic cycle.²³ This observation has important implications for the proposed reaction mechanism. The loss of labelled ¹⁸O as free phosphate suggests a mechanism which proceeds via a tetrahedral intermediate. Gunawan *et al*²³ proposed a C-O cleavage mechanism based on the results of their ¹⁸O labelling studies (Fig. 8). Initially PEP attacks the C-1 aldehyde

of ManNAc, yielding an oxocarbenium ion intermediate. Catalytic water present in the active site then attacks the electrophilic oxocarbenium carbonyl centre, generating a tetrahedral intermediate which spontaneously releases free phosphate via C-O bond cleavage. This yields open chain NeuNAc which can cyclise to its stable pyranose form in solution. This C-O bond cleavage mechanism is well documented in related PEP-utilising enzymes; 3-deoxy-D-manno-octulosonate 8-phosphate (KDO8P) synthase and 3-deoxy-D-arabino-heptulosonate-7-phosphate (DAH7P) synthase.^{30,31}

For this reaction mechanism to be plausible, the C-1 carbonyl of ManNAc requires activation to promote nucleophilic attack by PEP in the first step. Similarly, the nucleophilicity of the catalytic water must be increased to drive its attack on the oxocarbenium ion in the subsequent step. The crystal structure of *NmeNeuNAcS* shows the active site divalent metal ion occupies a position proximal to the C-1 hydroxyl of the ManNAc analogue. It could be imagined that the active site metal may coordinate the aldehyde oxygen of the native substrate, activating the aldehydic carbon to nucleophilic attack by PEP.²³ Several suggestions for the identity of the species responsible for activating water have been made. A glutamate residue (Glu-134) within close proximity of the active site water may act as a base, deprotonating the water and thereby promoting attack on the oxocarbenium ion intermediate. In addition, water coordination to the divalent metal ion in the active site may assist its deprotonation.²³

There is overwhelming evidence that a divalent metal ion is essential for catalysis of the sialic acid synthases.^{23, 32} This metal dependency can be rationalised if the metal is involved in such roles as activation of the ManNAc aldehyde and the catalytic water. Crystallisation of *NmeNeuNAcS* in the presence of a putative tetrahedral intermediate analogue provides strong evidence for a dual role of the divalent metal ion in catalysis.³² The orientation of the tetrahedral intermediate analogue within the active site strongly implies the role of metal in both activation of the ManNAc aldehyde, and delivery of water to the oxocarbenium ion in the following step of catalysis. This inhibitor bound crystal structure also suggests a strong preference for a tetrahedral intermediate with an (*R*)-configuration at C-2 due to the selectivity of the (*2R*) inhibitor over its (*S*)-diastereomer. The formation of this tetrahedral configuration would require a reaction mechanism that proceeds via the facial attack of catalytic water onto the *si*-face of the oxocarbenium ion intermediate.³²

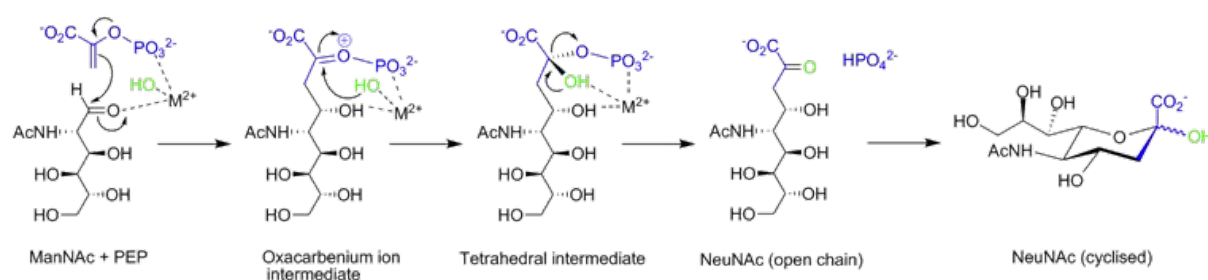


Fig. 8. Postulated mechanism of the reaction catalysed by *NmeNeuNAcS*.²³ Nucleophilic attack of PEP at the metal activated aldehyde gives rise to an oxocarbenium ion intermediate which is then attacked by water to form a tetrahedral intermediate. Decomposition of the intermediate via C-O bond cleavage releases NeuNAc and free phosphate to solution.

Decomposition of the tetrahedral intermediate in the final step of catalysis releases free phosphate and NeuNAc to solution. The driving force behind the collapse of the tetrahedral intermediate is thought to be ionisation of the C-2 hydroxyl group. Promoting deprotonation of the C-2 hydroxyl may be a third role for the coordinated metal ion, or this role may be played by a nearby basic residue.²³

There exists little mechanistic information pertaining to any of the other sialic synthases. However, sequence similarity implies that PEP and sugar substrate condensation may proceed via the same mechanism as is now established for *NmeNeuNAcS*. Glu-25 and Glu-234 are postulated catalytic residues involved in decomposition of the tetrahedral intermediate.²³ These residues, along with metal binding residues, are almost entirely conserved across phyla, suggesting a mechanistic commonality. The differential substrate specificity of the numerous sialic acid synthases would require general active site architecture modification, however the catalytic residues would be expected to remain largely unchanged if the same reaction mechanism is employed ubiquitously. A good example of this is the presence of a number of cationic residues near the human NeuNAc synthase active site that may encourage binding of the polyanionic substrate ManNAc-6-P. These charged residues are mostly absent in bacterial variants of the enzyme which utilise a neutral substrate, however other key catalytic residues are conserved. Furthermore, the metal dependency of all known sialic acid synthases suggests a common metallo-catalytic cycle. Further elucidation of the precise mechanism of the other sialic acid synthases will be made possible when high resolution crystal structures of these enzymes become available.

Conclusions

The sialic acids are a diverse family of nine-carbon keto-sugars, and the terminal residues of mammalian cell surface carbohydrate structures which facilitate cellular signalling and recognition events. Alongside their central biological function in mammals, sialic acids are involved in mediating bacterial and viral infection of mammalian hosts. The sialic acid synthases are an evolutionarily related family of enzymes which catalyse the formation of sialic acids via an aldol-like condensation of PEP with respective sialic acid precursor molecules. Biochemical and crystallographic analyses have provided insights into the structural and mechanistic detail of these enzymes. NeuNAc synthase from *N. meningitidis* exists as a unique domain swapped homo-dimer, each monomer of which contains a C-terminal (β)₈ barrel domain and an N-terminal antifreeze protein-like domain. This structure facilitates the condensation of PEP and ManNAc to form NeuNAc and free phosphate. ¹⁸O labelling studies have shown the reaction mechanism proceeds via oxocarbenium and tetrahedral intermediates, catalysis of which is highly dependent on divalent metal ions. Appreciable sequence conservation suggests that the structural and mechanistic understanding of *NmeNeuNAcS* can likely be applied to the other known sialic acid synthases for which such information is not yet available.

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Chemistry – an antidote to pseudoscientific thinking?

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Introduction

Knowledge of chemistry is a wonderful thing. It allows us to recognize and appreciate the many contributions chemistry has made to our modern way of life e.g., therapeutic drugs, new materials, safer foods, while also enhancing our understanding of how the world around us works. The ability to understand concepts such as kinetic theory, molecular structure, equilibrium, thermodynamics, and biochemical processes gives us a clearer picture of our world and can also help us make better decisions. It also has the potential to protect us from various forms of pseudoscience.

For those unfamiliar with the term, pseudoscience describes that which is portrayed as scientific but for which there is neither reliable evidence nor plausibility to support it. It is essentially “fake science”. Examples of pseudoscience relevant to chemists include homeopathy, detox therapies, “bio-identical” hormones, various nutritional claims as well as many of the arguments used against fluoridation and climate change.

The effects of pseudoscientific beliefs are not always obvious, particularly for those of us working in academia, where such beliefs are less likely to be encountered. However, they exist and can cause harm in a number of different ways. An area of particular concern is health “treatments” based on pseudoscientific beliefs. Pain, injury and even death can result when such treatments are embraced as an alternative to effective medical interventions. Examples of fatalities resulting from pseudoscientific beliefs include the death of a nine-month old girl in Australia from septicemia and malnutrition when her parents chose to treat her eczema using homeopathy – her parents were subsequently convicted of manslaughter¹ – and the death of a New Zealand woman when a cancerous lesion was allowed to grow to occupy a large part of her head and skull while under the treatment of a naturopath.² The website, whatstheharm.net,³ documents many other cases where belief in pseudoscience has had tragic consequences. So far over 300,000 deaths and a similar number of injuries have been attributed to such beliefs.

Pseudoscientific “treatments” can also be financially draining, particularly when they target the vulnerable, for example, a “detox” therapy at \$70 per treatment with a recommendation that consumers have between 10 and 20 treatments.⁴ The treatment was recommended for those suffering from a range of conditions including chronic fatigue, parasitic infections, arthritis, fibromyalgia and also as a post-radiation treatment. A description of how detox treatments are supposed to “work” is described in the next section.

Pseudoscientific beliefs can cloud public understanding of science, as demonstrated by ongoing public confusion

over climate change and water fluoridation. This is a major concern. Informed decisions can only be made when people understand the relevant science. It is vital that scientists (including chemists) participate in such discussions and communicate the science clearly and effectively.

Chemistry-related pseudoscience

Pseudoscience relies on an ignorance of science and the scientific method to convince people that it works. A knowledge of chemistry can help spot the flaws in different pseudoscientific beliefs and products, effectively acting as an antidote. Some examples of chemistry related pseudoscience are outlined below.

Detox therapies

There are several different types of detox therapies, the most common of which involves placing one’s feet in a warm salt water bath through which an electric current is passed. Within an hour the solution turns an orange brown colour which is claimed to consist of all of the toxins that have been pulled out of the body through the feet. A far more plausible explanation is that the electrodes placed in the water contain iron and that the discolouration is due to the iron salt produced in this electrolytic cell. This is a perfect example of how a knowledge of chemistry could help people avoid (and challenge) pseudoscience. A video explaining how this therapy is supposed to “work” can be found on Youtube⁵ for anyone willing to sit through 10 minutes of the most excruciatingly painful misuse of science terminology!

Another less expensive detox therapy involves sticking pads on the bottom of one’s feet overnight. By morning they will have turned a dark brown/black colour and smell awful. While those selling the pads claim this is the result of toxins pulled out of the body through the soles of the feet, a more scientific explanation is that the various compounds in the pads, including wood vinegar, absorb moisture from the feet overnight to produce the dark colour and pungent smell.

Homeopathy

Homeopathy is an alternative treatment that has been around for over 200 years, and has some high profile supporters including the British royal family. It is based on three interrelated beliefs:

1. The “Law” of Similars. The idea that something which causes similar symptoms to a disease can be used to treat the disease e.g., onion juice to treat conditions which cause teary eyes.
2. The more dilute a treatment is made, the more potent it becomes. Homeopathic treatments involve repeatedly diluting a substance by transferring 1 mL from a pre-

vious solution into 100 mL. Many treatments involve carrying out this process 30 times (to produce what is referred to as a 30C homeopathic solution). Of course a chemist will realise that once this dilution has occurred more than 12 times (a >12C solution) the chances of there being any of the original solution or active ingredient e.g., onion juice, becomes unlikely. Given that substances including arsenic and pus from an anthrax infected animal have been used in homeopathic solutions this level of dilution is somewhat reassuring.

3. After each dilution the solution is succussed (shaken) to supposedly transfer the properties of the original substance to the water molecules.

These beliefs make no sense based on what we now know about disease, how drugs work and basic chemical principles, so why do such beliefs persist? The first reason is that most people do not actually understand what homeopathy involves. A survey done in New Zealand about five years ago showed that over 90% of those surveyed thought it was some sort of herbal-based remedy. Simply explaining how homeopathy is purported to work is one way that its use could be discouraged. A second reason is that homeopathy was developed at a time when conventional medicine included treatments such as bloodletting and consumption of toxic mixtures containing arsenic and lead. Under such circumstances a treatment consisting of pure water would certainly be preferable! However, in the present day the decision to replace conventional and effective drugs with homeopathic remedies can have deadly results, with some homeopaths still recommending homeopathy as a viable alternative to antimalarial drugs and vaccines, and as a treatment for diseases such as cancer, dysentery and AIDS.

Miracle Mineral Solution (MMS)

Miracle Mineral Solution consists of a 28% sodium chlorite solution in distilled water which is “activated” with a food acid e.g., citric acid, before being taken orally. It has been sold as a treatment for a wide range of conditions, from acne to AIDS. It is sold largely via websites which use scientific misinformation to persuade consumers to buy it, for example by suggesting that because sodium chlorite works as a disinfectant (bleach) to kill micro-organisms externally then it must be effective internally. As well as being taken orally, MMS has been administered intravenously as a “cure” for cancer and as an enema to “treat” autistic children, an appalling example of how pseudoscience exploits the vulnerable and causes additional harm.

Vitamins and supplements

Vitamins and minerals are important for good health, but usually in trace amounts. Companies selling these products often distort the public’s understanding of our need for vitamins and other supplements by suggesting that if a little bit of something is good for you, then a lot must be even better. Instead, excessive vitamin and supplement use typically results in very expensive urine.

