Chemistry IN NEW ZEALAND

Volume 72, No.3, July 2008

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New Zealand Institute of Chemistry

supporting chemical sciences

July News

The 2008 International Year of Planet Earth paper in this issue is that by Matich, Rowan and Guenther on the analysis of volatiles — see page 88

Comment from the President

Politics and science are, of necessity, interconnected. As we draw closer to the 2008 election, matters of importance to scientists and the wider public are battling for attention. Science funding is one of these issues. The recent *Science Manifesto* (or plan for the recovery of NZ Science), produced by the National Science Panel (a group of senior NZ scientists, including Dr Mike Boland and Prof Jeff Tallon) is, of course, perfectly timed. This document (see: *www.rsnz.org*) highlights some of the key issues that the Government must address in order to recover NZ science's dwindling position in the international community. NZ science funding (at 0.5% of GDP) has been described by the *New Zealand Listener* as *woeful* – compare this with the likely target set by Singapore (a nation with a comparable population to NZ) of 3%. Most NZ scientists will attest that research funding can be very hard to secure. The *Science Manifesto* has lots of good ideas – let's hope that the politicians are listening.

Another topic receiving considerable current *airtime* is the increasing cost of petrol. While much blame for this rests quite rightly with the Government, the big oil companies have also come in for some serious criticism from the general public. However, we live in a society that is driven predominantly by money. In that respect, the oil producers are no different to any other product provider in today's economy– they have a product to sell and they want to make as much money as they can. Given the extraction, processing, and transport that crude oil must undergo, petrol (at least to me) is surprisingly cheap, especially compared to some other countries - but what it will become in the future?. It does not take a crystal ball or an economics degree to predict that because of increasing demand and decreasing supply, petrol is only going to increase in cost. Some believe that we are already experiencing peak oil, which if correct, means further price escalations are inevitable. As a chemist, burning a valuable hydrocarbon feedstock seems extremely wasteful compared to alternative uses such as making (recyclable) polymers. Of course, there is much talk of alternative energy sources yet the rate of implementation of these is slow. While petrol remains *cheap*, little incentive exists for alternative power sources to be progressed, or for us to change our petrol consumption habits. I am a firm believer that one of the most powerful ways to change people's behaviour is through their pockets. Think about speeding on the roads: the police receive much public criticism for *revenue collecting* through speeding tickets, yet, somewhat ironically, this is probably one of the most effective ways of actually preventing speeding. The politicians need to put the tax they take from petrol sales into developing alternative energy technologies - and chemists have a significant role to play here. Hydrogen is of course an exciting prospect. I often tell groups of visiting schoolchildren (with the aid of some hydrogen filled balloons and a candle on the end of a stick) that hydrogen is the *fuel of the future*, once we can store it safely and efficiently. As a parent of two young children, I often wonder what their world will be like in years to come, but I doubt that things will be all that different until petrol has become a lot, lot more expensive ……

Conferences

The **2008 NZIC Conference** is to be held in Dunedin from Nov. 30 to Dec 4. Appropriate details will appear in the July issue but a 75th jubilee celebration is planned. ***Mark your diaries now***.

NZIC Prizes

The Denis Hogan Chemical Education prize has gained sponsorship from ***ABA Books of Hamilton***; the value is $1000.

Sponsorship by NZIC

Council has agreed to sponsor The ***Rutherford Web Site*** (maintained by John Campbell) to the extent of $1000. The ***RSNZ Peter Spratt Scholarship*** has been given a one-off contribution of $1000 in memory of Peter Spratt, the Education officer for RSNZ who died suddenly last year. This award is aimed at assisting a Màori or Pacific Island student from a low decile school study, at a NZ university. A $500 prize in the ***RSNZ/Science Outreach Essay Competition*** has been agreed to mark the centenary of Rutherford's Nobel Prize in chemistry.

Branch Grants

Branch grants for 2008 have been distributed following the return of the essential financial statements for 2007 and submission of budgets for 2008.

BRANCH NEWS

AUCKLAND

The first Branch speaker for the year was *Graeme* ***Steel***, from Drug Free Sport NZ. He provided an intriguing look into the chemistry, biology, and sociology of drug testing in sports. He noted that there is now a move to *biological passports* for athletes, monitoring their steroid levels and red blood counts over extended periods of time. He suggested that such protocols may be more useful than random testing for compounds such as erythropoietin.

The following week the Branch co-sponsored a public lecture by Prof Richard Schrock, Nobel Laureate in 2005. He gave a very interesting talk that briefly described the work of his Nobel co-winners and his own group, together with a history of the Nobel Prize and his experience of the Prize ceremony and the Swedish nobility.

University of Auckland

Prof *Richard* ***Schrock*** (MIT), co-winner of the 2005 Nobel Prize in Chemistry, visited the Department in April as a Hood Fellow and gave two research seminars and a public lecture. The first seminar *Catalytic reduction of dinitrogen at room temperature and one atmosphere with protons and electrons* was also the first in the Departmental lecture series, and was followed by a convivial *sherry hour*, while the second *Thousands of catalysts for olefin metathesis. High turnover, variability, and asymmetry at the metal* was part of an informal one-day symposium on April 12 that was attended by 90 staff and students from Auckland, Waikato, Massey (Albany) and Victoria Universities.

Our female staff members have been maintaining a high profile. *Margaret* ***Brimble*** has continued to be recognised nationally and internationally, having recently been given a Kea World Class New Zealander award in Research, Science, and Technology; she was also a guest of honour at the 2008 L'Oreal-UNESCO Awards for Women in Science ceremony. She recently returned from visiting universities and institutes in Victoria, Australia as the Victorian Institute of Chemical Sciences (VICS) Distinguished Fellow. *Jadranka* ***Travas-Sejdic*** was featured in the most recent MacDiarmid Institute *Interface* newsletter, highlighting her growing profile in the fields of polymer electronics and sensor research. *Siew-Young* ***Quek*** was honoured for her teaching with the presentation of a University Award for Early Career Excellence in Teaching in May. Meanwhile, *Penny* ***Brothers*** has just attended an editorial board meeting for Chemical Communications (Cambridge, UK), which she linked with visits to the Universities of Durham, York, and Manchester.

Amongst other notable achievements, the LH Briggs Memorial Prize for best PhD thesis in Chemistry was awarded to *Prabhakar* ***Bachu*** (supervisor Margaret Brimble) at the Department's May graduation breakfast. *David* ***Williams*** has been awarded a FRST International Investment Opportunities Fund grant of $1.7M for a Microsystems Development project, while *Tilo* ***Soehnel*** has been awarded beamtime at the ILL (Institut Laue-Langevin) in Grenoble to do single crystal neutron scattering. ILL is one of the top facilities for neutron studies.

The Wine Science programme recently launched the 2007 vintage of their *Ingenio* Chardonnay, overseen by winemaker Randy Weaver, using grapes from the Waiheke Island vineyard that the University leases. This is the 5th vintage made in the programme, and the wine has already achieved a high standard. The, lead by Director *Paul* ***Kilmartin*** and *Laura* ***Nicolau***, has significant research projects on Sauvignon Blanc and Pinot Noir wines funded by FRST and NZ Winegrowers, respectively, with a focus on the chemicals responsible for the passion-fruit and capsicum aromas which make NZ Sauvignon Blanc wines so sought after worldwide.

To end on a more physical note, PhD student *Sumankalai* ***Ramachandran*** persuaded twenty staff and student members of the Department to participate in the Round-The-Bays fun run in mid-March, complete with suitably themed T-shirts.

ESR

Dr *Keith* ***Bedford*** is the new General Manager Forensic. Keith was educated at the University of Auckland, completing a PhD in physical-organic chemistry. He joined the Chemistry Division of DSIR in 1976, initially specialising in illicit drugs and forensic toxicology work. In 1984/5 he was on secondment with the Metropolitan Police Forensic Science Laboratory in London. Upon the restructuring, Keith moved to ESR, where he has taken on a number of management roles. He is a member of the Expert Advisory Committee on Drugs (established under the Misuse of Drugs Act) advising the NZ Minister of Health on drug classification issues. He is also a member of the Medicines Review Committee (an appeal body under the Medicines Act & Regulations in regard to certain decisions and rulings by the Ministry of Health or Medsafe).

Dr. *Robert* ***Winchester*** retired from ESR earlier this year. He joined DSIR Chemistry in 1976, becoming a gazetted food analyst in the Food Chemistry Group at Gracefield. After a sojourn with the Department of Health, he joined the Food Chemistry Group at Mount Albert before moving to the Forensic Biology section in 1989 and its Section Leader in 1992. The restructuring of ESR in 1996/7 led to him moving to the Illicit Drugs section, before his final role as Forensic Quality Coordinator.

CANTERBURY

The May meeting was a lecture *Chemists and Chemistry in Society* given by Prof *Leiv* ***Sydnes*** (Bergen, Norway) – see Wellington below for more details.

CPIT

The Year 12 Chemistry Competition was held in late May and was, by all accounts as successful as ever.

University of Canterbury

Suwannee ***Saisin***, a PhD student from Chulalongkorn University (Thailand) arrived in early April for 3-6 months to work with Profs *John* ***Blunt*** and *Murray* ***Munro***. *Lisa* ***Graham*** has joined the Department as a PhD student carrying a significant previous record in research. Lisa earned her BSc (Hons) and MSc degrees in Chemistry from McGill and Carleton Universities and worked at the Emissions Research and Measurement Division of Environment Canada (Ottawa) during 1991-2008 period. Having now joined her husband, *Darin* ***Graham*** (Director of NZi3 since last year), Lisa has embarked on a PhD with *Sally* ***Gaw*** and *Ian* ***Shaw*** working on the detection and effects on human growth and development of xenoestrogens.

Mick ***Sherburn*** completed his Erskine Fellowship and returned to Canberra early in April. *Akbar* ***Mobini*** has now returned to Iran after his nine month sabbatical leave from the Arak University. Akbar worked with *Peter* ***Steel*** and was a productive member of the group. Akbar gained his PhD from Otago some years ago.

Alicia ***Cavan***, a 3rd-year Honours student has been awarded both a NZ Federation of Graduate Women Undergraduate Award and an Australian Institute of Nuclear Science and Engineering scholarship to attend the Winter School on Applications of Nuclear Techniques at the Lucas Heights Science and Technology Centre. She is the second winner of an AINSE winter school scholarship for the Chemistry Department, the other being (current PhD student) *Daniel* ***Packwood*** in 2006.

The Science Graduation Ceremony was held 18th April, with Chemistry well represented. Among the PhDs were *Kelly* ***Anderson***, *Amy* ***Cruickshank***, *Annabel* ***Murphy*** and *Scott* ***Walker***. *Hemi* ***Cumming*** graduated MSc and there were twelve Chemistry and Biochemistry Honours student. *Emily* ***Parker***, *Jim* ***Coxon*** and *Murray* ***Munro*** were in the stage party.

MANAWATU

New Zealand Pharmaceuticals

NZP has entered into a global strategic alliance with Commonwealth Biotechnologies, Inc. (CBI) to provide a suite of small molecule chemistry products for the drug discovery, development and manufacturing markets. The Alliance will focus on providing glycotherapeutic products and services for research through to process scale-up and commercialization by way of an exclusive referral and co-marketing agreement. The CBI/NZP co-branded drug development services will be jointly marketed and promoted to both company's customer bases and to the broader pharmaceutical and biotechnology market.

OTAGO

Membership in the Branch Committee has recently changed. The current make up is *Julian* ***Eaton-Rye*** (Chair), *Jonathan* ***Kim*** (Secretary), *Guy* ***Jameson*** (Treasurer), *Kimberly* ***Hageman*** (Branch Editor), *David* ***Warren*** (Chemical Education Group Representative), *David* ***McMorran*** (Student Liason), and *Peter* ***Mace*** (Biochemistry Representative). Student representatives are *Scott* ***Cameron***, *Steven* ***Rusak*** and *Enitan* ***Ibisanmi***. Many thanks to *Sally* ***Brooker***, our most recent chair who served on the committee for the last 10 years, and *Kim* ***Currie***, who served as treasurer for the last 12 years!

In May, the branch organized a very successful visit to the Green Man Organic Brewery in Dunedin. Proprietor Tom Jones shared his intricate knowledge of the brewing process and provided samples of a selection of tasty beers. Employing an *environmentally sensitive philosophy*, this brewery uses a combination of NZ-grown hops, imported organic barleys, and proprietary yeast cultures to produce its character beers.