People can be encouraged to think more critically about vitamin and supplement use by reminding them that they are just one of many types of substances needed for good health e.g., fats, oils, proteins, carbohydrates, and that with

such substances there is usually an optimum dose beyond which there is no additional benefit, and even possible harm. Analogies can also be useful, for example asking if there would be any benefit in overfilling the oil in a car? It is also worth pointing out that for most people a well-balanced diet supplies all of our vitamin and mineral needs, while also providing other important nutrients, including fibre.

A more dangerous pseudoscientific view of vitamins and supplements is that they can be used as a “safe and natural” alternative to medicines, for example those who suggest that HIV can be effectively treated by use of vitamins and herbal remedies.

Herbal/natural remedies

Natural substances can possess potent medicinal properties. Indeed, many of our modern medicines were derived from research involving natural products. However, for every natural product which has been confirmed to have valuable medicinal benefits⁶ there are countless others for which claims are made which have never been verified, or which have been disproven.

The use of natural medicines can be made more hazardous by the erroneous belief that if something is natural then it is automatically safe to use. When encountering such beliefs, it is worth pointing out that some of the most lethal toxins known to humankind occur naturally, for example botulinum toxin, strychnine and tetrodotoxin (from the Puffer fish).

Faith in natural remedies, particularly when used instead of pharmaceuticals, often relied on a (unconscious) belief in vitalism – that substances derived from nature are somehow better than those made synthetically. Advocates of natural remedies may claim, for example, that vitamin C tablets made from natural materials are better than those which contain vitamin C which has been synthesized. Advocates of herbal medicines also ignore the fact that the dosage of beneficial compounds may vary significantly from batch to batch, and that as well as the beneficial compounds, herbal remedies may contain other less desirable compounds. Pharmaceutical preparations at least contain consistent and reliable doses of compounds which are known to be active.

Water fluoridation

The fluoridation of public water supplies has received great attention over the last year, largely due to the efforts of anti-fluoridation groups in regions such as Hamilton. There are many facets to this debate, and it is as much about societal values as it is about the science, for example is it reasonable to “mass-medicate” the population for the benefit of only some of the population?

Chemists can help bring some sense to the debate by clarifying the science behind fluoridation and also by countering poor arguments such as suggestions that fluoridation is a bad idea because fluorine is toxic and fluoridating agents are byproducts of fertiliser. Explaining that fluorine and fluoride are not the same, toxicity is dose dependent, and that just because something is a byproduct does not mean

it is harmful can at least help keep the debate focused on more rational arguments.

How to spot pseudoscience

Pseudoscience seeks legitimacy by pretending to be science. However, because it has neither plausibility nor evidence to support it, it can be easy to spot, particularly for those trained in science. The following list outlines some of the ways to spot pseudoscientific beliefs.

1. Misuse of scientific terminology. Terms such as “quantum”, “energy fields”, “vibrations”, “toxic overload” and “frequency” are often used to sound “sciency” while descriptions of basic science are just plain wrong, e.g., “electrolysis of water breaks the water molecule into H⁻ and OH⁺” (this description was used by a company providing detox treatments).
2. Explanations are implausible. Toxins being “sucked out” through the soles of the feet, and water “remembering” what it has been in contact with i.e., homeopathy.
3. Evidence to support pseudoscience involves misrepresentation of legitimate science, poorly run “experiments”, cherry picked evidence and anecdotes. Sometimes it is just made up.
4. May rely on dubious experts to support it.
5. Claims of conspiracy when challenged, e.g., the government (Big Pharma) is out to suppress the pseudoscientific “breakthrough”.
6. Attacks legitimate science. When denied the hard earned legitimacy of science, advocates of pseudoscientific beliefs often try to discredit science and medicine.

How do we counter pseudoscience?

Pseudoscience flourishes where there is a lack of understanding of science so one way to fight pseudoscience is to engage more with the general public. This could include getting involved with and/or giving talks to groups such as Rotary, Probus, Zonta and U3A. For those whose talents lie more with the written word, articles for newspapers and magazines, letters to the editor or contributing to a science-based blog are ways to help people understand science.

Chemists, by the very nature of our training, can contribute to public understanding of a wide range of important topics including:

- Toxicity is dose dependent (1 ppt of DDT in milk is not something to panic about)
- Natural compounds are not always safe and synthetic compounds are not always unhealthy
- Fluoridation
- Climate change (properties and reactions of carbon dioxide, methane, etc.)
- The chemical implausibility of homeopathy and other pseudoscientific beliefs
- How drugs work

When engaging with the public it is important to avoid the stereotypes that advocates of pseudoscience often promote,

such as that scientists are cold, disinterested and arrogant. Instead, communicating with enthusiasm, a genuine interest in your audience, and a sense of humour will provide an enjoyable time, not only for the audience but also for the presenter. A presentation’s content and delivery should be tailored to the audience to address their interests and background – a presentation to a group of year 13 chemistry students would of course differ from one given to a Rotary group. Scientific terms should be used judiciously and defined if your audience is likely to be unfamiliar with them. Giving a clear and concise explanation of scientific terms is one way to engage and include an audience in the topic. Asking questions of the audience during a talk is another way to include them and can be used to gauge their current views on a topic. It can also be a good way to get them to reflect on and question their existing beliefs. Making time to answer questions after a presentation is not only polite but also provides the opportunity to clarify points that the audience may not have quite understood.

Pseudoscience in advertising

Pseudoscientific products rely on advertising to attract new customers and the Advertising Standards Authority (ASA) provides an effective way to challenge them when the advertisements make claims which cannot be substantiated. Complaints can be made online⁷ and if successful require the advertiser to remove/rewrite the advertisement. So far I have laid 15 successful complaints against a range of companies including detox therapies, “chemical free” flea collars and BioMag magnetic underlays⁸ (for claiming that they induce melatonin production!). All one has to do is state the claims which cannot be substantiated and, where possible, provide evidence to demonstrate that the claims are wrong.

Summary

Chemists have a unique perspective on the world around us, one which makes us less vulnerable to pseudoscientific beliefs. We need to share this knowledge and challenge pseudoscientific beliefs as not only are they capable of doing harm to individuals, they also can result in poor decision making at a societal level. By engaging with our wider communities in an enthusiastic and respectful way we not only discourage people from pseudoscientific beliefs, we simultaneously encourage a greater interest in chemistry and the other sciences.

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Oxygen buster and other stories

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One of the items that arrived with the Christmas goodies was a pack of Canterbury Biltong Air-dried Beef Snacks. Apart from the tasty snacks, the pack included a sachet labelled "O-Buster" oxygen absorber. It was obviously included to absorb oxygen and, along with the drying of the meat, further minimise the risk of the product spoiling. But what did it contain? A quick check on Google and Wikipedia indicated the most likely composition of the sachet contents to be iron and sodium chloride, with maybe some activated charcoal. In other words, the oxygen content of the pack was being reduced by rusting as air and moisture permeate in. According to the website, the mix requires a relative humidity of 65% before rusting can take place and can reduce the level of oxygen in the surrounding atmosphere to 0.1%. The advantage of the iron/sodium chloride mix over other technologies is that it is cheap, there are no odours and it is food safe.

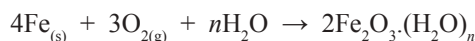


Beef snacks with a sachet of "O-Buster" oxygen absorber

Hand warmers

This reminded me of hand warmers that have a very similar technology. One type of hand warmer comes in a sealed plastic pouch. Inside is a porous sachet rather like a tea bag. After gentle shaking to mix the contents and allow air in, the temperature increases and the bag becomes quite warm and stays that way for an hour or more. The contents have been optimised to make the strongly exothermic rusting process take place as fast as possible; finely divided iron, salt, powdered carbon and vermiculite which has absorbed water. The only reactant missing is oxygen which is available once the sachet is removed from the sealed bag and shaken.

If the equation



is used to represent rusting, ΔH for the process is $-1648 \text{ kJ mol}^{-1}$. Rusting is normally so slow that this energy is dissipated as fast as it is released but under the conditions in the hand warmer the exothermic nature of the reaction is very apparent. The reaction can be temporarily halted by sealing the sachet in a self-lock plastic bag that has been smoothed, prior to locking, to remove as much air as possible.

Fencing wire

While on the topic of rusting, there is an interesting se-

quence in the development of fencing wire. Originally "pure" iron wire, which does not rust, was used. Sadly, a strand of wire stretched taut in summer contracted in the cold temperatures of winter and pulled the corner posts in. The next summer they expanded again, and sagged in loose loops. This was solved by using steel wire that has a much lower coefficient of expansion. But steel wire rusts and, after a season or two, weakens to the extent that animals could break it down and get out. This was solved by galvanising the steel wire and we had the ubiquitous No. 8 wire - the symbol of New Zealand ingenuity and mainstay of the farming industry.

How thick is the zinc coating?

A colleague of mine developed an elegant experiment in which an accurately weighed 3 cm square of galvanised iron sheet is dissolved in dilute hydrochloric acid. The zinc dissolves readily but under these conditions the iron is passive. Once the reaction is complete (and it is obvious when it is - no more bubbles and a uniform appearance on both sides of the metal) the square is removed, rinsed, dried and reweighed. The difference in mass gives the mass of zinc coating which is typically about 0.32 g. Using the mass and density of zinc (7.14 g cm^{-3}) the volume of zinc is calculated. Dividing the volume by the area (remember there is zinc on both sides) the thickness is calculated at 0.0025 cm. Taking the diameter of a zinc atom as $3.06 \times 10^{-8} \text{ cm}$ shows the layer is approximately 82,000 atoms of zinc thick.

Bluing

If the square of iron with zinc removed is heated strongly a blue coating forms. This is a coating of Fe_3O_4 which adheres to the iron and protects it from corrosion in the same way as aluminium oxide protects aluminium. It is a totally different process to rusting which is an electrochemical process unique to iron. Rusting creates a significant increase in volume and flakes off. Bluing is commonly used for protecting rifle barrels from corrosion. Commercially and industrially there are various techniques for bluing. In one, the items are heated in a solution of potassium nitrate and sodium hydroxide reaching temperatures of $135 \text{ }^\circ\text{C}$ to $154 \text{ }^\circ\text{C}$ (which indicates pretty concentrated solutions). Historically razor blades were blued, a necessity as they were constantly wet when in use. An interesting property of blued steel is that it has a non-linear resistance and World War II soldiers found they could utilise this feature and use razor blades as the detector in crystal sets.

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Wohlmann, water and whisky

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Introduction

Bottles of Lemon & Paeroa on supermarket shelves and television advertisements that include pictures of bathers in hot pools are the legacy of a nineteenth century Government initiative to exploit the numerous occurrences of geothermal springs as spas in the European tradition: bathing in hot waters and drinking cooled waters for the relief and possible cure of a variety of ailments. Central to this initiative was the appointment of Arthur Stanley Wohlmann in 1902 as the Government balneologist (Fig. 1).¹ His first task was to undertake a survey of New Zealand's hot springs in order to determine which might be most effectively used (Table 1).²



Fig. 1. A.S. Wohlmann. Appointed as Government balneologist in 1902, he was responsible for chronicling the chemical composition and alleged curative properties of New Zealand's hot springs. He is particularly remembered for his work in developing Rotorua as a spa town. Although he may have intended Rotorua to rival the spas of Europe, the reality was different: Rotorua, Te Aroha and Hamner instead provided an impetus to the fledgling tourism industry. [Photo: *New Zealand Illustrated Magazine*, vol. 7, issue 1, 1 October 1902, p. 4. Used with permission.]

Immersion in the waters

Ultimately the three occurrences of hot water that were identified as suitable for spa purposes were Rotorua and Te Aroha in the North Island and Hamner Springs in the South Island, of which Rotorua attracted most of the investment.³ All were used for bathing, but it remains un-

Table 1. The range of thermal waters investigated and classified by A.S. Wohlmann, Government balneologist²

Class	Description	Essential chemistry	No. of waters investigated
Simple thermal waters		Weakly mineralized	15
Muriated ^a waters		Chloride (Cl ⁻)	
I	Sodic muriated waters	Sodium (Na ⁺), chloride (Cl ⁻)	13
II	Calcic sodic muriated waters	Calcium (Ca ²⁺), Na ⁺ , Cl ⁻	11
III	Iodide muriated water	Iodide (I ⁻) 25 grains per gallon (0.036 g.litre ⁻¹), generally shown by the presence of iodine gas (I ₂)	27
IV	Magnesian sodic muriated water	Magnesium (Mg ²⁺), Na ⁺ , Cl ⁻	1
Simple alkaline waters ^b		Sodium bicarbonate (Na ⁺ , HCO ₃ ⁻)	2
Muriated alkaline waters		Na ⁺ , Cl ⁻ , HCO ₃ ⁻	2
Muriated sulphated waters		High in Cl ⁻ , with moderate Mg ²⁺ and SO ₄ ²⁻	1
Chalybeate waters		Iron (Fe ²⁺), HCO ₃ ⁻ and CO ₂ gas; only 6 of the 30 occurrences have all three components	30
Sulfur waters			
I	Alkaline sulfur ^c	High dissolved silica (SiO _{2(aq)})	21
II	Acid sulfur ^d	Less dissolved silica; acidic because of sulfuric acid (H ₂ SO ₄)	3 of 'innumerable'
III	Muddy waters	Quartz, amorphous silica, little feldspar; mud also contains 5 grains of gold and 6 dwt (24 grains) of silver per ton	unspecified
Arsenical waters ^e			unspecified
Borated waters ^f		Na ⁺ , borate	3
Mercurial ^g		Associated deposit contain globules of mercury	1
Minimum total of waters investigated			130

^a Muriatic acid is an old name for hydrochloric acid; thus, 'muriates' are 'chlorides'

^b Typical of Te Aroha

^c Typical of Rachel Spring, Rotorua

^d Typical of numerous springs in Rotorua, Wairakei, and Waiotapu

^e Only on White Island, although later found at Te Aroha

^f Typical of Hamner, where the concentration of sodium borate was reported as five times that in similar waters elsewhere; also later found at Te Aroha (see text)

^g Only at Ohaewai, in Northland

certain whether the specific composition of the water or simply the fact that the waters were warm was responsible for the waters' alleged curative properties when a human body afflicted by one or more of a wide range of medical conditions was immersed in the water.

As an example, there were suggestions that the waters in particular springs at Te Aroha were useful in relieving specific ailments: for example, water from Spring No. 8 "would relax the bowels", while water from Spring No. 15 would "confine" them; water from No. 2 bath was allegedly helpful in cases of rheumatic fever, while water from No. 3 bath was said to be helpful for eczema. However, it is difficult to find any single chemical characteristic of these waters (Table 2) that justifies these particular therapeutic claims.

Despite initial claims about the therapeutic value of bathing in hot water, until well into the 20th century, the spas were effectively under the control of the Tourist Department for most of their existence, and ultimately it was their recreational and tourist use that ensured their survival, whether under the control of local bodies or under private management.

Drinking the waters

The waters from Te Aroha were and are pleasant enough to drink (Fig. 2). Indeed, it was advertised by its bottler – Hancock and Company – as the 'autocrat of the dinner table'. Because the acidic water at the Rotorua baths was not drinkable, Te Aroha water was sold at the baths for a penny a cup, and a shilling a bottle at the nearby Grand Hotel.³ As well as chronicling the attendance at the baths, particularly at Rotorua, Te Aroha and Hanmer, sales of bottled Te Aroha water – some of which was exported to Australia – were reported annually by the Government Balneologist for a decade from 1926 to 1936 (Table 3). Drinking the waters was essentially the lifeline for Te Aroha, since there was never sufficient water available either from the natural springs or as a result of drilling for a large bathing establishment.⁴

Table 2. Composition of selected waters at the Te Aroha spa ¹¹

	Bath No. 2	Bath No. 3	Spring No. 8	Spring No. 15
<i>Concentrations (in grains/gallon)</i>				
NaHCO ₃	426.29	429.19	451.97	331.76
NaCl	60.45	60.51	66.14	43.11
KCl	1.90	Trace	1.96	-
Na ₂ SO ₄	32.67	32.82	32.91	22.16
CaCO ₃	7.12	7.24	7.47	6.91
MgCO ₃	4.21	4.20	4.21	3.61
silica	7.12	7.21	8.60	7.05
Al, Fe	Trace	Trace	Trace	Trace
Sum	539.76	541.17	573.26	414.60
Temperature (°F)	112	90 – 112	109	139

Table 3. Number of bottles of No. 15 spring water from Te Aroha sent to Rotorua and sold there, 1926-1936

Year	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936
No. of bottles	196	138	96	80	78	62	50	46	44	51	42

*Data from *Appendices to the Journal of the House of Representatives*



Fig.2. The gazebo built for No. 15 Spring at Te Aroha: "View of a man and two children in the summer house, a wooden gazebo with a thatched roof, at the 'No. 15' mineral spring in the Government Tourist Domain at Te Aroha. A hand pump for providing drinking water is in the centre, with a sign above it that reads: 'The public are warned against removing mineral water in bulk or using it at the spring for other than drinking purposes / by order'. Photograph taken circa 1910s, by Frederick George Radcliffe." [Photo: Alexander Turnbull Library, Ref.: 1/2-006352-G]

Wohlmann made copious comments about the suitability of the waters he encountered as potentially useful as medicinal waters, and as table waters, many of which have been reported in later works.³

Rather more recently, a classification scheme for the taste of mineral waters has been developed based on the contribution of six 'concepts': 'balance' ('carbonation', effectively the amount of CO₂),⁵ 'virginity' (NO₃-), 'minerality' (total dissolved solids), 'orientation' (pH), 'hardness' (Ca and Mg), and 'vintage' (age).⁶ For geothermal waters obtained from wells or fast-flowing springs, the concentration of nitrate is expected to be very low.

Thus, the influence of ‘virginity’ on their taste can be ignored. Moreover, most geothermal waters are hundreds to thousands of years old, so ‘vintage’ can also be ignored. The modern chemical compositions of a selection of geothermal waters considered by Wohlman to be particularly suitable as ‘table waters’ are mapped against balance, minerality, orientation and hardness concepts in Table 4.⁷ Of these ‘concepts’, balance, minerality and orientation are the characteristics of water believed to be most responsible for its taste, these three ‘concepts’ contributing 75%, 20%, and 5% to the taste respectively. The geothermal waters in Table 4 are shown on a ‘balance’ versus ‘minerality’ grid (Fig. 3). This grid shows that most of the waters contain high concentrations of total dissolved solids, and that they collectively encompass a wide range of dissolved carbon dioxide concentrations.

In a few cases, more exotic chemical components in or associated with the geothermal waters were identified and promoted. Wohlmann prescribed several glasses of ‘radioactive water’ each day for some visitors to Rotorua. However, the radioactivity was not derived from the geothermal water itself; rather, water was irradiated with radon derived from the decay of a small amount of radium bromide, rather than being naturally radioactive.⁸ In fact, the water from Te Aroha, which as mentioned above, was sold in Rotorua, could have been used instead, since it was found to be naturally radioactive in 1911: the radium content of Spring No. 8 being cited as $1.0 \times 10^{-14} \text{ g cm}^{-3}$, and that of Spring No. 15 as $3.1 \times 10^{-14} \text{ g cm}^{-3}$, respective-

ly.⁹ As analytical techniques improved other potentially harmful chemical elements were identified, which began to cast doubt on the advisability of drinking these waters. Prominent among these was boron. For example, analysis of the water at Te Aroha indicated that it contained significant boron and arsenic,¹⁰ and a sign was later erected advising against drinking it.¹¹

Among the warm and hot springs visited by Wohlmann, 27 were noted as containing iodine. In his particular classification of waters, these were “Class III – Iodide muriated waters”; and of the iodide in them he noted that there was “seldom more than 2.5 grains per gallon, but even this small quantity exceeds the amount present in most similar European waters”.

In Wohlmann’s time the therapeutic value of iodine for the thyroid was recognised, if not understood, and he further speculated that if the waters containing iodide had any benefit, it was because of iodine rather than iodide:

“There remains the possibility, however, that the essentially active factor is not the iodide, but the free nascent iodine which is almost always present. The pungent smell of the mineral may generally be detected for some distance around the source of an iodide spring, and where the thermal water is broken up by a fall into a spring or douche, under which circumstances free iodine seems to be liberated, the odour is particularly strong. It is conceivable that apart from the iodine that is taken into the system

Balance (as CO ₂)	Still				
	Effervescent		7	9	3 5
	Light				
	Classic			4	2
	Bold				8
	Super low	Low	Medium	High	Very high
Minerality (as total dissolved solids)					
<p>1 Te Aroha (Mokena well) – “the autocrat of the dinner table”; 2 Morere (spring), East Coast of North Island; 3 Waiwera (well), Auckland, said by a visiting doctor to be “not disagreeable, resembling diluted Wiesbaden water”; 4 Okauia – Crystal Springs, Matamata, of which Wohlmann noted this water was “Without medical value” but “would make an excellent and palatable table water”; 5 Parakai (well), Auckland; 6 Kamo, Northland, of which Wohlmann noted that the water was “foaming with a fierce effervescence of gas”; 7 Sapphire (well), near Tauranga, of which Wohlmann commented, “the fairly neutral water could be bottled as excellent table water”; 8 Paeroa (well), now combined with lemon juice or extract to make Lemon & Paeroa; 9 Jerusalem (spring), proxy for Pipiriki Spring, Whanganui River; 10 Puriri (spring), Coromandel Range, from which water was shipped to Auckland in kegs, bottled by Campbell & Ehrenfried and sold until the 1960s.</p>					

Fig. 3. Minerality vs balance for a selection of geothermal waters considered by Wohlmann to have potential as table waters.



Fig. 4. Left: Hatrick’s Accommodation House at Pipiriki, ca. 1900. [Photo: Alexander Turnbull Library, Ref: 1/1-020952-G used with permission]. Right: The paddle steamer ‘Waimari’ and passengers, on the Whanganui River, below Pipiriki, ca. 1900. [Photo: Alexander Turnbull Library, Ref: PA1-q-014-4405 used with permission].

Table 4. Masha's 'concepts' for fine drinking waters applied to selected New Zealand geothermal waters

Mascha's 'Concept'	Chemical characteristic		Selected North Island geothermal waters identified with potential for medicinal purposes or table waters*									
	Category	CO ₂ [†] (mg.l ⁻¹)	Te Aroha ①	Morere ②	Waiwera ③	Okauia ④	Parakai ⑤	Kamo ⑥	Sapphire ⑦	Paeroa ⑧	Pipiriki ⑨	Puriri ⑩
Balance	Still	0										
	Effervescent	0-2.5			0.07				1.87		1.03	
	Light	2.5-5.0										
	Classic	5.0-7.5		6.06		7.54						
	Bold	>7.5	56.3					54.2		1676		514
Minerality	Category	TDS [‡] (mg l ⁻¹)										
	Super low	0-50										
	Low	50-250							97.5			
	Medium	250-800				336					766	
	High	800-1500								1452		
Orientation	Very high	>1500	7249	26074	1933		1532	1635				4707
	Category	pH-range										
	Acidic	5.0-7.0								6.29		
	Neutral	6.7-7.3		6.95				6.73				
	Hint of sweet	7.3-7.8										7.30
Hardness	Alkaline	7.8-10.0	8.03		8.57	7.84	7.83		7.88		8.78	
	Category	Hardness [#] (mg l ⁻¹)										
	Soft	0-17.1									7.27	
	Slightly hard	17.1-60.0	28.6						53.3			
	Moderately hard	60-120			108	79.8						
Hardness	Hard	120-180				134.8						
	Very hard	>180		6328				804.5		937		404

Notes to Table 4

*For further details of these waters, see legend to Fig. 3.

†CO₂ calculated from $\alpha_{H_2CO_3}/\alpha_{HCO_3^-} = \alpha_{H^+}/K_1$, using K_1 values extrapolated and interpolated for values given in Drever (1982, p. 36) for the temperature range 0 – 50°C, assuming a logarithmic relationship between log K_1 and temperature

‡TDS calculated as the sum of concentration of cations Na⁺, K⁺, Ca²⁺, Mg²⁺, plus sum of concentration of anions SO₄²⁻, Cl⁻, and half of the concentration of HCO₃⁻.

#Hardness of water is calculated as {[Ca (in mg.l⁻¹) x 2.5] + [Mg (in mg.l⁻¹) x 4]}

when the water is drunk, quite an appreciable amount, and that in a highly active condition, may be inhaled with the water vapour and spray by the bather."²

At the request of the firm A. Hatrick and Co., which operated river steamers on the Whanganui River, Wohlmann investigated a hot spring near Pipiriki, recommending the water as a medicinal drinking water because of the presence of iodine. This information was used by Hatrick in 1906 to recommend to the Government that he erect a bath-house at the spring at his own expense and contribute to the cost of extending a nearby track to improve access. An extract from the Report on Scenery Preservation for 1907-1908 indicates that his request had fallen on responsive ears: "A spring of water near to Pipiriki on the banks of the Wanganui River was taken under the [Public Works] Act and has now been leased to Mr Hatrick, owner of the Pipiriki Accommodation House, who has by the terms of his lease, to keep it in order and erect a suitable drinking-fountain and bath-house thereon, which the public, on payment of a small charge can use. This will considerably popularize the spring which hitherto has been little known."¹² In fact, Hatrick did just that: the spring was advertised as a two-mile walk or boat-ride up-river along 'the Rhine of Maoriland' from his accommodation house (Fig. 4)¹³, and by the 1930s, posters promoted Pipiriki as important a tourist destination as the Chateau Tongariro and Waitomo Caves.¹⁴ Wohlmann's findings were highlighted in Hatrick's advertisements, an example of which is reproduced as Fig. 5. At the high pH of the Pipiriki Spring water (pH 8.78),⁷ the iodine is expected to be in the form of IO_3^- rather than I_2 , and little I_2 would be expected on the basis of the Eh-pH diagram of Fig. 6.¹⁵

Morere Springs on the East Coast of the North Island contains 1700 times the amount of iodide present in seawater: it "made the water so brown that bathers often thought it wasn't clean. People suffering from goitre drank Morere's special water; it was also drunk for the last stages of syphilis. The waters are now used for less desperate purposes."²³ The lower pH of these waters (viz., 6.95),⁷ means that the brown colour is unlikely to be caused by iodine dissolved in the water if the Eh-pH diagram for iodine under standard conditions is considered valid (see Fig. 6); but may result from the reaction $\text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$.