University of Otago

The Chemistry Department welcomes its newest lecturer, *James* ***Crowley***, whose research focuses on the development of molecular machines and other functional supramolecular systems. James recently completed post-doctoral research in Edinburgh, which followed PhD study at the University of Chicago.

The Department hosted a packed-house Morning Tea Celebration for its May graduates and their proud families. The graduate list included 10 BSc, 2 PGDipSci, 7 BSc(Hons), 2 MSc, and 6 PhD students. Each graduate received a *graduated cylinder* on a plaque as a gift from the Department.

Keith ***Gordon*** and *Sally* ***Brooker*** are co-chairing the AMN4 Conference on advanced materials and nanotechnology, to be held at the University on 8-12 February 2009. Distinguished Noble Laureates, Harry Kroto and John Hall, are confirmed keynote speakers who will also visit the University as James and Jean Davis Prestige Visiting Fellows. For more information see: *http://macdiarmid.ac.nz/amn-4*

Henrik ***Kjaergaard*** has returned from two months leave. The bulk of his time was spent working with Prof Wennberg at Caltech (Pasadena) developing a new technique for analysing atmospheric trace species. Henrik also visited the laboratory of Prof Vaida at the University of Colorado. PhD student *Ben* ***Miller***, postdoctoral felow *Daryl* ***Howard***, and Henrik have recently completed an exploratory research trip to the Australian Synchrotron Facility in Melbourne where they used the high resolution FT-IR beamline to record spectra of water vapour. Daryl will soon begin a permanent job working with the Microspectroscopy beamline at the facility. *Joseph* ***Lane*** completed his PhD and is continuing as a postdoctoral fellow on a new Marsden grant investigating phosphorus compounds in the atmosphere. *Mivsam* ***Yekutiel***, who recently completed an MSc at the Weizman Institute (Israel) has joined the group as a PhD student. Finally, we note that the 2007 paper on water dimer by *Daniel* ***Schofield***, Joseph and Henrik was one of the top 20 most-accessed papers published in *Journal of Physical Chemistry A* in 2007.

Sally ***Brooker*** was invited by the Sydney University Chemical Society to give the 2008 Francis Lions Memorial Lecture and spent several days visiting the Department as well. *Frederik* ***Kloewer***, a PhD student from Annie Powell's group in Karlsruhe left Brookers Bunch in May after a four month visit working on collaborative research. He had considerable success and has left another five sets of crystals for structure determinations. *Scott* ***Cameron*** has returned to start a PhD with Sally and *Matthew* ***Cowan*** has joined the team for his Honours project. Martin Albrecht (Fribourg, Switzerland), hosted by Sally, visited the department during March-April and gave a well attended honours module on self assembly at interfaces and a very well-received department seminar on non-classical carbenes.

Barrie ***Peake*** recently returned from a six-month sabbatical leave during which he worked with Bill Copper at the Urban Water Research Centre of UC - Irvine (USA). While there, his research focussed on advanced oxidation processes for the treatment of trace organic contaminants that have recently been determined in many sources of drinking and waste water in North American and Europe. He also studied the reaction of hydroxyl radical and solvated electrons with naturally occurring dissolved organic matter, which is a part of a broader study on the effect of solar radiation on natural waters. A number of students from Barrie's research group have recently graduated. *Michael* ***Gonsior*** completed his PhD (*Dissolved organic matter in NZ natural waters*), and *Reid* ***Forest*** (*The trace metal distribution in sediments and biota in the Motueka River Plume*), *Patila* ***Amosa*** (*The chemistry of rain water in Samoa*) and *John* ***Nielson*** (*Trace metal distribution in Otago Harbour sediments*) completed masters degrees.

Nigel ***Perry*** (Crop & Food Research) writes that FRST funding has finished for their pharmaceutical discovery and development programme, TerraMarine. Their FRST programme *Flavours of New Zealand* is assessing on flavour extracts from native plants used by Maori, which involves collaboration with the Federation of Maori Authorities and IRL. Another area of work concerns the control of insect pests; they have discovered a synthetic attractant for the small pest insect *thrips*, in collaboration with Crop & Food Research entomologists. This is now in commercial use in greenhouses in Europe. Sabbatical visitor Johan Svenson (University of Tromso in the Arctic Circle!) worked on pigments in the South American root vegetable ulluco. Another sabbatical visitor, Kjirsten Wayman (Humboldt State University, USA), worked on natural products from several NZ native plants. The most interesting concerned a new species related to horopito or bush pepper - *Pseudowintera insperata* - described in 2006 by Heenan and de Lange in the *NZ Journal of Botany*.

In the April issue of *Nature Genetics*, members of the Otago Biochemistry Department reported the first discovery of a mutation in the crucial cytochrome *c* protein. *Ian* ***Morison***'s group in the Cancer Genetics Laboratory found the surprise mutation in a search for the genetic basis of low platelet levels in an Otago family. The mutation can be traced back to a Cornish tin miner who immigrated during the nineteenth century. This family's overall good health overturns the prevailing view that cytochrome *c* is so finely tuned and important to health that mutations are practically impossible in healthy individuals. Cytochrome *c* has two important roles in the body, as an electron carrier in the production of energy and, when released, as a trigger of cell death. *Liz* ***Ledgerwood***'s group showed that the mutant form behaves normally for energy-production but is better at triggering cell death than the normal protein, accounting for the family's low platelet levels. Future studies will clarify the role of cytochrome c in mediating cell death and determine how the mutation makes cytochrome c a better trigger of cell death.

Guy ***Jameson***, an invited speaker at the Bioinorganic Chemistry International Conference in Vienna last year, has also been invited to speak at EUROBIC in Poland in September. *Doug* ***Mackie*** delivered an invited talk in the University's Statistics Department on the misuse of statistics in the *debate* about climate change.

WAIKATO

This year the student BBQ, which due to an unseasonably cold evening temperatures consisted of some prepared snacks, was held on March 31 and attracted a select group of students and academics from the Chemistry Department and external research institutions. We were entertained by a very interesting talk by Dr *Grant* ***Northcott***, a scientist in the Sustainable Land Use Science Team at HortResearch who spoke on *Emerging organic contaminants in New Zealand- an issue for concern or reticence?* His seminar introduction consisted of a description of emerging organic contaminants and their known and assumed effects. He then presented some NZ data on this and compared it to overseas scenarios before describing issues of specific concern in the NZ context. The lecture generated a lengthy discussion and all present appreciated the highly topical talk from Grant, a former BSc Tech graduate of Waikato.

University of Waikato

Recent seminar visitors to the Department have included Prof *Jerry* ***Antal*** Jr. from the Hawaii Natural Energy Institute of the University of Hawaii at Manoa who gave a fascinating talk entitled *Properties and Applications of Biocarbons* and Dr *Gareth* ***Rowlands*** from Massey University who gave an equally fascinating talk entitled *[2.2]Paracyclophane: Adventrues with Planar Chirality*.

NZBio Conference 2008

The NZBio conference was held at the SkyCity Convention Centre in Auckland at the end of March with the theme *Enterprising Technologies - Global Benefits*. Ther were many interesting talks on advancing technologies that could help aid some of the environmental issues facing the world today. The conference was attended by *Chris* ***Adams***, *Alan* ***Langdon***, *Benjamin* ***Deadman*** and *Jonathan* ***Puddick*** from chemistry. Ben and Jonathan presented posters *Isolation by HPLC and characterisation of the bioactive fraction of New Zealand Manuka* (Leptospermum scoparium) *honey* and *MALDI-TOF mass spectrometry of cyanobacteria: a global approach to the discovery of novel secondary metabolites*, respectivelyin the student competition. There meeting provided a good mix of talks over its the three days reflecting the mix of biotechnology researchers and executives in attendance. A highlight was a seminar on recent bioenergy research in NZ.

Richard ***Coll*** and *Chris* ***Eames*** have just had a special issue of the *Research in Science & Technological Education* dedicated to their major national science education research project they did as part of the Ministry of Education Teaching and Learning research Initiative. The project concerned the nature of the NZ higher education sector seen as *learning communities* and sought to understand in what ways teaching and learning occurs and the rationale behind pedagogical decisions.

NIWA

Hilke ***Giles*** is spending 3 months in Europe, supported by ISAT, working with A/Prof Pierre Regnier (Utrecht University) on the development of a reactive transport model of aquaculture impacts on sediment biogeochemistry with particular emphasis on simulating solute profiles and sediment re-suspension. She will also spend some time with Lars Hauer (Unisense, Aarhus, Denmark) familiarising herself with microprofiling equipment and a range of sensor types (O_2, pH, H_2S, NO_x biosensor). *Michael* ***Ahrens*** and *Mike* ***Stewart*** are examining emerging contaminants, *e.g.* marine antifoulants, in the Auckland region. *Craig* ***Depree*** and Mike Stewart have discovered some natural metabolites (sesterterpenes) from a marine sponge, that have potential use as antifouling agents in the marine environment. *Bob* ***Wilcock*** has recently co-authored a report assessing co-benefits of climate change mitigation strategies for the aquatic environment. These include land use changes and fertiliser management changes as well as the use of wetland denitrification techniques. *Micha* ***Rijkenberg*** will take up a 2-year postdoctoral post in the Aquatic Chemistry Group at the end of May. Micha, who comes from Southampton University, has a background in marine trace metal chemistry.

AgResearch

Dr *Chris* ***Miles*** has been awarded a 2-year, €289K, Marie Curie Incoming International Fellowship by the European Union (7th Framework Programme) to work on the chemistry and chemical biology of algal toxins. He took this up on June 1, and will be sharing his time in Europe between the National Veterinary Institute in Oslo, Norway and The Marine Institute in Galway, Ireland. He will return to NZ three times each year to work on NZ-EU collaborations and keep in touch with family and friends. Chris says his fellowship is a fantastic opportunity to be involved in applications for EU Research programmes.

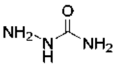
WELLINGTON

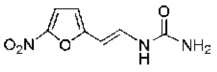
March saw the Branch actively target the new VUW students with a BBQ and then on the 12th Dr *Justin* ***Bendall*** (Fonterra Research Centre, Palmerston North) gave a very interesting presentation on *Semicarbazide: the chemistry that makes it a poor marker metabolite for detecting nitrofurazone abuse*. After an introduction to food contaminants and contamination, he described how regulatory authorities prescribe maximum residue limits (MRLs) for agricultural chemicals and drug residues, and then moved to available methods of chemical analysis outlining:

a. how semicarbazide came to be used as a marker metabolite for detecting the illegal use of the banned antibiotic, nitrofurazone, on agricultural animals,

b. the chemistry that makes its use as a marker metabolite completely inappropriate, and

c. the consequences of having analytical methods developed without considering either food chemistry or known reaction chemistry.


semicarbazide


nitrofurazone

Justin provided a good balance of the general interest material and the chemistry involved.

April saw a panel discussion on patents provided to a good-sized audienceunder the general guise of *The patent story*. *Duncan* **de Geest** (AJ Park) spoke on *Patent Protection - the first steps in NZ*, *Helen* ***Palmer*** (Baldwins) moved *Towards Commercialisation* and *Jeff* ***Tallon*** (IRL and VUW) provided his experience from the scientist's side with *Patently Unobvious - some lessons from our experience in superconductivity patents in Europe and the US*. And this illustrated the difficulties and frustrations that can beset the scientist. Most recently, Prof *Leiv* ***Sydnes*** (Bergen, Norway) provided a fascinating discussion on *Chemists and Chemistry in Society*. Leiv pointed out the raft of significant problems that face the world and need to be solved if we are going to secure a sustainable future. Whether the issue under consideration is related to energy supply, food safety, water quality, security, or development of new, affordable drugs the nature of the main challenges is in essence chemical. The chemical community therefore has a considerable responsibility to act on behalf of society, which, on the other hand, has a key role to play to enable us to take actions. Some of these measures have to do with funding of research and development, others with political initiatives to change school curricula and improve the education of the public. In order to achieve this cooperation between governments and NGOs appears to become more and more important. His discourse was based on his experience from many years in public service and six years as a member of the leadership of the IUPAC. Leiv also spoke to the secondary school teachers who came to the Branch ***Annual Quiz Night*** for secondary school pupils.

June saw the Branch annual dinner this time at Casa pasta in central Wellington. It was attended by a good number of members and a great night was had by all.

Industrial Research Ltd.

Tim ***Kemmitt*** visited collaborator Prof Ping Chen in Singapore in mid-May as the second part of a two year ISAT funded collaboration studying derivatives of light metal amides and imides with ammonia borane for potential application in hydrogen storage. Ping Chen will visit NZ as an invited plenary speaker at the MacDiarmid AMN4 conference early next year.

Graeme ***Gainsford***, *Martin* ***Ryan*** and *Mark* ***Bowden*** attended the 2008 NZ Synchrotron Group meeting in mid-April at Massey (Palmerston North) and the last two will follow this up with by using the powder diffraction beamline later in the year.

The executive and deputy directors of Singapore's Institute of Molecular and Cell Biology, Drs Neal Copeland and Dr Nancy Jenkins, visited the Carbohydrate Chemistry Team to investigate progress on work being carried out within the team on the identification and synthesis of stem cell activators.

Victoria University

Recent visitors to the School have included Dr. *Mick* ***Sherburn*** (ANU) who provided a fascinating lecture on entitled *Everything you always wanted to know about synthesis*. Dr *Peter* ***Tyler*** of IRL gave a seminar on *Drug Discovery by Rational Design* to a strong audience of students and staff and provided a synopsis of the successful Carbohydrate Group work from the past few years.

Prof *Leiv* ***Sydnes*** (Bergen University, Norway) spent a month in the School as a part of his recent sabbatical leave. Leiv has been a regular visitor to the School since 1990, mainly from ties with Prof ***Halton***. His arrival was nicely timed in that he was able to attend the may Science graduation at the Michael Fowler Centre and sit on-stage with the senior and emeritus academics. He gave an Honours level course on organic photochemistry, a research seminar on the ring opening of 1,1,2-trihalocyclopropanes (especially the synthesis and properties of 3,3,4,4-tetraethoxybut-1-yne, **1**) and a more general presentation on Organic *Chemistry and our Environment* as well as addressing the Branch at its May meeting and the Wellington Secondary teachers; he was even able to get on with some writing!

Dr *Ken* ***MacKenzie*** attended the International Conference on Smart Materials in Chiang Mai, Thailand last April and presented an invited paper encompassing the work of PhD graduate *Jeremie* ***Barrel*** entitled *Origin of the PE Offsets in Compositionally Graded Barium Strontium Titanate Thick Films*. He followed this with the 2nd International Conference on Science and Technology of Advanced Ceramics (Chiba, Japan) with invited paper *Development of Pyroelectric Ceramics for High-Temperature Applications* and then spent a few days at the Faculty of Engineering, Hokkaido University. In June he attend the 2nd International Congress on Ceramics in Italy giving another invited paper, this time *Science of Geopolymers: State of the Art and possible Future Developments* and presented posted on inorganic polymer research by post-graduate students Andrew Durant, Nils Rahner, Matt Bolton, Bryan O'Leary and Sean O'Connor.

Following this conference he attended the *World Academy of Ceramics* 2008 Forum, where he was inducted as an Academician.

Prof *John* ***Spencer*** and the six members of his group are attending the *16th International Symposium on Homogeneous Catalysis* meeting in Florence and then the *23rd International Conference on Organometallic Chemistry* in Rennes giving a range of oral and poster presentations; the students are using the timing in European summer to extend their stay and take vacation time off.

PACIFICHEM 2010

Honolulu, Hawaii 15-20 December 2010

The Congress, scheduled to be held in Honolulu in December 2010, is jointly sponsored by the Canadian Society for Chemistry (CSC), the American Chemical Society (ACS), the Chemical Society of Japan (CSJ), NZIC, the Royal Australian Chemical Institute, the Korean Chemical Society, and the Chinese Chemical Society.

The goal of Pacifichem 2010 is to promote collaborations among Pacific Basin chemical scientists that will improve the quality of life around the world. It is a very large chemical congress attracting ~15,000 chemists and a similar number of papers. It is organised around several hundred symposia, suggested by chemists from the region on the basis that they represent current cutting edge and 'hot' topics in chemistry.

At a recent meeting of the organizing committee approx 150 symposia were accepted for the conference and there will be a further round of symposia nominations submitted via the website over the period Nov2008 – Jan 2009. For information about the accepted symposia please view the website (http://www.pacifichem.org/)

If you would like more information about submission of a symposium proposal or a paper to this conference then please do not hesitate to contact the NZIC representative: Prof. Rob Smith (rajsmith@chemistry.otago.ac.nz, phone +64-3- 479-7924).

Deceit and Deception in Volatile Analysis

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*Dedicated to the memory of Dr. Cecil B. Johnson (1937-1998).
This article is the NZIC ***Planet Earth*** designated paper for this issue of *Chemistry in New Zealand*.

Introduction

Plant volatiles are low molecular weight ($M_r < 250$) organic molecules of long-standing scientific interest as natural pollutants, *e.g.* isoprene, 2-methylbut-3-en-2-ol, and pinenes,[1] as food flavours,[2] and as signalling molecules passing between plants and insects.[3] Modern genetic approaches have rejuvenated interest in this field of chemistry with an ongoing process of characterising the enzymes responsible for volatile production[4] and of the volatile signals that pass between plants and plants and herbivores - The Talking Trees Hypothesis.[5] There is speculation that volatiles might even provide cues by which we assess the nutritional value of our foods.[6]

Technology for the measurement of organic volatiles, *e.g.* gas chromatography and gas chromatography mass spectrometry (GC/GCMS), is well established and continues to advance. Newer techniques, such as solid phase micro-extraction (SPME) and the ability to back flush GC columns and automatically change the GC liner to enable the analysis of very complex samples are in place. However, as new workers enter the field, old skills need to be remembered, or sometimes restored. The technology provides us with new tricks but the underlying chemistry doesn't change.

Our interest lies at the interface of chemistry with biology, with the analysis of aroma and flavour biogenesis,[7,8] and the genetic mapping and use of functional genomics to identify genes responsible for flavour production.[9] In such interdisciplinary research, inter-generational memory can be stretched and old skills may need to be rediscovered. We would, therefore, like to dedicate this reflection on GC methodology to Dr Cecil B. Johnson (deceased), GC expert, lipid chemist and long-standing member of the NZIC.

The standard technology (GC/GCMS) for measurement of organic volatiles is well established and recent advances have focused on the MS detector (Time of Flight) and automated sampling and sample preparation techniques. The GC box with its split/splitless injector is often taken for granted, but the heated injector, itself, can be the source of some interesting chemistry. The reactivity in the GC injector of thiopropanal S-oxide (EtCH=SO), and several thiosulfinates [RS(O)SR] responsible for the onion and garlic flavour of *Allium* is well known[10] to produce artefact di- and trisulfides, and thiosulfonates, and serves to illustrate that without an understanding of the chemistry of the system under consideration it is possible for the analyst to be deceived.

Deceptive Analytes and Inappropriate Methods

The possibility for self-deception was demonstrated in the analysis of products of a terpene synthase enzyme expressed in *Escherichia coli*. Solvent extraction and GCMS analysis indicated a complex profile of sesquiterpene products (Fig. 1A) when using standard splitless injection into a 240 ºC GC injection port. One of the compounds, elemol, is a known thermal rearrangement product of the sesquiterpene hedycaryol (Scheme 1),[11] and so its presence in the chromatogram was viewed with some concern. When the sample was injected directly into the start of the capillary GC column before any heat was applied (cold on-column injection), the GC showed only germacrene D (Fig. 1B). An awareness of the value of cold on-column injections was helped by our remembrance of Cecil Johnson who specialised in this technique for lipid analysis. The germacrenes are known to rearrange thermally,[12] but to our knowledge there is no previous report of germacrene D rearranging to produce the isomers of elemene, nor of their subsequent reaction with water, present in the sample, to produce elemol. This may relate to the unknown and generally overlooked state of the GC injection port. The reported thermal rearrangement products of germacrene D are the stereoisomeric β-ylangene and β-copaene, isogermacrene D, and stereoisomeric ε-muurolene and ε-amorphene (Chart 1).[13]

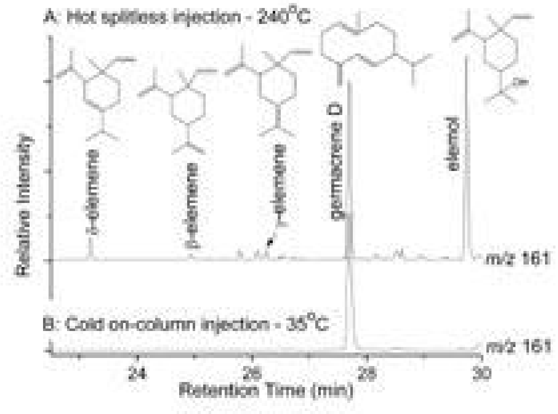
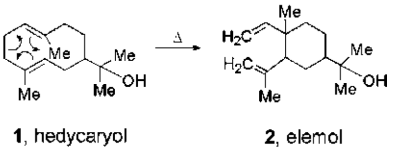
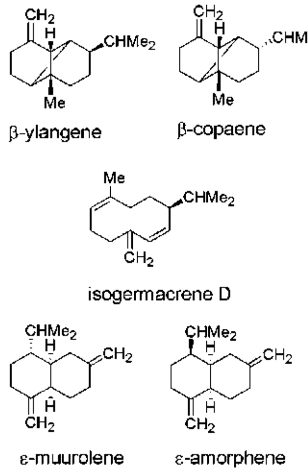


Fig. 1. Thermally labile analytes analysed by A) hot splitless GC injection, and B) cold on-column injection of a solution of germacrene D into the GC injection port



Scheme 1

Chart 1. Thermal rearrangement products of germacrene D



The more recent innovation of SPME in volatile analysis[14] has been widely adopted. It is convenient and easy to use in the extraction of organic volatiles from both headspace and aqueous samples with minimal equipment costs. In short, volatiles are concentrated onto an adsorbent coating, which is then inserted directly into the heated injection port of the GC from where the volatiles are thermally desorbed and pass into the GC in the normal way. In Fig. 2A, the SPME-GCMS analysis of an enzyme extract incubated with farnesyl diphosphate reveals the presence of seven sesquiterpenes; a mixture of products not atypical of such enzymes based upon published work.[15] A sesquiterpene synthase from the plant *Arabidopsis thaliana*, expressed in *E. coli*, produces some eighteen sesquiterpenes, all of which are found in the wild type plant. However, in our case, GCMS analysis of a solvent rather than an SPME extract revealed that nerolidol was the sole product of the enzyme (Fig. 2B). The other six sesquiterpenes observed by SPME sampling were all artefacts, presumably formed during thermal desorption from the SPME fibre in the GC injection port. The geometrical isomerisation of the remote (6*E*) double bond to the (6*Z*) isomer shown in the formation of (3*Z*,6*Z*)- and (3*E*,6*Z*)-α-farnesenes and (*Z*)-β-farnesene (not all shown in Fig. 2) indicates the extent and reversibility of the rearrangements taking place.

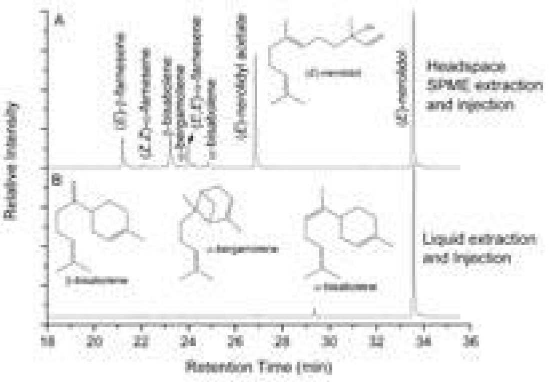


Fig. 2. GCMS following A) thermal desorption from an SPME fibre, and B) hot splitless injection of a solution of nerolidol into the GC injection port

With deceitful or *at-risk* analytes, it is not always clear where in the chain of extraction and analysis the problem lies. An example of this is the sesquiterpene zingiberene (found in ginger, *Zingiber officinale* L.), which can aromatize (-2H) in the injection port to curcumene. Fig. 3 shows that by SPME, oxidation to curcumene is extensive - only 2% of the zingiberene makes it through the system to the mass spectrometer. Based upon our experience with nerolidol, we attributed this to the SPME fibre. When a liquid injection was used zingiberene was detected at 16% but the outcome was still far from clear-cut. A liquid injection into a different GCMS system, presumably with a cleaner injection port, resulted in a chromatogram with 99% zingiberene. Problems with *at-risk* analytes can be circumvented by good GC house-keeping!