Although Morere Springs are somewhat unusual among geothermal springs in that they contain methane (which was used in gas lighting for the bath-house), natural gas seeps are common along the East Coast of the North Island.¹⁶

Whisky and water

A recent study has found that mixing iodide-containing water with whisky does affect its taste.¹⁷ Wohlmann made no comment about this, but he did note that water from Paeroa, 'blackened whisky', presumably on the basis of an experiment. He attributed this 'blackening' to the iron content of the water, going on to comment, "I am afraid that the universal use of tea in the Colony makes the demand for such a water very limited".³ This comment may seem strange until it is realised that water with a high iron content turns black when mixed with tannin-containing tea, coffee, or alcoholic beverages.¹⁸ This includes whisky

PIPIRIKI
Thermal Spring
BATHS.

Towels and Keys for Bath Rooms can be obtained from the Manager, Pipiriki House.

ANALYSIS OF WATER.

Sodium Chloride	121.88
Potassium Chloride	Traces	-52
Magnesium Iodide	Traces	
Calcium Sulphate	1.88
Aluminium Chloride	1.22
Sodium Carbonate48
Magnesium Carbonate	2.22
Silica	2.41
Total Solids				130.61

Dr. Wohlmann, Govt. Baineologist, states:
"Taken in regular doses, and on an empty stomach, it would act as a very gentle tonic in certain forms of Dyspepsia, by cleansing the stomach, and stimulating the gastric and intestinal mucous membranes. For internal administration the water is specially adapted. For this purpose it should be taken fresh at the spring before the three principal meals, the walk back to Pipiriki afterwards being rather an advantage, except in debilitated subjects. Aerated it should make an excellent table water.
The small amount of Silica present is an especial advantage in a country where most of the mineral springs are too Siliceous. The water would be classed as 'muriated' the chief constituent being Sodium Chloride; but the small quantity of Magnesium Iodide present is of much more importance than would be indicated by the analysis, as this Iodide tends to decomposition at the source, with the consequent liberation of free Iodide. Iodide in this 'nascent' condition has more powerful properties than in its ordinary state."

THERE IS A DRINKING FOUNTAIN AT THE SPRING
Also Bathrooms for Ladies and Gentlemen.

A. HATRICK & Co.,
Proprietors Wanganui River Steamer Fleet.

Fig. 5. Advertisement for Pipiriki Thermal Springs (National Archives, Ref. No. T0164, Item Ref. No. 1906/314). The second paragraph of Wohlmann's statement in the advertisement also featured in 'Advance Wanganui River', *Wanganui Herald* (1907, November 20).

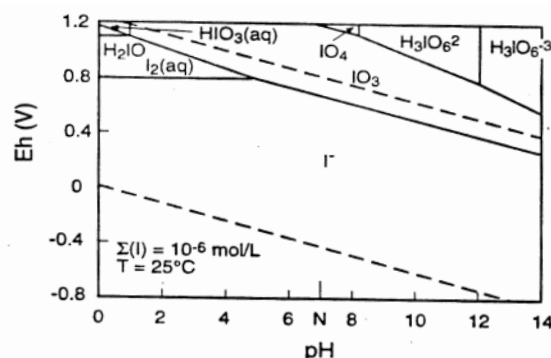


Fig. 6. Eh-pH diagram for iodine at 25°C.¹⁵

because even though iron-free calcium-bearing waters are sought in the making of the beverage,¹⁹ it is generally aged in wooden barrels, from which tannins enter the whisky.

The modern-day Lemon and Paeroa carbonated soft drink contains 160 mg kg⁻¹ of sodium,²⁰ similar to the natural Paeroa spring water.⁷ It also has lemon juice or lemon extract added. Adding strong tea to modern-day Lemon and Paeroa produces no 'blackening', suggesting that it is either not made from the natural Paeroa water, or that it is made from the Paeroa water from which the iron has been removed. Of course, had the experiment worked, the black material made from the combination of tannins and irons would have been gall ink²¹ and could have been used in the writing of this article, had a computer not been available.

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Science in the News: Marsden Fund celebrates 20 years

On Tuesday 18 February this year scientists, researchers and politicians celebrated 20 years of the Marsden Fund. The Fund was established by the New Zealand government in 1994. The event was hosted in Parliament by the Hon. Steven Joyce, Minister for Science and Innovation. Over the course of its lifetime the Marsden Fund has allocated over \$600 million to support research excellence in the areas of science, engineering, mathematics, social sciences and the humanities. Recommendations for funding are made by the 11 distinguished scientists who comprise the Marsden fund council.

The panel includes:

- Professor Juliet Gerrard: Chair of the Marsden Fund Council
- Professor Vicky Cameron: Convenor, Biomedical Sciences panel
- Dr Ian Ferguson: Convenor, Cellular and Molecular Physiology panel
- Professor Robert Hannah: Convenor, Humanities panel
- Professor Margaret Hyland: Convenor, Engineering and Interdisciplinary Sciences panel
- Professor Jari Kaipio: Convenor, Mathematical and Information Sciences panel
- Professor Jarg Pettinga: Convenor, Earth Sciences and Astronomy panel
- Dr Grant Scobie: Convenor, Economics and Human and Behavioural Sciences panel
- Professor Linda Smith: Convenor, Social Sciences panel
- Professor Graham Wallis: Convenor, Ecology, Evolution and Behaviour panel
- Professor David Williams: Convenor, Physics, Chemistry and Biochemistry panel

Professor Gerrard gave a speech at the event as did Professor Jason Tyljanakis

"Looking back over the last two decades, it becomes clear how Marsden-funded research has benefited all New Zealanders," says Professor Juliet Gerrard, chairperson of the Mars-

den Fund Council. "Many projects have a long lead-in time, but increasing our basic understanding of the world has now brought improved environmental outcomes, new technologies and better medicines and healthcare.

"What's important about the Marsden Fund is that it gives our best and brightest researchers the freedom to explore their most exciting ideas. This is how important breakthroughs are made," says Professor Gerrard.

"Who would have thought that finding a sheep that kept on having triplets would result in better IVF treatment for women? Or that investigating brain development would lead to a new product for healing wounds?"

"The research being funded by the Marsden Fund today – ranging from understanding New Zealand drinking culture to investigating how pests will respond to global climate change – is work that will benefit New Zealand for decades to come."

She also stated: "In particular, the Marsden fund has supported over 1200 postdoctoral researchers and approaching 3000 PhD students. The fast start fund has also provided a vital boost to emerging researchers establishing their research careers in NZ."

The Marsden fund council assesses proposals under the themes: Biomedical Sciences; Cellular, Molecular and Physiological Biology; Earth Sciences and Astronomy; Ecology, Evolution and Behaviour; Economics and Human and Behavioural Sciences; Engineering and Interdisciplinary Sciences; Humanities; Mathematical and Information Sciences; Physics, Chemistry and Biochemistry and Social Sciences. Funding equating to over NZ\$59 million was allocated across 109 successful research projects in 2013.

The Marsden fund is named after the physicist Sir Ernest Marsden (1889-1970). He worked with Ernest Rutherford on research which led to the Nobel Prize winning model of the atom. He was appointed Professor of Physics at Victoria University Wellington and was also appointed head of the government's Department of Scientific and Industrial Research.

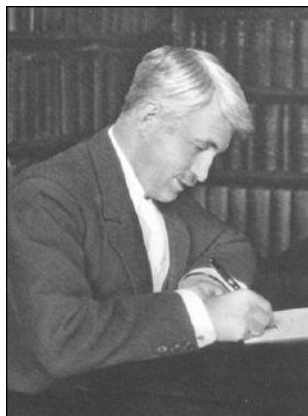
Some Unremembered Chemists

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.

Joseph William Mellor, CBE, FRS (1869-1938)

Brian Halton

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



Joseph William (Joe) Mellor was born on July 9, 1869, in the small town of Lindley some two miles from the centre of Huddersfield in Yorkshire, the third child of Job and his wife, Emma (née Smith). His elder brother Frank had died at two years of age in March 1869 before Joseph was born leaving his sister, Ada, his only sibling at birth. His parents sub-

sequently had a further six children of whom younger brother Oliver (1874) and sister Amy (1875) each survived only a matter of months. His other sisters Ada, Agnes and Gertrude came to New Zealand with Joseph and their parents when they emigrated from the UK in 1879. The youngest child, Nellie, was born on the voyage and given Hurunui as her middle name, after the sailing ship in which they had passage. A youngest brother, Alfred, was born in Dunedin in 1883.¹

The family arrived in Lyttleton on December 6, 1879, after a 114 day voyage.² Job Mellor found work in the mill of the Kaiapoi Woollen Manufacturing Company and the family settled in the north Canterbury town. The then newly established company took on many workers from the north of England because of their skill in spinning and weaving, but the Mellor family's time there was a mere two years as Job found better prospects in Dunedin. He settled his family there permanently in 1881 when he gained work in the Ross and Glendining Roslyn Worsted and Woollen Mills.³ The firm had begun operations in 1879 in the Kaikorai valley as one of a number of factories and Job Mellor settled and built his house in the valley. The children went to the local Linden (the original name for the area) School, which became the (New) Kaikorai School in 1884. As noted above, the last of Job and Emma Mellor's children, Alfred, was born in 1883 in Kaikorai, but little is known of him. It appears that he was a jeweller prior to serving in WWI in 1918 as a Private in the 34th Reinforcements Otago Infantry Regiment, D Company, but his life span is unknown.

The Mellor family was not wealthy and Joe left the Kaikorai School at age thirteen in 1882 to begin work as free secondary education did not exist at that time. Initially, he was a handy-boy for Mr. H. S. Fish, the then MP for Dunedin South and former (1870-73) and subsequent (1893-95) Otago City Mayor. From there Joe went to Si-

mon Brothers boot shop and then to McKinley's boot factory, finally spending several years in the boot factory of Sargood, Son and Ewen, which employed upwards of 250 workers after its move from Cresswell Street to its site adjacent to the Rattray Street wharf in 1889. As recorded in the *Railways Magazine*³ (and elsewhere), the young Mellor was a 'boot clicker', the person who cuts the uppers for shoes or boots from a sheet of leather and named as such after the sound that the machine made. However, A.H. Reed in his summary of Mellor⁴ cites first-hand evidence that Joe was a finisher, rubbing down soles to provide a good appearance and water-proofing, blackening and waxing the boots.



Sargood, Son & Ewen Boot Factory boot factory 11 November 1918 (<http://hockensnapshop.ac.nz/nodes/view/5436>)

Mellor's foreman in the factory recollected him as being studious, pondering over mysterious books during the lunch hour and whenever the factory was at standstill.^{3,4} Joe Mellor took to self-education, even building himself a small 1800 x 1800 mm corrugated iron shed in the garden at home for the purpose. The shed became his evening retreat, heated by a brick put in the kitchen oven over the evening meal by his mother and then wrapped in a flannel to keep his feet warm; it was lit by a small kerosene lamp. Here Joe carried out those experiments that his limited savings would allow and he read much. He borrowed books from wherever he could and then copied out the contents in longhand. His parents had much hope and expectation for their studious son. In his early teens, Joe confided to Arthur Ellis (a life-long friend who married his sister Agnes on Christmas Day in 1894) that he was determined to become the foremost chemist of his generation. Perhaps this enthusiasm came from his father's interest in anything scientific.

In any event, Joe's endeavours gained the attention of Mr. Thompson, the science master at Otago Boy's High School who was a founder, director and teacher at the

Dunedin Technical School that opened in 1889. The twenty-year old Mellor took immediate advantage of the evening classes offered and matriculated in 1892, gaining the respect of Thompson to the extent that a scholarship to the University of Otago was arranged for him; Thompson even negotiated the time off work from Sargood's so that Mellor could attend lectures. As a part-time student it took Mellor until 1897 to graduate with his BSc degree. Under the university's inaugural Professor of Chemistry, J. G. Black, Joe Mellor was awarded the Senior Scholarship in chemistry that year and he proceeded directly to Honours from which he graduated first-class and was offered the 1851 Scholarship in Science in 1898. This proved to be not as straightforward as might be imagined. The examination papers were set by specialists in England and the scripts returned there for marking. However, the steamship carrying them sank off Cape Horn and the candidates were re-examined.⁴ Once offered, Joe accepted the 1851 electing to study chemistry at Victoria University (Owens College) in Manchester. Since the funds from the scholarship did not become available until later in 1899, the young graduate was employed as a lecturer in Natural Sciences at Canterbury (later Lincoln) Agricultural College until the middle of the year. On June 25 in Dunedin, Joseph William Mellor married Emma Cranwell Bakes, a gracious young lady from Lincolnshire, England, who had been brought up in Auckland and lived with her mother in Stanley Street, Mornington. She was a music teacher and the organist at Dunedin's Mornington Methodist Church. The newly married couple sailed from Port Chalmers for England a short time later and Joe took up his scholarship, never to return to New Zealand. The Mellors had no children and Emma remained her husband's constant companion, assisting him throughout his busy and hectic life. A.H. Reed records that Mellor was her 'Joe' and Emma his 'boss'.⁴

Owens College in Manchester was the first constituent part of the federal Victoria University, England's first civic university comprising of Owens and colleges in Leeds, Liverpool and Birmingham. Once there, Mellor came to experience the subsequently noted organic chemist, W.H. Perkin Jr. and started work with him. His exploits into organic chemistry led to a 1901 publication 'Some α -alkyl substitution products of glutaric, adipic and pimelic acids',⁵ which showed the chain extension of ethyl 4-chlorobutanoate [ClCH₂(CH₂)₂CO₂Et] with the sodium salt of diethyl malonate [NaCH(CO₂Et)₂] to be just as effective and more judicious with 1-chloro-4-cyanobutane [ClCH₂(CH₂)₂CH₂CN].