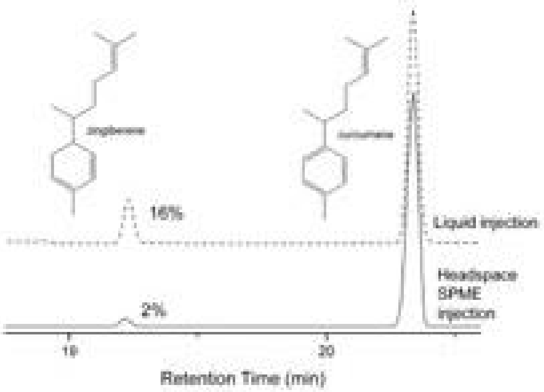


Fig. 3. Thermal lability and injection port maintenance – SPME vs liquid sample injection of easily oxidized zingiberene (to curcumene); injection into a totally different GCMS system provided a chromatogram with 99% zingiberene

When Good Labels Go Bad

The use of isotopically labelled compounds as internal standards is widely regarded as the gold standard for quantitative chemical and biosynthetic analysis. However, the use of such compounds is subject to the same assumptions as for any internal standard or tracer, i.e. identical chemical properties and consequently identical metabolism, complete and equal spatial equilibration with analyte, and non-perturbation of the system. These assumptions are known to break down in complex, heterogeneous biological systems. The commonly observed separation of deuterated and non-deuterated isotopomers in a GC capillary column demonstrates their chemical non-equivalence (Fig. 4).[16] Deuterated skatole shows reduced toxicity compared with the non-deuterated compound, and this difference has been used to infer both the mechanism of toxicity and a structure for the reactive intermediate generated *in vivo*.[17] The following examples are intended to illustrate both the usefulness and the need for care in use of isotopically labelled compounds in biological systems; they stem from our experience in this area.

α-Farnesene synthase is an enzyme identified in a number of plant species. It converts farnesyl diphosphate into the sesquiterpene, α-farnesene (Fig. 4). Expression of the apple enzyme in *E. coli*, and treatment with a number of alternative precursors, suggested that this enzyme was also able to assemble the 15C α-farnesene molecule directly from a C10 geranyl diphosphate and a C5 isoprenyl diphosphate precursor.[9] Evidence for this novel combination of activities was provided by feeding the deuterated versions of all precursors to the purified enzyme. Analysis by headspace SPME-GCMS (Fig. 4) showed the formation of (*E*,*E*)-d_{10}-α-farnesene in addition to (*E*,*E*)-d_0-α-farnesene from the endogenous d_0-farnesyl diphosphate, which had remained bound to the protein throughout its purification. The MS fragmentation pattern indicated head-to-tail coupling of the two fragments. In this case, the two isotopomers (d_0- and d_{10}-) were completely resolved on the GC column, with the heavier deuterated isotopomer counter-intuitively eluting first. This chromatographic isotope effect is colloquially known as the reverse isotope effect.[18]

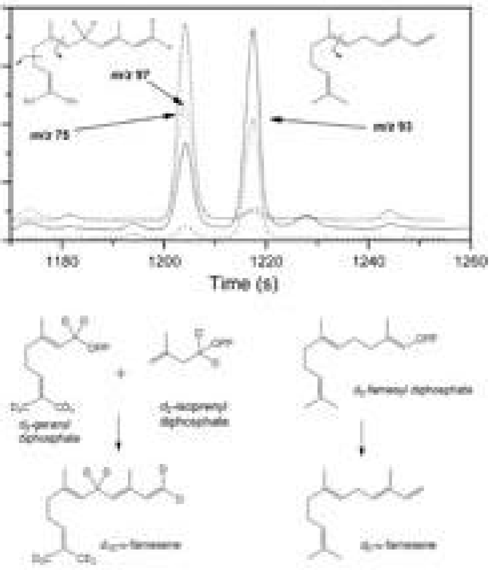


Fig. 4. Deuterium labelling of precursors to determine biosynthetic pathways; d_{10}-α-farnesene produced by incubation of a farnesene synthase gene with d_6-geranyl diphosphate, and d_2-isoprenyl diphosphate and α-farnesene produced by endogenous farnesyl diphosphate – see ref. 9.

Fruit kept in cold (or controlled-atmosphere) storage lose the ability to produce flavour volatiles resulting in a noticeable loss of flavour. In particular, apples lose their ability to produce fruity esters such as hexyl acetate and 2-methylbutyl acetate. However, not all flavour volatiles are equally suppressed and ester production can be artificially enhanced by infusing flavour precursors into the fruit tissue. This provides opportunity for identifying which enzymes in the biosynthetic pathways are being inactivated during storage.[8] Addition to the apple tissue of [6,6,6-$^2H_3$]-hexanol, a precursor for hexyl acetate, leads to the production of deuterated hexyl acetate. This suggests that the concentration of the alcohol precursor is limiting hexyl acetate production by the fruit. However, the addition of deuterated hexanol to younger, but not older, fruit also increases the production of non-deuterated hexyl acetate (Fig. 5). Presumably sufficient *total hexanol* is now available to meet the needs of other unknown biosynthetic pathways, thus allowing more non-deuterated hexanol to be converted to acetate ester.

The above example, perturbation of the biological system, was not a problem because the deuterium labelling has been used only as a tracer to test the biosynthetic capability. However, if the deuterated compound is used as a quantitative internal standard then the matter may have become more serious. In a study of sulfur esters present in kiwifruit, deuterated internal standards d_5-ethyl 2-(methylthio)acetate and ethyl 3-(d_3-methylthio)propanoate were dissolved in ethanol and then spiked into kiwifruit pulp. Upon addition of the deuterated internal standards, kiwifruit samples that did not previously contain d_0-ethyl 2-(methylthio)acetate developed levels approaching 5% of the amount of the d_5-ethyl 2-(methylthio)acetate internal standard. We assumed that this problem was caused by the presence of transesterase enzymes in the kiwifruit pulp. These would remove the d_5-ethyl moiety from the internal standard and replace it with a d_0-ethyl moiety from endogenous and added ethanol.

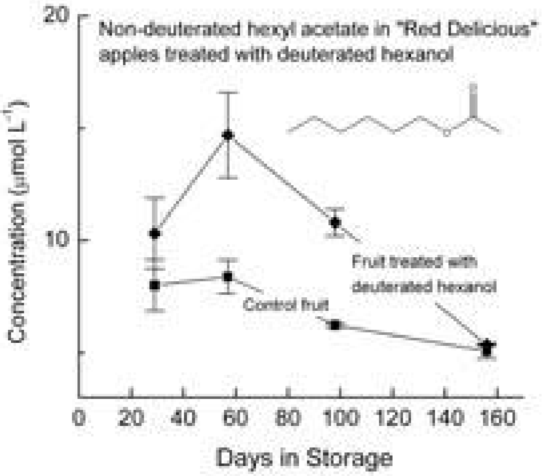


Fig. 5. Perturbation of biological systems by addition of biological precursors; elevation of endogenous hexyl acetate production in controlled-atmosphere-stored 'Red Delicious' apples treated with deuterated hexanol

Adding carboxyesterase inhibitors to the fruit pulp partially clarified matters. The cysteine protease inhibitor E-64 [*trans*-epoxysuccinyl-L-leucylamido-(4-guanidino)butane] that is used to block serine carboxy esterases, and 50% sodium dodecyl sulfate solutions caused 4- and 2-fold reductions, respectively, in the levels of d_0-ethyl 2-(methylthio)acetate. More of the story was revealed when deuterated standards dissolved in isopropanol rather than ethanol were added to the kiwifruit pulp. No non-deuterated esters were formed. Full clarification was reached only after the powerful esterase inhibitors paraoxon [diethyl 4-(nitrophenyl)phosphate] and DMCP (dimethyl chlorophosphate) were used in addition to isopropanol as solvent. Not only was there no formation of the d_0-ethyl 2-(methylthio)acetate, but also the peak areas of both deuterated internal standards, d_5-ethyl 2-(methylthio)acetate and ethyl 3-(d_3-methylthio)propanoate, increased 6- to 7-fold above those in the control samples. Thus, what had appeared to be the major problem, exchange of d_5- and d_0-ethyl moieties on one of the deuterated standards was, in fact, a minor problem. Moreover, it assisted in revealing the massive, and therefore much more serious, loss of both deuterated internal standards due to occult esterase enzyme activity. In previous studies of the biosynthesis of apple flavour volatiles,[19] apple tissue samples had been incubated with deuterated esters to assess transesterase activity, and the fates of the deuterated moieties in those esters. The present case appears to be an example of re-learning something we already knew. Internal standards placed in biological systems may not be inert and can be quite misleading when used for the purposes of quantitation.

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Dates of Note

Sir *Geoffrey* ***Wilkinson***, joint recipient with Ernst Fischer of the 1973 Prize for Chemistry on sandwich compounds, was born on July 14, 1921.

Paul ***Walden***, the Latvian chemist who iscovered the reversal of stereochemical configuration phenomenon in 1896 – the Walden inversion – was born on 14 July 1863.

On July 15 in 1869 margarine was patented by *Hippolyte Mège* ***Mouriés*** in France. His formula included a fatty component that mixed to a pearly luster, so he named the product after the Greek word for pearl (*margaritari*).

Sir *Frederick* ***Abel*** was the English chemist and military explosives specialist who invented cordite (1889) with Sir James Dewar; he was born on July 17, 1827. This day is also the 10th anniversary of the publication (*Science*) of the genome sequence of the bacterium that causes syphilis.

July 24 marks the 70th anniversary of the introduction of Nescafé instant coffee in Switzerland, but Dr. *Satori* ***Kato*** (Japan) presented the first instant coffee in 1881 at the Pan-American World Fair. It was patented in 1903 in the US.

Stephanie ***Kwolek***, the DuPont chemist who invented Kelvar®, was born on 31 July 1903 and *Friedrich* ***Wöhler*** on this day 103 years earlier (1800).

Aug 3 of 1926 saw installation of the first traffic lights – at Piccadilly Circus.

August 13 marks the 90th birthday of *Fredrick* ***Sanger*** who has twice received the Nobel Prize in Chemistry [1958: proteins especially insulin; 1980 (with Paul Berg and Walter Gilbert) for the base sequences in nucleic acids]. *Anders* ***Angstrom*** was born on this day in 1814.

Aug 14 is the 50th anniversary of the death of *Frédéric* ***Joliot*** (b.1900) who, with wife Irène (Curie) received the 1935 Nobel Prize for artificial radiation.

Linus (Carl) ***Pauling***, twice made a Nobel laureate, died on 19 Aug in 1994. He charted the chemical underpinnings of life, worked for nuclear peace, and proffered vitamin C as especially beneficial.

Sir *Hans Adolf* ***Krebs*** (of Krebs cycle fame) was born on Aug 25, 1890. In 1973 on this day the first CAT (Computer Assisted Tomography) scan was recorded.

On Sept 4 in 1888 *George* ***Eastman*** was issued the landmark US Patent 388,850 for his box camera. He registered the trademark name *Kodak* on the same day.

Felix ***Bloch***, the Swiss-born American physicist who, with E.M. Purcell, received the 1952 Nobel Prize for Physics for developing NMR, died 25 years ago – 10 Sept 1983.

Sept 20 is the 155th anniversary of the day of sale of *Elisha Graves* ***Otis***'s first safety lift equipment.

27 Sept 1910 was when US Patent 971,501 for the production of ammonia was granted to *Fritz* ***Haber*** and *Robert* ***Le Rossignol***.

Sept 30 marks the 65th birthday of German *Johann* ***Deisenhofer*** who (with Hartmut Michel and Robert Huber) received the Nobel Prize for Chemistry in 1988 for the determination of the three-dimensional structure of certain proteins that are essential to photosynthesis. It is also the 69th birthday of Nobel laureate *Jean-Marie* ***Lehn***, a recent visitor to Otago.

Oct 1, 1908 saw the the first car to be made on an assembly line. Ford's Model T sold for $US825.

October 5th marks the 50th anniversary of the death of *Earl Silas* ***Tupper***, inventor of Tupperware.

8 Oct is the 125th anniversary of the birth of *Otto Heinrich* ***Warburg*** who received the 1931 Nobel Prize in medicine or Physiology for his discovery of the nature and mode of action of the respiratory enzyme.

October 9th marks the 90th anniversary of the birth of *Kenichi* ***Fukui*** who introduced the frontier orbital theory of reactions. He received the 1981 Nobel Prize jointly with Roald Hoffmann.

Enantioselective Radical Reactions and Organocatalysis

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Introduction

…most chemists have avoided radical reactions as messy, unpredictable, unpromising, and essentially mysterious – Chryssostomos Chatgilialoglu[1]

For many years, radicals – molecules that contain a single unpaired electron – were considered too reactive to be used productively in organic synthesis. This myth has been dispelled and, somewhat ironically, it is now clear that radicals frequently offer higher levels of selectivity and predictability than analogous ionic reactions.[2] Even with increased understanding, dogma dictated that radicals could not participate in highly stereoselective reactions despite them being simple organic species, subject to the same steric and electronic interactions as all other molecules. This too has proved incorrect as the last decade has seen tremendous progress in enantioselective radical reactions.[3] The majority of naturally occurring compounds are chiral and not superimposable on their mirror images. One of the major challenges for organic chemists is to develop enantioselective reactions, *i.e.* reactions that can discriminate between mirror image enantiomers. The domination of enantioselective transformations by metal-based reagents is coming to an end as it becomes clear that small, metal-free molecules, or organocatalysts,[4] can achieve complementary reactions without recourse to potentially toxic or expensive metals.

The recent introduction of radical intermediates into organocatalysis by MacMillan[5] and Sibi[6] has attracted considerable attention and there is no doubt that the principles underpinning this methodology will have a major impact on organic synthesis. It is often overlooked that radical chemistry has always been conducive to organocatalysis, with many of the general characteristics of radicals being ideally suited for a synergistic relationship with organic-based catalysts. Radicals are largely impervious to the effects of water, display greater functional group tolerance than ionic reagents and operate over a wider pH range. It is the aim of this article to briefly outline the shared history of radicals and organocatalysis and speculate on the future directions of this profitable partnership.

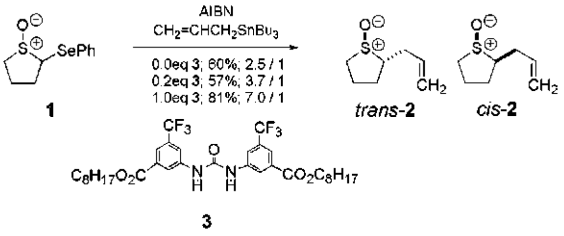
Organic Reagents and Organocatalysts in Stereoselective Radical Chemistry

When the spatial alignment of two interacting reagents is controlled, it is possible to achieve a stereoselective reaction. For this to occur, at least one of the reactants must have a well-defined shape; this can arise if either the molecule has a specific configuration or if it forms a temporary bond to a second molecule with a well-defined shape. This article will cover three strategies for achieving stereoselective radical reactions - the interaction of a substrate with a Lewis acid, the interaction of the substrate with a chiral reagent, and the temporary incorporation of chirality into the substrate.

Chiral Lewis Acid Activation

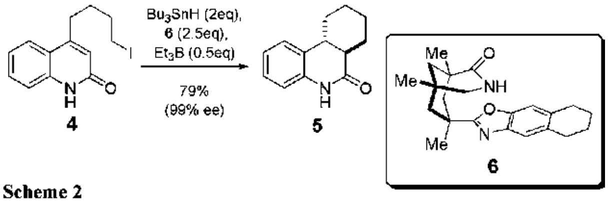
Lewis acids activate a substrate by accepting electrons and lowering the energy of the lowest unoccupied molecular orbital (LUMO) of the molecule, thus encouraging nucleophilic attack. The smallest Lewis acid is the proton and its use in catalysis is often termed Brønsted acid catalysis. The last five years have seen a renaissance in the use of Brønsted acids in asymmetric catalysis[7,8] but it is clear that the ground work was laid over a decade ago. Brønsted acids can be classified into two categories: neutral acid catalysts such as ureas, which are often termed hydrogen-bond catalysts, and stronger acid catalysts that are proton donors, such as phosphoric acids. Both classes have been employed in radical chemistry.

Since Jacobsen's seminal work in 1998,[9] (thio)ureas have rapidly become one of the *privileged* motifs for asymmetric organocatalysis,[8] yet the first example of a urea being used as a hydrogen-bond catalyst was four years earlier in Curran's diastereoselective allylation of cyclic sulfinyl radicals formed from **1** (Scheme 1).[10] Urea **3** was shown to increase both the yield and the *trans/cis* ratio of **2**, with as little as 0.2 equivalents of **3** increasing the ratio from 2.5/1 with no catalyst to 3.7/1. Urea **3** is thought to clamp the sulfinyl oxygen and increase the steric bulk of one face of the molecule whilst activating the incipient radical to allylation. Considering this promising result it is shocking that there have been no other reports of the use of (thio)ureas in radical chemistry.



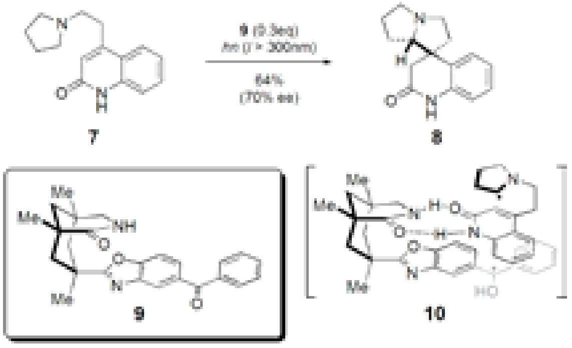
Scheme 1

Chiral lactam **6** has been employed as a hydrogen-bond catalyst for a host of enantioselective reactions including the cyclization of iodide **4** to furnish **5** in excellent yield and selectivity (Scheme 2).[11] Lactam **6** binds to amide **4** by complementary hydrogen-bonding between carbonyl and N–H moiety and thus induces high enantioselectivity. Whilst super-stoichiometric quantities of **6** give the best results (2.5 equiv. gives 99% e.e.), use of sub-stoichiometric quantities still results in chiral amplification with just 0.1 equivalents affording **5** in 55% e.e. The correct choice of solvent is pivotal for high enantioselectivities in the catalytic variant; the reaction mixture must be heterogenous throughout the reaction with the substrate dissolving only on its complexation to **6** thus forcing cyclization to occur in a chiral environment. The same complexing reagent has been successfully used in the enantioselective radical cyclization of piperidines[12,13] and the synthesis of fused tetracycle cyclobutanes via either inter- or intramolecular [2+2]-photocycloaddition reactions.[13]



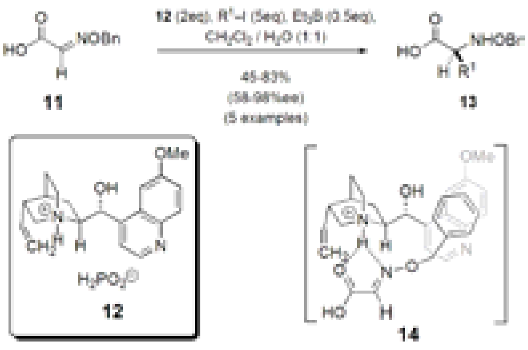
Scheme 2

An exciting variation on this system has permitted a highly enantioselective, catalytic, photoinduced electron transfer reaction that furnishes tetracycle **8** (Scheme 3).[14] Key to the success of this reaction is catalyst **9** that acts as both the chiral template and an antenna for harvesting the light required to activate the substrate. Excitation of **9** expedites electron transfer from the amine **7** to **9** and permits formation of the α-aminoalkyl radical **10**. Cyclization of the complexed radical **10** occurs from the top face as the catalyst blocks the bottom face of the alkene. Just 0.3 equivalents of **9** are required for the reaction to occur in high yield and enantioselectivity. The simplicity of this methodology and its use of just two reagents coupled with the rapid increase in molecular complexity ensure that this methodology has a bright future.



Scheme 3

A stronger Brønsted acid catalyst is the chiral quaternary ammonium salt **12** that has been used in the synthesis of amino acid derivatives **13** under mild, aqueous reaction conditions from **11** (Scheme 4).[15] Salt **12**, prepared from a *Cinchona* alkaloid and hypophosphorous acid, plays a multitude of different roles; it acts as the radical chain carrier, as a surfactant to increase the water solubility of the organic components, and as a chiral additive capable of inducing high stereoselectivity in the addition (up to 98% ee). The enantioselectivity is thought to arise from hydrogen bonding between **11** and **12** coupled with the π-stacking of the aryl groups as depicted in **14**. Whilst a catalytic variant has not been developed yet, the reaction still has many advantages over conventional nucleophilic additions: no metal reagents are utilised, all reagents are cheap and readily available, aqueous solvent mixtures are preferred to organic solvents, and the chiral amine can be recycled readily. With these benefits in mind, further applications of this and analogous systems can be anticipated in the future along with efforts to develop catalytic variants.

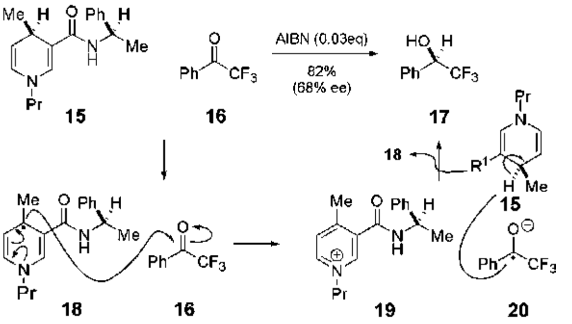


Scheme 4

Enantioselective Hydrogen Atom Transfer

It is possible to transfer a hydrogen atom from a radical chain carrier to a substrate radical in a stereoselective manner. There are two distinct methods that achieve this selectivity, the first involves an achiral hydrogen source and a chiral Lewis acid, whilst the second involves the use of a chiral hydrogen donor. Curiously, whilst the former method is the more common with metal-based systems it has not been achieved under metal-free conditions. On the other hand, the second strategy permitted some of the earliest examples of asymmetric organocatalysis.

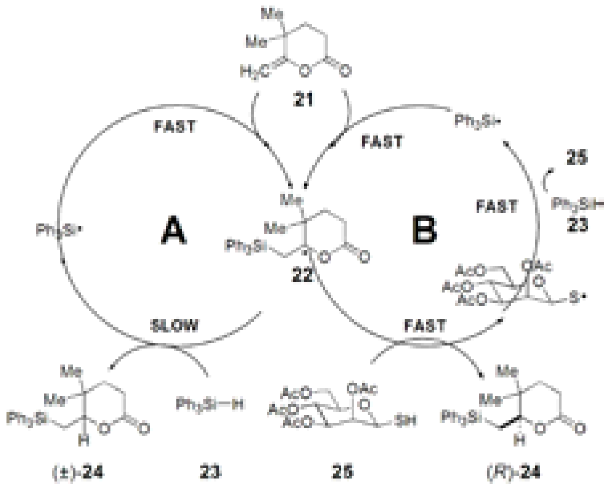
Nearly thirty years ago, Ohno synthesized nictotinamide **15** as a chiral model of the coenzyme NAD(P)H and found that it reduced certain carbonyl compounds with high selectivity (~70% e.e.).[16] Later, Tanner showed that the reaction proceeded *via* a radical pathway and was in fact the first radical chain reaction whose propagation steps contained an enantioselective hydrogen atom transfer (Scheme 5).[17] Radical initiation with azobisisobutyronitrile (AIBN) abstracts a hydrogen from **15** to give the doubly allylic stabilised radical **18**. Electron transfer from this to **16** is driven by aromatisation that provides **19** and generates the ketyl radical anion **20**. Interaction of this last intermediate with chiral hydrogen source **15** furnishes the desired product **17** and propagates the chain by reforming **18**. Once again, this reaction appears to have been consigned to history with little study outside of biochemistry reported, even though it offers an intriguing route to enantiopure alcohols.



Scheme 5

It is often forgotten that radical chain reactions rely on polarity effects for efficient propagation; smooth hydrogen atom transfer only occurs if an electrophilic radical interacts with a nucleophilic source of hydrogen or *vice versa*. If the polarities are mis-matched then the reaction will be a non-chain process and will be sluggish at best.