Despite this, it was physical chemist H.B. Dixon who had the greater influence on Joe and it was he who set him on his subsequent career^{6,7} from research into the combination of hydrogen and chlorine that ran to a series of seven papers in the various Chemical Society publications (Proceedings, Transactions and Journal).⁸ In essence, Mellor repeated the earlier 19th century studies of Draper, Bunsen and Roscoe, and Pringsheim, showing the first two works to be correct while that of Pringsheim, who had suggested Cl₂O as the reaction intermediate, was not; Mellor proposed an alternative mechanism.

In addition to his research studies, Joe Mellor began his 'second' career, namely that of an author, and a noted one at that. It was in 1901 that he had the idea of writing a book to make it easier for students to grasp concepts of the mathematics that one of his contemporaries in particular had had difficulties with when trying to follow chemical developments. Dixon encouraged him, the outcome of which was *Higher Mathematics for Students of Chemistry and Physics*⁹ that ran to four editions and was reprinted in 1926. Prior to the completion of Mellor's Manchester studies, Professor Black at Otago University retired and it was suggested to him that Mellor be appointed as his successor; Black decreed that "he would be wasted here" envisaging a distinguished career for the man in England.³ Thus, with his doctoral studies completed and an Otago University^{10,11} (not Owens College¹²) DSc degree, Dr Mellor applied in 1902 for and accepted appointment as Science Master at Newcastle High School (now Newcastle-under-Lyme School). It seems that his application for this position was made on the mistaken assumption that he was applying for a post in Newcastle-upon-Tyne in north-eastern England.¹¹ Thus, one may regard Joe Mellor's subsequent major contribution to the pottery industry as arising by chance since it was as a Staffordshire schoolmaster that he became fascinated by clay technology and pottery manufacture. It was during this time that he wrote his second book, *Chemical Statistics and Dynamics*, that appeared¹³ in 1905.

In 1900, the North Staffordshire Ceramic Society was formed to foster discussion on matters relating to the clay working industries.¹¹ Past and current students of local pottery classes were invited to attend the first meeting of the society. From its small beginnings it evolved and expanded into the English (then British) Ceramics Society that is now a part of the Institute of Materials, Minerals and Mining. Dr Mellor became associated with the society in about 1903, became a member in January 1905, and within six months was appointed vice-president and secretary, holding the latter post until his death in 1938; it is perhaps surprising that he never held the presidency.¹¹ The six pottery towns of Tunstall, Burslem, Hanley, Stoke, Fenton, and Longton (amalgamated in 1910 as Stoke-on-Trent) put pottery classes on a firm foundation by starting a pottery school in Tunstall in 1904 to which Dr Mellor was appointed lecturer and head in pottery manufacture. The school provided technical and scientific training for managers in the pottery industry but the early years of the school were not easy. By 1907 the school had moved to temporary buildings in Stoke alongside those where mining classes had commenced the previous year.¹⁴ Despite the rather meagre facilities, Mellor turned down the offer of the Chair of Chemistry at Sydney University in 1908, instead staying on in Stoke.¹⁵ In 1910, after amalgamation of the six towns, land in Stoke was set aside for an educational institution. Largely due to the efforts of Dr Mellor, plans for the building were drawn up and it opened in 1913 as the Central School of Science and Technology. It comprised large chemistry and physics laboratories, a large pottery laboratory, an analysis room, a grinding room, classrooms and lecture rooms, and other accommodation, while also providing for mining classes.¹⁶ The

old Pottery Department became the Ceramics Department to which Joe Mellor was appointed head where he established courses leading to degree level qualifications and organised research projects to help manufacturers produce better quality ware. As a teacher Mellor was popular with his students as his own early struggles gave him a deep insight into the difficulties of the evening-class student. Shortly before his death he is credited with saying "I think I spent some of the happiest years of my life with those early students".¹⁷

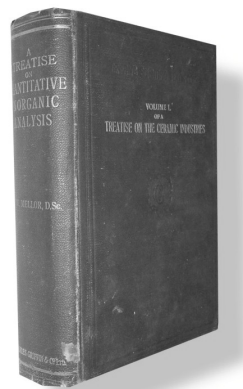
The early contributions that Mellor made to the ceramics industry were a 1904 paper in *Transaction of the English Ceramics Society*⁵ and a lecture to the North Staffordshire Ceramics Society on Saturday April 15, 1905, entitled *Crystalline glazes*, which was accompanied by a note with J. Rodgers on pink glazes.¹¹ In all, Mellor contributed over 100 papers to the British (originally English) Ceramic Transactions ranging widely over the field. These included studies on the constitution of clay and the crazing, peeling and durability of glazes of which he was especially interested. However, his studies extended to the action of heat on refractory materials, the specific heat of firebricks at high temperature and the fine grinding of ceramic materials. In presenting his work¹⁸ on the clay molecule (kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), Mellor apologised to the English Ceramic Society for its purely chemical nature going on to say "But clay is the lifeblood of pottery, and it is difficult to live with clay day after day without trying to form some idea of its nature and character. Today we may not know enough to see the practical bearing of this work but who dare predict what we shall see tomorrow".⁵ In presenting this work he acknowledged proofreading by the noted English potter Bernard Moore, a 1905 vase of whose is illustrated below and with whom Mellor had a life-long friendship. Mellor's early studies form the basis of understanding of clay firing, beyond which he contributed further to industry by providing his third text *The Crystallisation of Iron and Steel. An Introduction to the Study of Metallography*¹⁹ in 1905. This book was based on the six lectures he delivered to the engineering students at the Staffordshire County technical classes in November and December of 1904.



1905 Bernard Moore Porcellaneous stoneware vase with a flambé glaze; Victoria & Albert Museum C.175-1984 (reproduced with permission).

Despite his active involvement in the creation of the Central School of Science and Technology, Dr Mellor continued to perform research, write, and continue his teaching duties. In 1912 he published²⁰ his book *Modern Inorganic Chemistry* that went to eight editions (154,000 copies during his lifetime¹⁵), the last being prepared in 1939 by Dr G.D. Parkes a year after Mellor's death. It ran to 871

pages in its initial edition and became the standard inorganic textbook throughout the English speaking world and beyond. It was reprinted until 1951 and was abridged to provide three independent titles: *Introduction to Modern Inorganic Chemistry* (1914),²¹ *Intermediate Inorganic Chemistry* (1930)²² and *Elementary Inorganic Chemistry* (1930).²³ Following the initial 1912 release came *A treatise on quantitative inorganic analysis, with special reference to the analysis of clays, silicates, and related materials* in 1913 and this became a standard work on silicate analysis, also until well after his death.²⁴



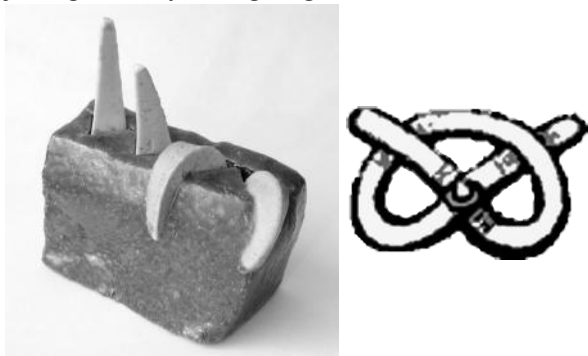
Mellor's 1913 Quantitative Inorganic Chemistry.

It was Mellor who recognised that almost every industry employing high temperature manufacturing processes in the early 20th century was limited in scope and efficiency by the durability of the refractory materials employed. He linked difficulties in the ceramics industry with those in firebrick manufacture. Indeed, it was largely as a result of his effort that the Refractories Committee of the Institution of Gas Engineers was formed in 1909, which instigated research into manufacture, properties and durability of refractory materials. Following from this came the 1920 British Refractories Research Association (BRRA) to which Dr Joseph Mellor was appointed the first research director, a position he held until his retirement in 1937. That year the pottery industry was required by the Import Duties Advisory Committee to create a research association and the British Pottery Research Association was formed. This and the BRRA merged in 1948 as the British Ceramic Research Association and a new building was opened in 1951 in Penkull, a dormitory suburb of Stoke-on-Trent.²⁵

At the outbreak of war in 1914, the British steel and pottery industries were faced with a major crisis. The steel industry was desperately short of suitable refractory linings for the existing furnaces and needed more fire bricks to build new ones to increase output for the shipbuilding, engineering and munitions industries; the pottery industry needed temperature-indicating cones in order to continue. Importation of the traditional magnesite (calcined MgCO_3) bricks from Austria was banned as were the Seger cones from Germany. Liverpool University geologists showed that the UK had sufficient raw materials to manufacture furnace linings and fire bricks except for magnesite. Greece was to become supplier but the composition of Greek magnesite bricks differed in composition from the Austrian ones and required additional

working. Aware of the problems the country was facing, and unable to join the armed forces because of ill health, Joseph Mellor approached government with an offer to use his expertise in the design of a new brick for the steel industry.²⁶ Working with his Staffordshire students in the Ceramics Department he developed a successful furnace lining that allowed the steel industry to maintain its production without even one day's interruption.

This work of Mellor appears to have been linked with that which followed an emergency meeting of the School's Governors that led to his services being offered to government to manufacture the vital pyrometric (Seger) cones commercially at the School.²⁶ These cones are triangular pyramids used to determine the internal furnace or kiln temperature and show when a material had been fired from placing inside a set of three or four cones and recording their bend at different temperatures. Working in a dedicated laboratory at the Central School of Science and Technology, Mellor developed a cone that became the *Staffordshire Cone*, stamped with the de Stafford knot, the traditional symbol of the English county of Staffordshire and of its county town. A workman was employed and paid 25 shillings (\$NZ 2.50) a week to make the cones under Mellor's supervision. The venture became so successful that Mellor's salary was increased to GBP 100 p.a. and two boys were employed from early 1915 to assist with the work and paid five shillings a week each (GBP 13 p.a.). Late that year an order for 200,000 cones was received. For the contributions that he made towards the war effort, Joseph was offered a peerage but he turned it down saying that he had given of his scientific knowledge freely to help his country because ill health prevented him joining the army and fighting in France.

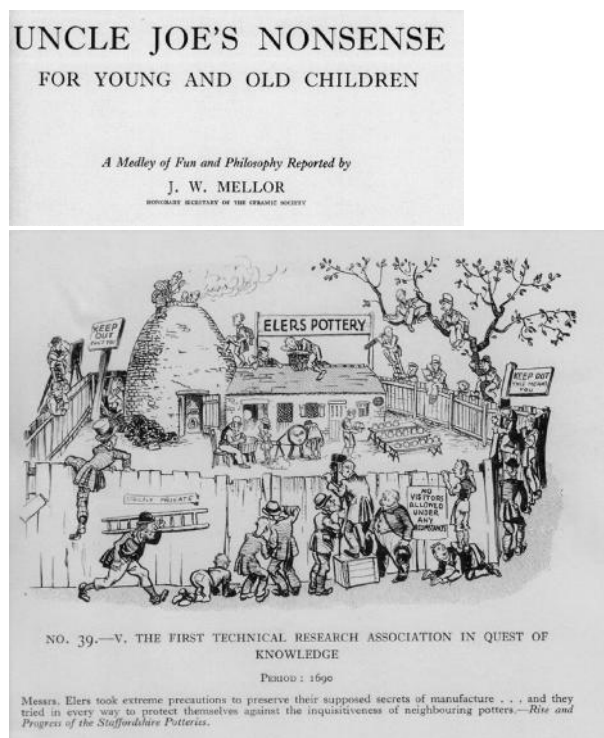


Left: Four pyrometric (Seger) cones (from <http://en.wikipedia.org/wiki/File:Segerkegel.jpg>); right: The Staffordshire knot (from http://en.wikipedia.org/wiki/File:Stafford_badge.png)

Throughout the remainder of his career as a teacher and researcher in the pottery industry Joseph Mellor maintained his position at the forefront of development and the British ceramics industry owes much of its 20th century reputation to the efforts of this man. As a major interest he researched glazes although his significant publications in the area did not appear until late in his career. Thus, his noted *The Cracking and Peeling of Glazes* and *The Durability of Pottery Frits, Glazes and Enamels in Service* appeared only in 1935 after his retirement from the Pottery Department at age 65 the previous year. However, Mellor was prodigious in his writing and from the early 1920s his attention focused more closely on what

became his monumental *Comprehensive Treatise on Theoretical and Inorganic Chemistry* that was published in 16 volumes between 1927 and 1937 by Longman, Green and Co. It started with the information collected for his 1912 *Inorganic Chemistry* text. Mellor collected all the information, wrote out every word of the every volume including all the citations given and had but one secretary with a standard manual typewriter to produce copy for the publisher. This *opus magnum* provided what has undoubtedly been the major reference work in the field. Each of the 16 volumes received much praise and supplements were produced under an editorial board until 1980. For a 21st century chemist to contemplate the time and effort required for Mellor to produce some 15,320 printed pages of detailed science from longhand written script with no computer is incomprehensible. It is not surprising therefore, that Joseph W. Mellor is best remembered among the chemical fraternity as an academic author *par excellence*. But Joseph W. Mellor made equal contributions to academic chemistry from his writings and to applied chemistry from his work with pottery materials.