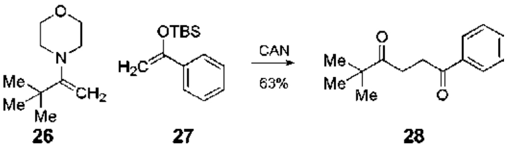
Polarity-reversal catalysts alleviate this problem, facilitating hydrogen atom transfer *via* the addition of an extra propagation step.[18,19] In the radical hydrosilylation of electron-rich alkenes such as **21**, the hydrogen atom transfer step from silane **23** to prochiral radical **22** is slow (Cycle ***A***, Scheme 6) as both donor **23** and acceptor **22** are nucleophilic. Thiol **25** acts as a polarity-reversal catalyst and overcomes this problem; the slow propagation step of the previous reaction is replaced now by two fast propagation steps (Cycle ***B***) as the thiol provides an electron deficient (or electrophilic) hydrogen atom. By making the polarity-reversal catalyst a chiral carbohydrate derivative (**25**), it is possible to enantioselectively transfer hydrogen to radical **22**. Furthermore, since **25** is regenerated in the second propagation step of Cycle ***B*** a sub-stoichiometric quantity of chiral reagent can be employed. In this example just 0.05 equivalents of **25** in the presence of a radical initiator gives lactone (*R*)-**24** in 90% yield and 95% e.e.[18] It should be noted that this is a general principle and should allow enantioselective organocatalytic radical reactions for a range of transformations. It is somewhat surprising that, with the exception of Roberts's work, very few examples of chiral polarity-reversal catalysts have been reported so this appears to be an area ripe for exploitation.



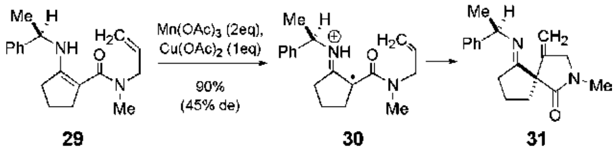
Scheme 6

Aminocatalysis/Enamine Activation

The new radical activation strategy reported by MacMillan[5] and Sibi[6] is based on aminocatalysis or enamine catalysis popularized by List and MacMillan,[20] but has its roots in older radical methodology. In 1992 Narasaka reported the cerium(IV) ammonium nitrate (CAN) mediated oxidation of an enamine **26** to a radical cation and the addition of this radical to electron rich alkenes such as **27** to give **28** (Scheme 7).[21] Whilst this undoubtedly laid the foundations for the current methodology, it was limited by the need to pre-form the enamine and because it was non-stereoselective. Arguably, Cossy reported[22] the first solution to the latter shortcoming with the manganese(III) acetate/copper(II) acetate-mediated oxidation of a chiral β-carboxamido enamine **29** to a radical cation **30** (Scheme 8). The radical then underwent cyclization to give the spirocycle **31** in moderate diastereoselectivity (45% d.e.). The enamine was formed from a primary amine and it is entirely possible that use of a secondary amine would have led to an iminium cation with less rotational freedom and thus would have resulted in better stereochemical induction. Again the reaction was limited by the need to pre-form the enamine precursor, but it clearly revealed the plausibility of this strategy for asymmetric radical chemistry.



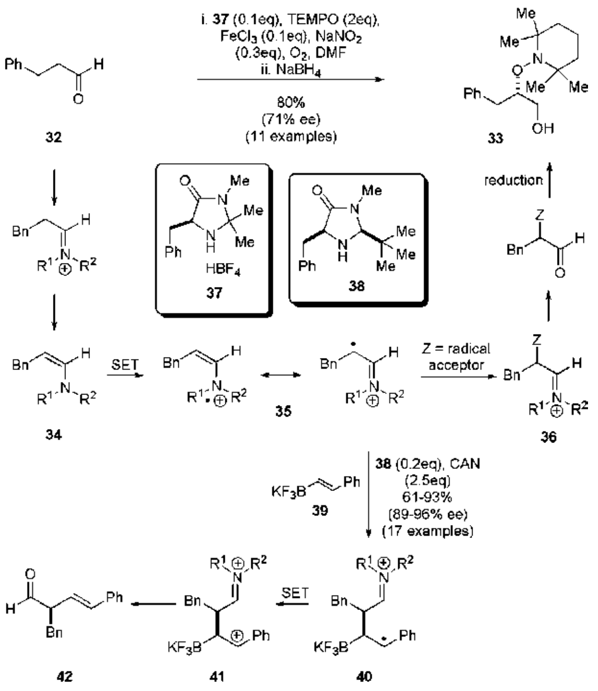
Scheme 7



Scheme 8

By refining these early examples both MacMillan[5] and Sibi[6] have developed a truly exciting method for conducting enantioselective radical reactions that shows great potential to encompass many different transformations. Both methodologies combine radical chemistry with enamine-based organocatalysis to functionalise the α-position of aldehydes; condensation of an aldehyde **32** with a sub-stoichiometric amount of a chiral secondary amine (**37** or **38**) gives enamine **34** (Scheme 9). Oxidation of the enamine by single electron transfer then furnishes iminium radical cation **35** that reacts with the appropriate radical acceptor to give the cation **36** (or **40**), which finally undergoes hydrolysis to product **33** (or **42**) and regenerates the chiral catalyst (**37** or **38**), ready to repeat the reaction. The fate of the alkyl radical **35** differentiates the two methodologies. In Sibi's methodology[6] the radical is trapped with the persistent *O*-centred 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), resulting in the α-oxyamination of the initial aldehyde (Scheme 9). The chiral imidazolidinone **37** gives moderate to excellent enantioselectivities for a range of aldehydes, and although a variety of aryl-substituted aldehydes were tolerated, simple alkyl aldehydes containing no aromatic rings or double bonds gave no selectivity suggesting that π interactions are important.[5] The benefit of this system is that oxidation is achieved with a catalytic quantity of iron(III) chloride in conjunction with a stoichiometric amount of a co-oxidant comprised of sodium nitrite and oxygen. The disadvantage is that products of type **33** are accessible by more conventional chemistry.

MacMillan's methodology[5] appears to be more versatile and permits the reaction of the radical cation **35** with a host of electron rich acceptors including allylsilanes, silylenol ethers, heteroaromatics and alkenyl potassium trifluoroborate salts. Thus, reaction of **35** with the alkenyl potassium trifluoroborate **39** gives **40** in good yield (Scheme 9). In MacMillan's reactions two distinct oxidation steps occur; the first gives radical cation **35** whilst the second is required to oxidise radical **40** to cation **41**. As a result, the methodology currently needs an excess of the metal-based oxidant CAN. The reaction appears to be quite general as a range of aldehydes can be employed whilst the alkenyl component **39** can be alkyl- or aryl-



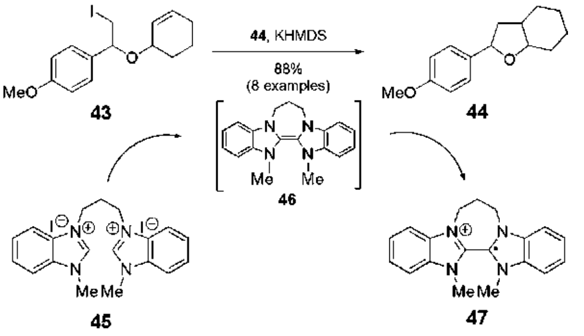
Scheme 9

substituted with little variation in the yield or selectivity. Not only does this methodology permit the facile synthesis of enantiomerically pure homoallylic aldehydes that would be difficult to form by conventional means, but also it is undoubtedly just the tip of the iceberg; it is easy to imagine this general strategy, the formation of a chiral radical cation from enamines, being employed in a wide range of novel transformations and it will be fascinating to see how this work progresses.

Currently, neither methodology is ideal. Sibi's system[6] involves a single oxidation and so appears to be limited to the addition of persistent radicals. MacMillan's protocol[5] is far more impressive in scope but it uses an excess of oxidant. A combination of the two would have a major impact on both radical chemistry and organocatalysis, and is undoubtedly being investigated.

Future Directions for Organocatalysis in Radical Chemistry

Hopefully, the discussion above has shown that most forms of organocatalysis can be applied to enantioselective radical reactions. No doubt the area will continue to develop rapidly in order to take advantage of all the benefits proffered by both radical processes and organocatalysis in terms of both clean reaction conditions and the range of transformations possible. It is obvious that the radical enamine-activation strategy will have a major impact and many new applications can be expected in the future. Improvements to the oxidation protocol that allow for use of sub-stoichiometric amounts of metal-based oxidants and more environmentally benign terminal oxidants are major goals. It will be interesting to see if the antithetical strategy, the reductive formation of radical intermediates, will be applicable to enantioselective organocatalysis. Already organic electron donors have been developed for the reduction of halides to radicals.[23] Tetraazaalkene **46** is a neutral ground-state organic molecule capable of donating an electron to a suitable acceptor due, in part, to the considerable aromatisation energy residing in its derived radical cation **47** (Scheme 10), and the stability imparted to the carbocationic centre by the adjacent nitrogen atoms. This allows **46** to reduce unactivated aryl and alkyl iodides such as **43** to C-centred radicals that can then undergo cyclization to give, *e.g.* **44**. The major drawback here is the high reactivity of **46** towards air, which requires that it normally be prepared by deprotonation of the stable salt **45** immediately prior to use. If this limitation can be overcome related reagents could be of considerable value.

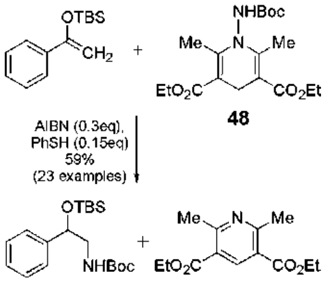


Scheme 10

The use of hydrogen-bond donor catalysts (or Brønsted acid catalysts) in radical chemistry is ripe for exploitation; the groundwork has been laid, examples of enantioselective templated reactions[11-14] and chiral proton donors[15] are known. Now it is necessary to take these precedents and pursue more general and valuable examples. It is surprising that chiral (thio)ureas have not been employed in radical additions or cyclizations. Likewise, the use of chiral phosphoric acids appears to be an obvious progression; logically, the use of chiral acids to activate various C=N moieties to radical attack would be the first step before tackling more general activation/addition methodology. It should be remembered that the last decade has seen considerable progress in the use of metal-based Lewis acids for enantioselective radical reactions whilst at the same time, Brønsted acids have begun to replace Lewis acids in many ionic transformations.[7]

The development of new chiral hydrogen atom sources as simple chain carriers or polarity-reversal catalysts is likely to continue. Not only do phosphorus hydrides show great promise as radical reagents due to their stability, low toxicity and water compatibility,[24] but also they are readily incorporated into chiral frameworks offering considerable scope for optimization. Currently, the use of chiral phosphorus hydrides has met with little success[25] perhaps because of a poor choice of chiral manifold - more sterically demanding structures may result in better diastereo- and enantioselectivities.

An interesting possibility for the development of an enantioselective transformation is the thiol-catalyzed radical transfer-hydroamination of alkenes with the N-aminated Hantzsch ester **48** (Scheme 11).[26] This reaction involves **48** as both a source of an aminyl radical and a hydrogen atom donor. The latter requires hydrogen atom transfer from a carbon atom to a carbon radical, a generally inefficient transformation that can be facilitated by the use of a polarity reversal catalyst. The reaction proceeds in moderate yield for a range of alkenes but ,more importantly, it can proceed with good diastereoselectivity (up to 90% d.e.) suggesting that possibly it could be developed into an enantioselective process either by the correct choice of polarity reversal catalyst or hydrogen-bond catalyst. Such transformations hold plenty of potential especially as they are complementary to metal-based systems, which generally give the product of Markownikov addition.



Scheme 11

Summary

It is clear that organocatalysis is going to play an important role in the future of enantioselective radical reactions. The recent reports of Sibi and MacMillan have highlighted the potential this combination displays and it is hoped that this summary shows that radicals, by their very nature, have always been good partners for organocatalysis, and have in fact been employed in some of the earliest examples of this now ubiquitous field. It is also hoped that the article offers an insight into the potential of this powerful marriage of chemistries and inspires others to forget their fear of radicals and enter this fascinating field of chemistry.

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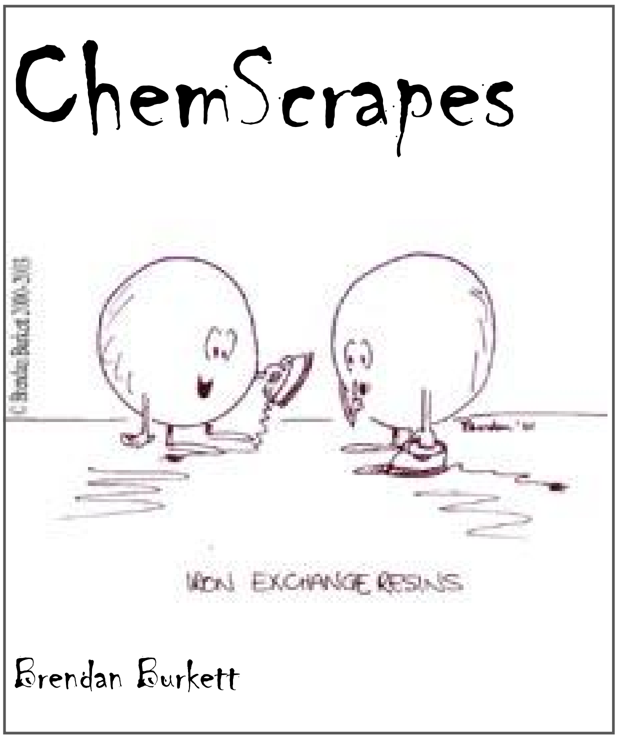

From the lab to the factory – considerations for synthetic product development

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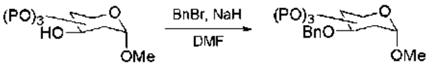
Introduction

When presenting their work, many synthetic chemists will comment on a synthesis being readily scalable. However, the product development scientist often makes drastic changes to the protocols when starting to make the process suitable for scale.[1] These changes can be due to a number of factors, but generally they fall under three main banners of safety, manufacturing considerations and environmental impact.

This article does not attempt to give an in-depth discussion of all of the factors that are considered in the development process. Rather, it attempts to highlight some of the issues that we have learned at NZP[2] through taking processes from laboratory through pilot plant and on to manufacturing scale. Naturally, many issues are specific to a given organization such that no chemist or engineer outside of that institution can design a process that takes these into account. However, there are some generic considerations for which a greater awareness at bench scale will flow through development and make for easier scale up.

Safety

Safety is (or should be) the foremost consideration when taking any process beyond bench scale. Inevitably, a chemist who has worked in a synthesis laboratory will have stories of fires, explosions, over pressurizations, and/or other incidents that have caused damage to equipment and/or people. These are accidents that occur on an operating scale from a few milliliters to, at most, a few liters. When tens, hundreds or thousands of litres of chemicals are involved the effects of an accident are potentially much worse as there is the potential to cause death and ruin factories; for businesses a major accident can be a company ending event.[3] The term *process safety* is very broad and the present discussion covers only those aspects that are relevant to the synthetic chemist - the engineering aspects of process safety are highly complex and likely of limited interest to the bench chemist. However, when an industrial chemist thinks of safety, both chemical and processing considerations do need to be taken into account. For instance: what chemicals are to be used and how are they best safely handled? What is happening to them in the reactor? What by-products are being formed? Is the reaction exothermic and, if so, can the equipment cope with this? How will the reaction be quenched and/or made safe? What will be in the waste streams? How will these be made safe and disposed of? How will an emergency be dealt with? While the answers to these questions could fill many pages and papers, an overview of the factors that must be taken into account when considering safety are illustrated by a suitable and appropriate example.



Scheme 1. Benzyl protection of a sugar

Benzyl protection of a hydroxyl group is a well used reaction, particularly in carbohydrate chemistry. This is usually carried out using benzyl bromide and sodium hydride with dimethylformamide (DMF) as a solvent (Scheme 1).[4] While this is a very useful and high yielding synthetic reaction, it is not optimal from a safety stand point. Benzyl bromide is a severe lachrymator and highly corrosive. DMF is a high boiling point solvent with significant handling issues. As a solvent it does not have concerning acute toxicity, but it does have chronic health issues. It targets the liver, kidney and central nervous system, and it is also a reproductive effector. The most concerning reagent in the benzylation mixture is sodium hydride. When used with DMF, NaH is especially prone to spontaneous ignition - to the extent that fires on scale up led to investigations into the optimal method of extinguishing them.[5]

The best way to consider such hazards such is to use the OSH mantra of *eliminate*, *isolate*, *minimize*, in that order. In the present example, sodium hydride is the reagent of greatest concern and should be replaced. Even a quick literature search provides a lengthy list of alternate reagents that have been used in this reaction.[4] A specific replacement used in collaboration by NZP and IRL Glycosyn was potassium hydroxide flakes. This triggered replacement of the DMF by acetonitrile which, while having a slightly heightened acute toxicity, is much easier to handle on scale and does not have the health concerns associated with DMF.

The last chemical to receive attention in the benzylation is benzyl bromide and this proved the most difficult to replace. Other benzyl halides such as the chloride are arguably less of a hazard than benzyl bromide, although anyone who has ever worked with them will attest to the fact that even the slightest exposure is very unpleasant. The removal of benzyl bromide from the reaction is possible only by re-designing the synthesis. If the molecule is being made as a starting block for further synthesis, particularly for an external customer, this may not be practical. An alternative is to include a quench at the end of the main reaction. The idea behind this is to convert any residual benzyl bromide (or for that matter any other hazardous reagent), into a less hazardous product thereby allowing safer handling of the final product mixture and the process wastes.

There has to be a limit to which the elimination of hazardous chemicals from a process can proceed. Was one to attempt to remove everything hazardous then there would be no process left to work on. Thus *isolation* and *minimization* now take precedent. To isolate an operator from the chemical process requires engineering solutions that are not discussed here. The concept of minimization involves reducing to acceptable levels the impact of a chemical hazard on the operator; usually this is achieved by the use of personal protective equipment (PPE). Basic chemical safety often was not covered well in tertiary training courses, although the increased emphasis of occupational safety and health (OSH) standards is changing this. People working with chemicals need to know how to find the relevant safety and toxicity information to ensure their own safety and those in the environs, and this applies to laboratories as much as processing plants. Copies of material safety data sheets (MSDS) for all reagents are now required in all laboratories but people must know where they are kept and refer to them regularly. Where an MSDS sheet is not available for an intermediate or product expected from a given process then relevant assessment must be made prior to any experimentation commencing. The information must then be supplemented prior to any processing being undertaken, *e.g.* use of glove compatibility charts. It is well known that nitrile gloves generally offer more protection than latex but for some solvents latex is the better option. The Environmental Risk Management Authority of NZ (ERMA) website can be consulted for the hazardous substances and new organisms (HSNO) classifications for approved chemicals[6] while the OSH website contains information on the NZ workplace exposure standards.[7]

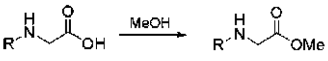
Finally, when discussing the safety of a process, thermodynamics considerations are important especially when exothermic reactions are involved. Calorimetry can provide much useful information although it must be applied to the process as a whole, including all reagent additions and quench reactions. Once this information is gathered it needs to be applied to the specific vessels in which the process is to be carried out. Each reactor has its own characteristic heat transfer properties and each heater/cooler unit has different capacity for dissipating changes in internal reaction temperature. This information will be used by a process engineer or technician to ensure that no more material is loaded into the system via header tanks or transfer vessels than the reaction system can cope safely with in the event of a catastrophic failure.

The present discussion is far from exhaustive and the reader is directed to the American Institute of Chemical Engineers quarterly journal *Process Safety Progress* as a valuable source of information.

Manufacturing considerations

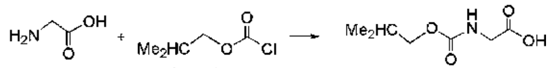
Manufacturing considerations cover issues specific to a given facility such as the equipment involved, and many can only be worked on in-house by people who know the equipment well. These can include the material the vessels and equipment are made from, the practicalities of loading and unloading the reactor, and how material is transferred around the plant. The synthetic chemist should consider scale up factors when designing a synthesis. Thus one should avoid reagents that cannot be used under certain circumstances, *e.g.* halogenated acids attack many grades of stainless steel while strongly basic hydroxide solutions etch glass.

Process-specific considerations must also be taken into account and these are best more fully investigated in the laboratory prior to moving into development. The critical points in a process must be identified and tested. For example, if an acidic product is being precipitated by adjustment to pH 3 what will happen if the pH is accidentally adjusted to pH 2.5, or pH 2 or pH 4? At what point in a process is the product sufficiently stable to be left overnight? When must operations be carried out within a specified time, temperature or other range? For example, if a process uses a glycine conjugate where, due to product solubility, the conjugate is taken up in methanol but recovered by precipitation from a less polar solvent, will the free glycine react with methanol and form its methyl ester (Scheme 2)? As methyl ester formation is temperature dependent its presence can be eliminated by temperature control. Were this not the case, other options such as converting the free acid into the sodium salt would need to be considered.



Scheme 2. Methylation of a glycine residue

While side reactions of the main product are often discussed in the literature, unwanted reactions between reagents are often overlooked. The formation of the glycine conjugate discussed above uses isobutyl (2-methyl-1-propyl) chloroformate in the conjugation step. This is because this compound is more stable and more user friendly than the more common laboratory reagent, ethyl chloroformate, including its added stability in water. Early conjugations employing ethyl chloroformate could result in quenching of the excess simply by washing with water. In contrast, isobutyl chloroformate persists through multiple water washings and goes on to react subsequently with amino acid forming a carbamate by-product (Scheme 3). To circumvent this, the carbamate either needs to be removed by purification or an alternate quench step included so as to ensure that there is no chloroformate remaining for reaction with the amino acid.

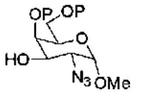


Scheme 3. Formation of glycine carbamate

Generally, optimization of a reaction is one of the quicker parts of the development process since much of the work is carried out in the research laboratory prior to transfer to the development chemist. However, product purification is usually a different story. For most synthetic chemists the focus is on how best to make a given compound. Purification is easy - pass it through a column. While flash chromatography is a very useful technique, it has significant problems as the scale increases. Industrially, a number of systems are available for large scale chromatography, many with pre-packed cartridges allowing for safer working systems. However, these add significantly to the cost. For fine chemicals, particularly those early in commercial life, this cost can be justified. For commodity products or chemicals for which there is significant price competition, chromatography is simply too expensive. This often leads to a significant amount of development work on chemical purification.

The best place to start working on improving product purity is by examining the reaction itself. While reactions are often worked on in a laboratory to optimize yield, process development requires a trade off between what is economic in terms of reagents and purification. Thus, while precious metal-containing reagents may be fine for laboratory use thay are too expensive for commercial production. Other reagents, such as those containing tin oxides, are very difficult to remove from the product and may be prohibited when manufacture is for human end users. Side reactions, such as the chloroformate example discussed above, need to be identified so the process can be modified to eliminate them.

The techniques used to purify a given chemical will depend on the purity levels targeted. Many common laboratory techniques such as bi-phasic washings and crystallizations are far more effective than chemists often give them credit for. However, this requires that the product and its impurities have appropriate solubilities that allow for efficient separation in an economically small number of washings. It is often assumed that organic molecules, such as fully protected sugars, are insoluble in water, but this is not always the case and it should always be checked. Knowing the solubility of both the products and impurities can often lead to greatly simplified purification techniques. An example of this is an azide transfer reaction worked on by NZP and Glycosyn. The product **1** was a protected sugar with an azide at C-2, the major impurity was an organic amide formed during the reaction. In laboratory work this sugar had been purified by chromatography but attempts to crystallize it from a variety of solvents did not remove the amide impurity; the amide proved to be soluble in water while the sugar was not! This led to a purification protocol in which the sugar was precipitated from organic solvent by the addition of water allowing for recovery in greater than 99% purity.



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Environmental impact

Much of the discussion concerning the environmental impact of a process is covered when safety and manufacturing considerations are discussed. Despite this, it is always useful to look at a process from a purely environmental angle. Can the solvent volumes be reduced? Can any environmentally dangerous chemicals be replaced? What is going to happen to the waste streams and will they need treatment? How is the process going to be contained? What is going to be released? How are any gasses produced going to be scrubbed, and how do we tell when the scrubber medium requires changing? How do we contain all chemicals in the event of fire? A spill? Another emergency situation? To answer these questions effectively requires engineered solutions that are specific to the given site and beyond the scope of this article.