Mellor had yet another side – that of the humourist. Although he had no children of his own he maintained contact with his nephews and nieces in New Zealand writing letters and illustrating them with cartoons. These culminated in a book published for the Ceramics Society by Longman Green in 1934 entitled as shown below and illustrated by the cartoon.²⁷ In addition to this Mellor was a part of the 1929 Ceramic Society delegation to the US on the Cunard liner, R.M.S. Laconia. For this Joe produced a 36-page log-book of the voyage, which contains the menus of the eight day voyage each adorned with two full-page cartoons. It has been described appropriately by Alexander Silverman who describes him not only as a wit but an artist *par excellence*.²⁸



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For his work Joseph Mellor became the second person connected with the ceramics industry elected Fellow of the Royal Society in May 1927. The first was Joshua Wedgewood (January 16, 1783), the noted potter who invented the pyrometer to measure internal furnace temperatures in 1782. Upon retirement from the BRR in 1937 Mellor received the CBE in the Coronation Honours and several authors have suggested that this was hardly fitting for someone who had made so many contributions to his country. He died in London on May 28, 1938 and, by 1960, the Mellor Building was constructed on the North Staffordshire Technical College site, now Staffordshire University.



Former technical college, Stoke, now part of Staffordshire University, UK; copyright Steven Birks reprinted under the Creative Commons Attribution-ShareAlike 2.0

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I am grateful to Dr. Ian Brown for comments on the manuscript and for providing the NZ records on Alfred Mellor.

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NZIC Conference 2013

The biennial NZIC conference held in Wellington from 1-5 December 2013 at Victoria University of Wellington's Rutherford House was a success. The organising committee, chaired by Dr **Richard Furneaux** (Callaghan Innovation) with the day-to-day running by Drs **Rob Keyzers** and **Matthias Lein** (VUW) provided a well balanced programme. Their efforts were strengthened by contributions from Drs **Joanne Harvey** (VUW), **Tim Kemmitt** (Callaghan Innovation), **Wendy Popplewell** (ESR) and **Ralf Schwörer** (Callaghan Innovation).

Section chairpersons were: Analytical: Dr Rob Keyzers, Education: Dr **Suzanne Boniface**, Inorganic: Prof **John Spencer**, Materials: A/Prof **Richard Tilley**, Organic: Dr **Ralf Schwörer** and Physical: Dr Matthias Lein. Dr Popplewell retired from the committee on maternity leave several months prior to the conference. It should also be noted that with the exception of Dr Lein (who was Treasurer for the Auckland Branch conference in Rotorua), none of the committee had had prior experience with organising large conferences.

The conference had fewer delegates than hoped. Initial predictions (and budget) were based on the numbers of attendees at the 2011 NZIC conference organised by Waikato with a "break-even" number of about 150. However, with a venue able to host 300, the ideal target number was 250. The conference attracted 174 delegates, including students, members, overseas visitors and chemistry education symposium attendees. In addition, 18 sponsor representatives attended the meeting. The reasons for the low number of delegates are likely the financial constraints of employer organisations (funding is getting harder and harder to obtain!), and the number of conflicting major conferences; NZ chemists often have to decide which meetings are best for them to attend. In 2013, many chose meetings other than the NZIC conference in Wellington.

Notwithstanding the above, the meeting was well received with unsolicited comments that came after the conference complementing an enjoyable event with a broad programme. The five international and one local plenary speaker were especially congratulatory. They were:

Ben Davis (Oxford) organic chemistry; Pieter Dorrestein (UC-SD) analytical chemistry; Tina Overton (Hull) chemical education; Jeff Tallon (Callaghan Innovation) physical chemistry; Tony Hill (ANU) inorganic chemistry; and Jim Watkins (Massachusetts) materials chemistry.

Each plenary was very well received. The inclusion of a specific education speaker was designed to improve the impact of the chemistry education symposium held concurrently as a separate "stream" on the second day. This initiative was successful and several attendees opted for the chemistry education sessions in preference to the more traditional conference break-out sessions; many indicated that this was a useful and thought-provoking opportunity for them. Unsurprisingly, most of these comments came from academic staff rather than students or CRI representatives.

It is worth noting that the break-out sessions were not overtly "streamed" by topic in order to encourage delegates

to go outside their area of interest, and many took advantage of this. In one case, a physical chemist (Sarah Masters) chaired an organic session and did an excellent job, surprising many of the speakers with her probing questions.

Delegates were not provided with a book of abstracts, but a preloaded 8 GB memory stick containing all the relevant conference information, supplemented with a small booklet with useful information and the abstracts for the plenary talks. This initiative was met with mixed reviews because not all attendees had mobile devices capable of using USB sticks and they were unable to read the abstracts. Whilst the provision of a hard-copy abstract book to write in during meeting provides a link to a topic after the conference, the committee felt digital abstracts offers a better, more practical option. The companies sponsoring the meeting were allocated trade-stall space and complementary registrations. The allocated mezzanine floor space in Rutherford House was alongside the poster display area and food servery.

Outside the scientific programme, options were available for delegates to relax with a conference session mixer on the Sunday evening, two optional excursions and the conference banquet. The mixer was a great success with the conference being opened by Prof Jim Metson, now the official scientific advisor to MBIE. The excursions were attended predominantly by our overseas international visitors. That to Wellington's South Coast and the local seal colony by a 4WD "wildlife" safari apparently caused several delegates to be "out of their comfort zone"! The other to the Weta Cave was followed by a tour and tasting at the Garage Project micro-brewery that apparently resulted in quite a few take-away sales!

The Conference Banquet, held at the Shed 6 entertainment venue on Wellington's waterfront, had been planned for the Amora Hotel but it was undergoing earthquake repairs to its ballroom. It was their staff that undertook to find a new venue, and Shed 6 proved ideal. The dinner entertainment was provided by the Mulligans, an excellent jazz quartet comprised of students from VUW's NZ School of Music. Those in the know rated it a top quality performance. The banquet provided a very fitting end to the conference entertainment and everyone had a good time.

Thursday 5 December, the last day of the conference, comprised the final lectures and presentations that included Jim Watkins' plenary. After this, the new Dean of Science and Engineering at VUW, Prof Mike Wilson, officially closed the conference around 1 pm in time for most attendees to make their way home.

The meeting was a success save for dissatisfaction by some of the sponsors. The quality of the catered food was amazing, and surprisingly, there was never a shortage of anything. This was supplemented by a quality selection of beverages at each event. Keeping the attendees well fed and well watered has to lead to success.

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Book Review

A Tale of 7 Elements by Eric Scerri

That a mere seven elements from the periodic table are selected for this book is an immediate attraction to open its covers to find out more.¹ In fact, the focus of the book is on the discovery of the seven elements in the periodic table which fill the gaps in Mendeleev's original periodic table. But Eric Scerri wants to do more than this for his reader; he sets the scene in the Intro-

duction by addressing the central issue of how the discovery of a chemical element should be defined, and the criteria by which priority of the discovery should be determined, showing that the latter is a good deal more fraught than might initially be imagined. The significance of the Introduction only becomes apparent later in the book.

Interesting though the two chapters that follow are – on the development of periodic table and its ‘invasion’ by physics, respectively – they do distract from the flow of the book. To be fair, Scerri notes that these chapters are effectively condensations of his earlier works,² and indicates that the reader might wish to skip to Chapter 3.

That said, the most significant section of these first two chapters for the development of this book is the 1½ pages devoted to Henry Moseley's work. His 1913 paper recognised the importance of atomic number rather than atomic weight in assigning the position of elements in the periodic table,³ and is an important precursor for the ultimate discovery of the seven chemical elements with which the book is concerned.

Following some discussion about the merits of several orders of presentation, the seven elements are presented in the order of their discovery, as shown in Table 1.

Table 1.

Chapter	Three	Four	Five	Six	Seven	Eight	Nine
Element	Protactinium	Hafnium	Rhenium	Technetium	Francium	Astatine	Promethium
Symbol	Pa	Hf	Re	Tc	Fr	At	Pm
Atomic no.	91	72	75	43	87	85	61
Earliest claim	1899	1911	1909	1827	1925	1931	1927
Discovery year*	1917	1923	1925	1937	1939	1940	1945
Senior Discoverer*	Meitner†	Hevesy†	Ida and Walter Noddack	Segrè†	Perey†	Segrè	Marinsky
Co-discoverer	Hahn†	Coster	Berg	Perrier		Corson† MacKenzie	Glendenin
Pages (% of text)	27 pp. 13%	17 pp. 8%	17 pp. 8%	29 pp. 14%	22 pp. 11%	11 pp. 5%	21 pp. 10%

*From *A Tale of 7 Elements*, figure 0.1, p. xvi

†Photographs included in *A Tale...*, some of which are portraits on postage stamps, evidence of the nationalism that has accompanied the discovery of these elements.

As each story unfolds, Scerri successfully incorporates information on the relevant experimental techniques needed or developed to enable the discovery and the impediments to progress brought about by war, international pride, and personal circumstances: providing a delightful if complex mix of technological development and sociological issues.

The co-discoverers of protactinium, Lise Meitner and Otto Hahn, for example, were respectively a physicist and a chemist who initially worked together, but became separated in their endeavours, firstly by the demands of the First World War, and then by the anti-Jewish sentiments of the inter-war period. Although Meitner and Hahn are recognised as co-discoverers in the text of this book, it was Hahn alone who received the Nobel Prize. For some elements, the controversy of priority of discovery continues to this day, albeit in somewhat muted form. The discovery of hafnium by Dutchman Dirk Coster and Hungarian György Hevesy was contested by the French researchers Georges Urbain and Alexandre Dauvillier, the scientific claims being complicated by feelings of partisanship in the interwar years. Much more recently the implications of the involvement of Niels Bohr and Fritz Paneth in prompting the direction of the research undertaken by Coster and Hevesy has come under renewed scrutiny by Scerri and others.

The discovery of rhenium (element 75) by Walter and Ida Noddack is portrayed as less controversial than the other elements.⁴ Over many years the claim of the one other serious contender for priority, Masataka Ogawa's ‘nipponium’, has been persistently reconsidered, but consistently dismissed. This narrative of this particular chapter is complicated by the Noddacks' involvement in the hunt for Element 43 – technetium – a quest in which they were not successful. The chapter on technetium is the longest in the book. This is not only because the earliest claim for discovering Element 43 dates back to 1823, and was followed by several unsubstantiated claims from around

the world, but because the story details a protracted controversy related to Noddack, Tacke and Bern's discovery of the element they called 'masurium'. Regardless of the science, their naming an element after a disastrous battle won by the Germans against the Russians, when scientists of both countries were vying for prominence in the discovery of the elements was both provocative and unhelpful. Ultimately, the Italian Emilio Segrè discovered element 43, 'mining' it from a cyclotron. As the first artificially produced element, this raised a further issue about the validity of the claim, which Scerri discusses in some detail.

By comparison, the story of the discovery of francium appears rather more straightforward, complicated only by Fred Allison's alleged discovery of element 87 (and also element 85) based on an ultimately refuted approach using a development of the Faraday effect first noted in 1845. Scerri observes that Allison's approach and other spectroscopy-based attempts were unlikely to succeed in discovering elements beyond bismuth (atomic number 83) because these elements were radioactive, i.e., "any researcher hoping to discover element 87 had to be working in the field of radiochemistry if they stood any chance of being successful" (p. 154). Allison and Segrè feature again in the chapter on astatine, being unsuccessful and successful, respectively; and, as with the other elements, "the various claims for its discovery reveal many nationalistic traits" (p. 165). Scerri appropriately acknowledges the contribution to this particular chapter from recent work by Brett Thornton and Shawn Burdette, who he describes as "two young chemists".⁵ International controversy, albeit less connected with post-First-World-War sentiments than for some of the other seven elements, swirled around the discovery of promethium – the element of the book's penultimate chapter. For this element, claims based on relationships of chemical properties (Bohuslav Brauner, from Bohemia) and X-ray spectra (Luigi Rolla and Lorenzo Fernandes, from Italy; Charles James, from Britain; Smith Hopkins, from the United States) ultimately foundered in the face of the conclusions drawn by Jacob Marinsky⁶ and Lawrence Glendenin from analysis of fission products using ion-exchange chromatography.

Each chapter concludes with at least one section on the properties and applications of the element. While the chemistry of and uses for these lesser known elements are interesting in their own right, these sections tend to distract from the theme of the book, and add little to its overall narrative.

Surprisingly, the book does not attempt to weave the commonalities and differences of the individual stories into a concluding chapter. Such a chapter could have picked up on the themes of the Introduction; it could have explored the effects of interwar and postwar nationalism or perhaps the delaying influence of outdated or inappropriate inves-

tigative techniques. Instead, Scerri uses his last chapter, 'From Missing Elements to Synthetic Elements' to traverse new ground. Even this chapter does not really reach a conclusion; thus, at page 208 the narrative just stops.

The text is supported by notes which cite additional research material and provide further anecdotes about the discovery process; and by a bibliography, which includes many primary sources, but not necessarily the papers written by the discoverers, as well as secondary sources that generally provide more recent comment and perspectives.

A Tale of 7 Elements will be an enjoyable read for those with a chemistry background, but those who supervise research in other disciplines may also find it insightful. This book reminds us all that real research does not neatly fit into a narrowly prescribed linear model, that its progress is constrained by technological and sociological factors, but is no less worthwhile for that. For at least the non-chemist audience, it would have been helpful for the periodic tables that head each chapter to also show atomic numbers, especially as in the text elements are frequently identified by atomic number, as is appropriate for the time before the name of the particular element was formally accepted.

In concluding this review, I can do no better than note Oliver Sacks' comment in the Preface to *A Tale...* that Scerri "allows us to see chemistry, and science generally, as an essentially historical enterprise – a human adventure that shows the best, and sometimes the worst, of human nature" (p. x), and agree that the book has succeeded in doing exactly that.

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3. Moseley, H.G.J. *Nature* **1913**, 92, 544. *A Tale...* does not include a photograph of Moseley, but one is available at: http://en.wikipedia.org/wiki/Henry_Moseley.
4. *A Tale...* does not include photographs of the senior discoverers of this element, but a photograph of Ida Noddack is available at: http://en.wikipedia.org/wiki/Ida_Noddack.
5. Thornton, B.F.; Burdette, S.C. *Bull. for the Hist. of Chem.* **2010**, 35, 86-96.
6. *A Tale...* does not include a photograph of Marinsky, but one is available at: http://en.wikipedia.org/wiki/Jacob_A._Marinsky.

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Dates of Note

Paul Karrer, the Swiss chemist who investigated the constitution of carotenoids, flavins, and vitamins A and B₂, and was 1937 Nobel Prize Laureate (with Haworth), was born on April 21, 1889. **Donald J. Cram**, the 1987 Nobel laureate in chemistry (with Pedersen and Lehn) for host-guest work, was born on 22 April 1919 and atomic scientist **J. Robert Oppenheimer** the same day in 1904. On April 26 in 1954, mass testing of the Salk polio vaccine began and involved about 1.8 million children. **Abraham Pineo Gesner**, the Canadian chemist and geologist who pioneered the extraction of kerosene (which he named) by the dry distillation of asphalt rock and realised its usefulness as a cleaner-burning fuel in lamps than whale oil, died on April 29, 1864 – 150 years ago.

Alexander William Williamson, the English chemist whose research on alcohols and ethers clarified organic molecular structure and for whom the etherification synthesis named, was born on May 1, 1824, as was **Hilaire Chardonnet** the same day in 1839; he was the French chemist and industrialist who first developed rayon, the first commonly used artificial fibre. **Frederic Stanley Kipping**, the British chemist who pioneered the chemistry of silicones, died on May 1, 1949, as did **John Walker** in 1859; he was the English chemist who invented friction matches made from small wooden sticks coated with sulfur, then tipped with a mixture of potassium chlorate, antimony sulfide and a binder of gum Arabic. May 1, 1964 was the day that saw the first BASIC program run on a computer. **Sergey Vasilyevich Lebedev**, the Russian chemist who developed a method for industrial production of polybutadiene in 1910 and whose process was begun in Russia in 1932-33 using potatoes and limestone as raw materials, died on May 2, 1934, as did **Giulio Natta**, the Italian chemist who contributed to the development of high polymers through the Ziegler-Natta catalysts, in 1979.

Wilbur Olin Atwater, the American scientist who developed agricultural chemistry, was born on May 3, 1844. **Max Delbrück**, the German chemist who developed the fermentation industry, established a school for distillation workers, a glass factory for the manufacture of reliable apparatus and instruments, and an experimental distillery, died on May 4, 1919. **Paul Lauterbur**, the American chemist who shared (with Mansfield) the 2003 Nobel Prize for Physiology or Medicine for discoveries concerning magnetic resonance imaging, was born on May 6, 1929. **Alexander von Humboldt**, the German natural scientist, archaeologist, explorer and geographer, after whom the cold ocean current along the Peruvian coast is named after (the Humboldt Current) and who has given his name to the noted German Foundation, died on May 6, 1859. **Sidney Altman**, the Canadian-American molecular biologist who shared the 1989 Nobel Prize for Chemistry with Cech for discoveries concerning RNA, has his 75th birthday on May 7.

Antoine-Laurent Lavoisier, the father of modern chemistry, was guillotined in Paris on May 8, 1794. **Paul-Louis**

Toussaint Héroult was the French chemist who invented the electric-arc furnace, widely used in making steel. Independently of the simultaneous work of Charles M. Hall of the US, he devised the electrolytic process for preparing aluminium; he died on May 9, 100 years ago. **Roy J. Plunkett**, the American inventor of Teflon (the DuPont trademark name for polytetrafluoroethylene - PTFE), died on May 12, 20 years ago, the same day that **Charles-Adolphe Wurtz** died in 1884. **Lars Frederik Nilson**, who discovered the oxide of scandium, scandia, in 1879 in the rare-earth mineral gadolinite, died on May 14, 1899. **Georg Ernst Stahl**, who developed the phlogiston theory of combustion and of such related biological processes as respiration, fermentation, and decay, was born on the same day in 1734. **Pierre Curie** was born on May 15, 1859, while **William Hume-Rothery**, the British metallurgist, internationally known for his work on the formation of alloys and intermetallic compounds was born on the same day in 1899. **Roy Patrick Kerr**, the New Zealand mathematician who solved in 1963 Einstein's field equations of general relativity to describe rotating black holes, has his 80th birthday on May 16. **Alfred O. C. Nier** who refined the mass spectrometric process to distinguish isotopes, died on May 16, 20 years ago. **Thomas Midgley**, who discovered the antiknock effectiveness of tetraethyl lead (C₂H₅)₄Pb in 1921, was born on May 18, 1899, the day 100 years ago that the first commercial cargo entered the Panama Canal. **Max Ferdinand Perutz**, the Austrian-born British biochemist and co-recipient of the 1962 Nobel Prize for Chemistry for his X-ray diffraction analysis of the structure of haemoglobin, was born on May 19, 100 years ago.

Bengt Ingemar Samuelsson, the Swedish biochemist and co-recipient (with fellow Swede S.K. Bergström and J.R. Vane) of the 1982 Nobel Prize for Physiology or Medicine for the isolation, identification, and analysis of numerous prostaglandins, has his 80th birthday on May 21. **William Whewell**, the British scientist, best known for his survey of scientific method and for creating scientific words (*scientist* and *physicist* by analogy with the word *artist*), founding mathematical crystallography, and developing Mohr's classification of minerals, was born on May 24, 1794. **Waldo Semon** who invented plasticised PVC (vinyl), died on May 26, 1999. Sir **Joseph Wilson Swan**, the English scientist, chemist, physicist and inventor, who produced an early electric incandescent lamp, died on May 27, 100 years ago, the day 20 years ago that the highest temperature produced in a lab was a plasma temperature of 510,000°C in the test reactor at Princeton University. **Antoine A. B. Bussy**, the French chemist who first prepared magnesium in a coherent form, was born on May 29, 1794, while **Sir Humphry Davy**, who discovered several chemical elements and compounds, invented the miner's safety lamp, and epitomised the scientific method, died on the same date in 1829.

June 2 marks the 280th anniversary of the founding of the Royal Swedish Academy of Sciences (Kungl. Vetenskapsakademien). On June 4, 1794, Joseph Priestley arrived

at New York in the US, having emigrated from England. Soon after, he settled in Northumberland, Pennsylvania. The day also marks the birth in 1739 of **Johann Beckmann**, the German chemist and economist who established the science of agriculture. **Adolf Windaus**, the German organic chemist, who was awarded the 1928 Nobel Prize for Chemistry for services rendered through his research into the constitution of the sterols and their connection with the vitamins, died on June 9, 1959. **Fritz Albert Lipmann**, the German-American biochemist who shared (with Krebs) the 1953 Nobel Prize for Physiology or Medicine for the discovery of coenzyme A, was born on June 12, 1899. The Cavendish Laboratory opened at the University of Cambridge on June 16, 1874. **Anders Jonas Angstrom**, the Swedish physicist whose pioneering use of spectroscopy is recognised in the name of the angstrom unit of length (10^{-10} metre), died on June 21, 1874.

Walther Hermann Nernst, the German scientist and one of the founders of modern physical chemistry was born on June 25, 150 years ago (1864). In 1889, Nernst devised his theory of electric potential and conduction of electrolytic solutions (the Nernst Equation) and introduced the *solubility product* to explain precipitation reactions. In 1906, he showed that it is possible to determine the equilibrium constant for a chemical reaction from thermal data, and in so doing he formulated what he himself called the third law of thermodynamics. **Lord Kelvin (William Thomson)** was born on June 26, 1824. **Mikhail Semyonovich Tswett**, the Russian father of chromatography, who developed and named the adsorption chromatography technique of separating plant pigments by extracting them from leaves with ether and alcohol and percolating the solution through a column of calcium carbonate, died on June 26, 1919. **James Smithson**, the English scientist who provided funds in his will for the founding of the Smithsonian Institution in Washington, DC, died on Jun 27, 1829. June 30 marks 75 years since the 60-in. diameter cyclotron was set in operation at University of California, Berkeley. Seven elements were discovered or made using it, beginning with the discovery of neptunium (Edwin McMillan), plutonium (Glenn Seaborg and his team), americium (atomic number 95), curium (96), berkelium (97), californium (98) and (by 1955) mendelevium (101).

Gerald Maurice Edelman, the American biochemist whose contributions concerning the chemical structure of antibodies won him (with Porter) the Nobel Prize for Medicine or Physiology in 1972, has his 85th birthday on July 1. The day also marks 80 years since the first X-ray of the whole body was taken in a one-second exposure. **Thomas Anderson**, the Scottish organic chemist who discovered pyridine, was born on July 2, 1819. **Marie Curie** died on July 4, 80 years ago. **Edward Robinson Squibb**, the US chemist and pharmaceutical manufacturer who improved the purity and reliability of drugs while a Navy medical officer, was born on July 4, 1819. **Georg Ohm**, the German physicist who showed by experiment that there are no perfect electrical conductors and was followed by his famous 1826 Ohm's law, died on July 6, 1854. **Lyman C. Craig**, the American chemist who developed the counter-current distribution (CCD) method for fractionation of complex mixtures with an apparatus that could simultaneously accomplish 20 quantitative extractions in a single step, died on July 7, 1974. The day also marks the 1954 death of **Saul Dushman**, the Russian-American physical chemist who was world leader in vacuum science. **Robert Burns Woodward**, the noted American organic chemist who received the Nobel Prize for Chemistry in 1965, died on July 8, 1979 as did **Torbern Olof Bergman** in 1784; he was the Swedish chemist who experimented with carbon dioxide, which he named *aerial acid* and successfully prepared artificial mineral water. **Emil Fischer**, the German chemist who was awarded the Nobel Prize for Chemistry in 1902 in recognition of his investigations of sugar and purine, died on July 15, 1919. This day in 1869, **Hippolyte Mège Mouriés** patented margarine in France. **Harold Dadford West**, the American biochemist and college president, who was the first to synthesise the essential amino acid threonine, was born on July 16, 1904. **Samuel Colt**, of Colt 45 fame, was born on July 19, 200 years ago. Sir **Ed(mund Percival) Hillary** was born on July 20, 1919, the day 50 years later (1969) that Apollo XI astronauts Neil Armstrong and Edwin "Buzz" Aldrin became the first men to walk on the moon.

Brian Halton

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The monetary value of natural gas condensate: a New Zealand perspective

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Introduction

I have recently¹ been examining the published condensate yields of a number of gas fields, in particular in Kazakhstan and in the North Sea. In this article I wish to perform a similar analysis for a source of natural gas in New Zealand. I go on to argue that the same analytical results in numerical terms for a gas field, say in the US, would be viewed and acted upon differently there from in New Zealand. My choice of 'source of natural gas in New Zealand' is the Cardiff-3 well in Taranaki, recently spudded in and therefore not yet producing. Resources there are quoted as 160 billion cubic feet of natural gas and 5.49 million barrels of condensate.² The operator is TAG Oil and, spudding having been completed, the drill tube of a narrower diameter than that close to the surface is being installed. The accompanying illustration² shows the drill tube at Cardiff-3 awaiting well installation.



Drill tube for use at Cardiff-3. Image reproduced with permission from TAG Oil Ltd.²

Calculations

Unlike oil or coal, natural gas is sold on a heat basis, not on a quantity basis. A widely used benchmark price is the Henry Hub price which, at the time of writing this article, is \$US3.62 per million BTU (British Thermal Units) of heat. One million BTU is equivalent to 1.06 GJ. Using a value of 37.5 MJ m⁻³ for the calorific value, the gas at Cardiff-3 is therefore worth:

$$[(160 \times 10^9 \text{ ft}^3 \times 0.028 \text{ m}^3 \text{ ft}^{-3} \times 37.5 \text{ MJ m}^{-3} \times 10^{-3} \text{ GJ MJ}^{-1}) \div 1.06] \text{ million BTU} \times \$\text{US}3.62 \text{ per million BTU} = \$\text{US}573 \text{ million at present-day prices.}$$

There appears to be no widely accepted benchmark price for natural gas condensate. It often seems to attract the same price as low-sulfur light crude and to be bracketed with it for pricing purposes. For example, prices of about \$100 for crude and condensate, by 2013 reckoning, are given without distinction between the two.³ The condensate at Cardiff-3 is therefore worth about \$US549 million. This is about 4% lower than the value of the gas and, having regard to approximations made and uncertainties in future prices and trends, we can cautiously conclude that the gas and the condensate at that particular source have approximately the same monetary value.

Discussion

As previously pointed out,¹ internationally there are fields where the condensate significantly exceeds the gas in finan-

cial value. At the Cardiff-3 well it will be about 50:50 according to the above calculations. It has also been pointed out that crude and condensate are sometimes considered jointly (although OPEC does not recognise any equivalence of one to the other), so to compare Cardiff-3 with an oil well having major amounts of associated gas would be reasonable – there are many such around the world. More importantly, the monetary value of a particular source or supply of natural gas is less of a 'hard number' than the price of a barrel of oil. A sufficiently interested reader can show, by converting a benchmark price for oil (OPEC, NYMEX, Brent) to units of \$US per million BTU and comparing that with Henry Hub, that unit heat from natural gas is worth only something like a fifth of unit heat from oil. This has been so over the history of the industry and is a major factor in there having been so much flaring of natural gas. This is now largely prohibited for GHG emission reasons, and has been replaced by reinjection of unwanted gas into the well after separation from the oil with which it was 'associated'.

New Zealand is still a long way from being self-sufficient in hydrocarbons, so thrift in the use of her reserves is required. In a country where hydrocarbons are more abundant, a case for treating a particular quantity of natural gas as being of negligible worth could be made much more easily than it could in New Zealand. Price comparisons like the above for Cardiff-3 based on US experience, therefore, have to be modified conceptually for the conditions prevailing in New Zealand. One consequence of the superfluity of natural gas in some parts of the world is that it can be made available at very low prices to refineries, keeping down refining costs. The only refinery in New Zealand is that at Marsden Point. This has a capacity of just under 0.1 million barrels of oil per day, making it a small refinery in world terms. I do not know the extent of natural gas usage at Marsden Point or where the gas is sourced, but quantities of gas which in other regimes might have been seen as hardly worth collecting would meet the energy requirements there.

Concluding remarks

I recall that not many years ago Air New Zealand was interested in biodiesels as jet fuel and that some related research was carried out. To get jet fuel from condensate is of course straightforward, and countries producing jet fuel in this way include the UAE. I note that Marsden Point is set up for condensate refining as well as for oil refining. That aviation as well as the 'motoring public' stand to gain from expansion of activity in condensate production and refining in New Zealand is clear.

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Can I patent my dinner? Protection of food technology innovations

Tim Stirrup

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The food and natural products industries generate innovations in a number of technology areas. These include packaging, bulk production apparatus and methods, texture and taste modifier compounds, health supplements and nutraceuticals to name but a few. As patent attorneys working closely with innovators in these industries, we are often asked to advise on strategies for protection of innovative food and beverage products and recipes. Such strategies generally include leveraging a number of different forms of intellectual property (IP) in order to protect the investment in innovation as well as to successfully compete and increase market share.

Trade marks are regularly used by food manufacturers to build brand awareness and reputation, as well as to deliver a particular taste perception by visual means.

Registered designs are used to protect innovative and distinctive packaging of foods and drinks.

Trade secrets are particularly important in protecting novel formulations and recipes, a classic example being the Coca Cola™ recipe which has purportedly been a closely guarded secret since 1886.

Patents are appropriate in some situations to protect innovative foods and beverages, especially where the method of production or the product itself includes unexpected results. For example, foods which exhibit novel textures, visual effects or cooking properties may be patentable.

It is often preferable to rely on trade secrets over patents where a patent will be hard to obtain or where disclosure of the details of the recipe and ingredients is undesirable. Trade secrets also need no registration and, as long as the recipe can be kept a secret and cannot be reverse engineered, the term of protection is unlimited. Innovations involving the optimisation of parameters of a known process often fall into the category of innovations best protected by trade secret.

In reality, modern analytical methods make it likely that most products could be reverse engineered given enough time and resources. In addition, employee mobility and the ease of copying electronic documents mean that trade secrets can be easily compromised. Once a competitor can replicate the recipe, often nothing can be done to prevent its use.

Next we'll look at the requirements of patentability in more detail and how they apply to food and beverage products and recipes.

Novelty

The most fundamental criterion to obtain grant of a patent is that the invention being claimed has not been previously published or used, i.e. it is novel. The date on which

novelty of the invention is judged is the filing date of the patent application. Its novelty is typically measured against all information that has been made available to the public in any form before that date; otherwise known as the *prior art*. Prior to the new Patents Act coming into force in New Zealand next year, prior publication or use outside of New Zealand does not compromise novelty of a New Zealand application. However, after it comes into force, prior publication or use of the invention anywhere in the world will compromise novelty for the New Zealand application.

Although confidential development and testing of a recipe is allowable, any previous publication by the inventor or any other person on the internet, in magazines, journals or by word of mouth will generally mean that the invention is not novel and a valid patent cannot be obtained. The test for whether a food or beverage is novel is fairly strict – has an identical product been previously published or used? If so, you will likely be out of luck in pursuing a patent for your product.

Inventive step (otherwise known as *obviousness*)

Obvious variations of known products or methods are not patentable. Therefore, even if your recipe contains ingredients that are not *identical* to a prior art recipe, if the ingredients are trivial variations that would routinely be used by a chef/product formulator, then the invention will be deemed to lack inventive step. For example, if a published recipe requires egg and you use a known egg substitute, then your recipe may meet the requirement for novelty (since it is not identical to the prior art) but it will likely be obvious and therefore unpatentable.

A combination of known components?

Recipes that merely combine known ingredients to yield a product whose characteristics would be expected are similarly unpatentable on the basis that they do not meet the definition of an *invention*. In order to be an invention in New Zealand, the combination of ingredients must result in some enhancement or improvement over what would have been expected by a person with skill and knowledge of the field. Alternatively, there must be some kind of surprising synergistic interaction between the ingredients to result in a new product.

Most recipes would fail the test for patentability on this criterion because the result would be expected. For example, adding an unusual flavouring compound to beaten egg whites and sugar then baking would be expected to create a meringue. Even though the meringue may be novel (if the flavouring hasn't been used in a meringue before) it would likely be unpatentable because the meringue produced would simply be a combination of known components with an expected result.

However, if the unusual flavouring compound had the unexpected result of adding stability to the resultant meringue, such a recipe could be classed as an invention and may be patentable assuming all other criteria are met. In this case there is something occurring between the egg whites and the flavouring compound which results in increased product stability.

Full disclosure of the invention

The patent system is fundamentally based on a bargain between the inventor and the State; the inventor makes a full and complete disclosure of the invention and how best to make it, and in exchange, the State provides a limited term (20 year) monopoly to exclude others from making, using, selling or importing the invention. The aim of the bargain is to encourage disclosure of information that others can use to further advance technology and to incentivise the research, development and commercialisation of new technologies.

In line with this bargain, the inventor must disclose all the details about how to make the new food/beverage product including ingredients, ratios, concentrations, methods of production/extraction etc. The disclosure must be sufficiently detailed that a skilled person in the industry can use the instructions in the patent document to replicate the food/beverage without extensive further experimentation. If a full disclosure is not given, the patent may be held invalid.

Where the invention is not sufficiently innovative to gain broad and commercially significant patent protection, the innovator may decide that giving away such sensitive information with scant reward is unpalatable. In these cases the innovator may prefer to rely on other methods to protect

the innovation such as branding (trade marks) and trade secrets.

Innovating our way to success

It is generally agreed that innovation in the food and beverage sector will play a large part in the future fortunes of New Zealand. A key step in developing the sector will be for innovators to recognise and protect that innovation in appropriate ways. There is no one-size-fits-all strategy to protect an innovative food or beverage; the key is to pursue a multi-tiered IP strategy tailored to the product and market. Innovators can then look to provide innovative products to the public while protecting their investment in innovation and growing their domestic and overseas business.

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

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Chemistry in the News

International Year of Crystallography

The International Year of Crystallography (IYCr2014) celebrates the 100th anniversary of the Max von Laue's Nobel prize. He was the German physicist who won the Nobel prize in Physics in 1914 for the discovery of the diffraction of X-rays by crystals. It also celebrates the 400th anniversary of Kepler's observations in relation to the symmetrical form of ice crystal structures.

Some of the aims of IYCr2014 are:

- To increase public awareness of the science of crystallography and how it underpins most technological developments in our modern society
- To inspire young people through public exhibitions, conferences and hands-on demonstrations in schools and to

illustrate the universality of science

- To intensify the programme Crystallography in Africa and create similar programmes in Asia and Latin America
- To foster international collaboration
- To promote education and research in crystallography and its links to other sciences
- To involve the large synchrotron and neutron radiation facilities worldwide in the celebrations of IYCr2014

There was an official launch of IYCr2014 and the opening ceremony took place at the UNESCO House in Place de Fontenoy, Paris on 20-21 January 2014. Details of events can be found on the website: www.iycr2014.org/home

Conferences

Challenges in Inorganic and Materials Chemistry ISACS 13

1-4 July 2014, Dublin, Ireland

Challenges in Inorganic and Materials Chemistry will be the follow-up event to successful conferences ISACS 3 and ISACS 8 held in 2010 and 2012 respectively, by bringing together leading scientists from across the world to share scientific developments. The Scientific Committee warmly invites you to take part in ISACS 13 and looks forward to welcoming you to Dublin.

This conference will bring together world leading experts from several disciplines and encourage the cross fertilization of ideas. Extensive poster sessions will form a key part of the symposia and there will be questions after each talk.

Themes: main group chemistry, metals in biology, organometallic chemistry and catalysis, porous and solid state materials and supramolecular materials.

Submit your poster abstract by 21 April 2014.

See: www.rsc.org/ConferencesAndEvents/ISACS/ISACS13/index.asp

Green Chemistry, Gordon Research Seminar, Applications for a Sustainable Future

26-27 July 2014, The Chinese University of Hong Kong, Hong Kong, China

The Gordon Research Seminar (GRS) on Green Chemistry is a unique forum for graduate students, post-docs, and other scientists with comparable levels of experience and education to present and exchange new data and cutting edge ideas. The focus of this meeting is on novel research in green chemistry, with an emphasis on industrial applications (but all interesting and innovative topics using a green chemical approach are welcome to be submitted). This second GRS on green chemistry is an excellent chance to build a collaborative network within the green chemistry community, working together towards a better, sustainable future.

Applications for this meeting must be submitted by 28 June 2014

See: http://www.grc.org/programs.aspx?year=2014&program=grs_green

Challenges in Organic Chemistry ISACS14

7-10 August 2014, Shanghai, China

'ISACS 14 Challenges in Organic Chemistry' will bring together world leading experts in the field of organic chemistry and synthesis.

The conference will take place at the Shanghai Institute of Organic Chemistry and the Scientific Committee warmly invites you to take part in ISACS 14 and looks forward to welcoming you to Shanghai.

Themes: organic and metal based catalysis, total synthesis, new synthetic methodologies, physical organic chemistry, bioorganic and medicinal chemistry.

Submit your oral abstract by 7 April 2014 or submit your poster abstract by 2 June 2014

See: www.rsc.org/ConferencesAndEvents/ISACS/ISACS14/index.asp

Challenges in Nanoscience ISACS15

17-20 August 2014, San Diego, USA

The conference will take place at the University of California, San Diego and the Scientific Committee warmly invites you to take part in ISACS 15.

The conference will bring together world leading experts from several disciplines - all leading names in their field - for an outstanding programme, complimented by contributed talks, together with extensive poster sessions that will provide many networking opportunities.

Themes: Nanomedicine/Bionanotechnology, Programmable Materials, Response nanomaterials, Energy and Catalysis and Characterisation and preparation - new materials.

Submit your oral abstract by 14 April and your poster abstract by 9 June 2014.

See: www.rsc.org/ConferencesAndEvents/ISACS/ISACS15/cfp.asp

Chemeca 2014 – Processing Excellence; Powering Our Future

28 September – 1 October 2014, Perth, Western Australia

Chemeca is an annual conference for the Australian and New Zealand community of chemical and process engineers and industrial chemists who come together to discuss latest developments in the field, recognise outstanding achievement and share lessons learned. Chemeca 2014 will provide an excellent platform for chemical engineers and researchers to showcase their latest research and technologies. It will give opportunities to share vision with some prestigious leaders from industry, government and academia to discuss solutions to the grand challenges humanity faces, such as energy, water, food and the environment

Early bird registration closes July 2014. Registration closes 15 September 2014

See: www.chemeca2014.com/