Conclusion

When a process is given over to a development chemist for scale-up there has often been much work done in the laboratory to optimize the product yield. However, this does not mean that the process is ready for scale up. The development chemist will often need to carry out extensive research and make significant changes to the laboratory process before it can be safely scaled for the equipment available at the particular facility. This brief discussion has covered some of the concerns of the development chemist when assessing a new process. While it provides a brief introduction to the area, examples of the scale-up improvements made to synthetic pathways can be found in the ACS journal *Organic Process Research and Development*.

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CHEMICAL EDUCATION TRUST

APPLICATIONS REQUESTED

Applications are invited from secondary school teachers (via Head of Chemistry and Head of Science) for grants from the ***NZIC Chemical Education Trust*** to promote the teaching of chemistry in their school. For the 2008 distribution, grants of around $400 are envisaged, but greater or lesser amounts can be applied for.

Closing date for applications: 1 August 2008

Applications must include full details of the item(s) for which funding is requested together with an up-to-date quotation, and sent to:

Professor A. M. Brodie,
NZIC Chemical Education Trust,
Institute of Fundamental Sciences,
Massey University,
Private Bag 11-222,
Palmerston North.

Fax: 06 350 5682; e-mail: *A.Brodie@massey.ac.nz*

Late applications will not be considered.

Laboratory Education in New Zealand

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Laboratory work is one of the main forms of teaching used in chemistry, physics, biology and medicine. Studies carried out in the 1970s and 1980s showed that students did not enjoy this type of work, which is hardly surprising when one considers the effort (workload, commitment) and risks (chemical burns, poisoning, *etc*.) associated with it.[1] Since then, safety technology has been improved to a point where laboratory work is safe and, in principle, enjoyable. However, the technology of improving laboratory conditions came with significant increase in costs and effort to equip and maintain practical work areas, and as a result, raised questions regarding its necessity and viability. The NZ tertiary education budget is above average for OECD countries at 1.7% compared to 1.4% of GDP (Ireland 1.3 %; Finland and Sweden 1.7 %; Australia 1.5 %) specifically to address continuing skills shortages.[2] The GDP of New Zealand is approximately three quarters of that of other OECD countries, *e.g.* Finland and Ireland, and thus the actual amount of funding available for tertiary education is rather low. Furthermore, the market-driven nature of NZ universities and educational institutions places limitations on the willingness of financers and managers to approve comparatively costly forms of education.[3]

Doubts about education in laboratory environments are not just limited to managers and financiers; teachers, lecturers and students have discovered new technologies that can be applied at a fraction of the costs and effort of laboratory education.[4] The discussion about laboratories and other educational techniques is very opinionated, with many scientists arguing heatedly either in favour,[5] or against laboratory education.[6] Recently, the online journal *Chemistry Education Research and Practice* dedicated a special issue in 2007 to *Experiments and the Laboratory in Chemistry Education*,[7] and several of the articles discuss the history, development, and current standard in laboratory education with a focus on technique and procedures.

One question is often ignored in this context: What do *students* think about laboratory education? In 2006 Polles wrote a PhD thesis investigating student perspectives on chemistry teaching laboratories.[8] He found that students' experiences were strongly dependent on their learning environment and the stance of their teachers, lecturers, demonstrators, and technicians. This dependence raised questions for Polles about the validity of assessing student opinion. Many academics feel that students tend to give overly positive replies that do not adequately reflect their true opinions regarding different forms of education.[8]

Presented here are the results of a survey using independent indicators. Students were asked to comment on how a set of strategic aims formulated by Victoria University staff and management are realised in laboratory education (For the questions, see Appendix 1). The outcome was a good spread of results with the aims used as indicators appearing to be largely unconnected, meaning that the responses presented are statistically valid, thus alleviating the concerns academics usually have towards the collection of student opinion. The results are presented here to inform academics and researchers about the views of students regarding laboratory education and the effectiveness of this form of teaching of chemistry.

An Investigation of Students' Opinions Regarding Chemistry Laboratory Education

Based upon statements from Victoria University of Wellington's strategic plan, and conversations with the Dean of Science, lecturers in chemistry, and the School Head, a list of the seven most important joint strategic goals for the University and the School was collated. The goals are directly linked to generic, course-independent attributes, which a chemistry student at Victoria University should have or attain during study. The list was limited to seven items based on the importance attributed to the individual goals in the discussions. Between the selected seven items (and other items not included in this study) a perceivable step in importance was noticed. According to University and School guidelines, the goals assessed in this study should be realized in the teaching curriculum as provided, *e.g.* in the university calendar, course outlines, and reports.

The seven attributes thought to be the most important (in no particular order) are:

i. Confidence,
ii. Interest,
iii. Linking theory with observation,
iv. Critical thinking,
v. Scientific methods like analysis, observation and the deductions on observations,
vi. Leadership skills, and
vii. Practical skills

A questionnaire was formulated and distributed in chemistry lectures and laboratory classes to students at all levels (see Appendix 1). Ethical standards were strictly obeyed in the collection and handling of the questionnaire. Answers to the questionnaire were categorical to avoid confusion, with five categories given – the positive always being on the left-hand and the negative always being on the right hand side. Students were told that they could choose two categories to express that their answer lay between the categories given. Thus a total of nine categorical answers were possible for each question. For the evaluation of the answers, the five main and four intermediate categories were translated into a 9-point scale of numbers, ***5*** standing for most positive and ***1*** for most negative possible. After compilation of statistical data (calculation of means, errors, chi-tests, *etc.*) and construction of box plots, the numbers were transformed back into categories for interpretation of the results so calculated.

Return Rate and Survey Statistics

One of the issues facing any survey is whether it is representative. The population selected for the survey was all enrolled chemistry students. No sampling was undertaken, so representativeness is not an issue for this study. The survey was carried out close to the end of a trimester, a time when students are pre-occupied with exams, assignments and presentations; attendance levels in classes and response rates to questionnaires can be low. This was weighed against the higher level of experience that the students have accumulated by the stage of the course when the survey was undetaken. As experience of laboratory teaching is important for the purposes of this study, a lower response rate was accepted as a risk and, as expected, attendance levels had dropped (Table 1). However, even an attendance of 77.8 %, as at the 100-level (1st year students) is respectable. Thus the return rate of 72.8 % means that 56.6 % of all 100-level students enrolled in chemistry participated in this study. The values for 200-level students and 300-level students are even better: 86.1 % and 75.0 %, respectively. This means that a total of 65.6 % of all undergraduate students enrolled in chemistry at Victoria University participated in the study. A detailed examination of the survey statistics (statistical data and histograms comparing the distribution of results) is available upon request.

Table 1. Return rate

Level	No. Enrol	Distrubuted Surveys No. (%)	Returned Surveys No. (%)	Return Rate (%)
100	189	147 (77.8)	107 (72.8)	56.6
200	72	67 (93.1)	62 (92.5)	86.1
300	24	22 (91.7)	18 (81.8)	75.0

Opinions Regarding the Realization of Strategic Aims

Results in terms of the strategic aims are diverse (Fig. 1).[9] Aims for confidence, interest, linking theory with observation, and scientific method have been achieved well, with replies being between neutral and positive. Critical thinking is not realized as well as the other aims: opinion tending more towards a neutral position. It is likely that the relatively narrow knowledge base of the undergraduate student does not allow them sufficient opportunity to train themselves in the evaluation and discussion of concepts. Pending findings among postgraduate students, this might be an issue that should be discussed amongst, and remedied by, the academic staff and students. Leadership was the only strategic aim not fully realized in chemistry laboratories. The undergraduate laboratories leave little room for the students to take leadership roles. Owing to safety considerations, instructions, guidelines and requirements are precise and strict, especially for 100-level students, allowing little room for taking leading roles. Only at 300-level do students start to embark on self-guided, independent research and start to get involved in leading functions (outreach programs, providing guidance for first year students, chairing discussions, *etc.*). One other strategic aim is prominent – practical skills, which owing to the nature of laboratory courses is not surprising. Opinions regarding the acquisition of these skills are positive to very positive; the median lies above the positive category with a value around 4 (indicating a high degree of approval; the maximum value possible is 5).

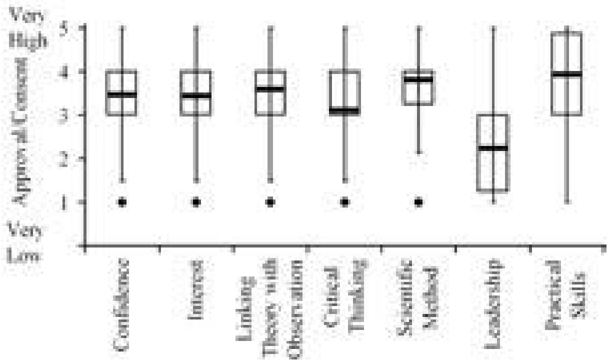

Fig. 1. Box plot showing the spread of opinions of 100-level students regarding laboratory education assessed by independent indicators. Key: Thick horizontal line – median; box – 2nd & 3rd quartile (middle 50 % of opinions); whiskers: spread between 1st & 4th quartile; dots outliers.

Several researchers have investigated the relation between laboratory work, lectures, and other teaching techniques.[4] DiBase and Polles both came to the conclusion that a good alignment between the different forms of teaching needs to be achieved for maximum effectiveness.[8,10] DiBase and Deters have both suggested strategies for how this may be achieved.[10,11] The effectiveness of the link between the different teaching techniques, lectures and laboratories at Victoria University was represented in the ranking of the corresponding question (see Fig. 1) and in the free-form part of the questionnaires, where 31.3 % of the students stated that laboratories helped them understand concepts. Further positive points mentioned by approximately a quarter of the students were visual learning (22.9 %) and the acquisition of practical skills (27.7 %). The only negative remarks were comments on the high workload and the time required were stated by a significant number of students (28.2 %). In general only 33.2 % of all participating students used the free-form questions.

The raw data have been submitted to Chi-square tests to see if group (other than level) specific trends would be noticeable by correlation of the replies to demographic data collected at the beginning of the survey. The result was overwhelmingly negative, with the error in the Chi-square test being unacceptably high (22 %). This means that no statistical significance for differences between any of the demographical groups has been observed.

The spread of results includes negative as well as positive opinion. Nonetheless, the overall trend is quite positive, with student opinion being quite favourable towards laboratory education.

The Development of Opinion through the Levels

Student opinions, regarding the alignment between laboratory education and strategic aims, improve as students advance through their undergraduate career. While there is a noticeable improvement in opinion between 100- and 200-level (Fig 2), the opinions expressed by 300-level students are very positive (Fig. 3). Generally the spread of opinions becomes narrower over the years, which could indicate that the students' perception and understanding of the strategic aims become clearer and more refined. If this is the case, the results concerning leadership and critical thinking might be due to a lack of student understanding of these concepts. Victoria University has a policy of research-led teaching in line with good teaching practice as formulated by Vallarino, Polo, and Esperdy.[12] At 300-level the students become involved in independent three-week research projects. Here almost all opinion is in the range between positive and very positive. Only the opinions regarding the realisation of critical thinking and leadership in laboratory education remain lower than the rest, but even they are improved, with critical thinking tending towards a positive rating and the opinions regarding leadership being expressed relatively evenly around the neutral mark.

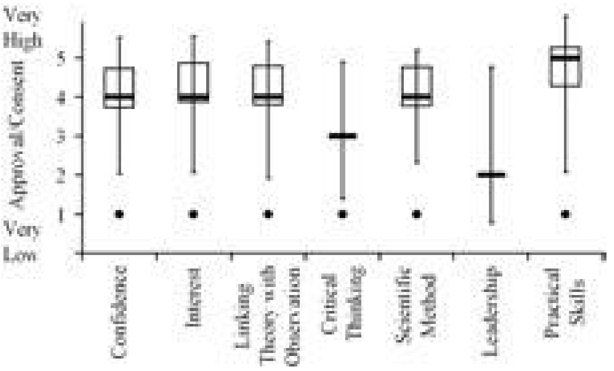

Fig. 2. Box plot showing spread of opinions of 200-level students regarding laboratory education assessed by independent indicators. (Key as for Fig. 1)

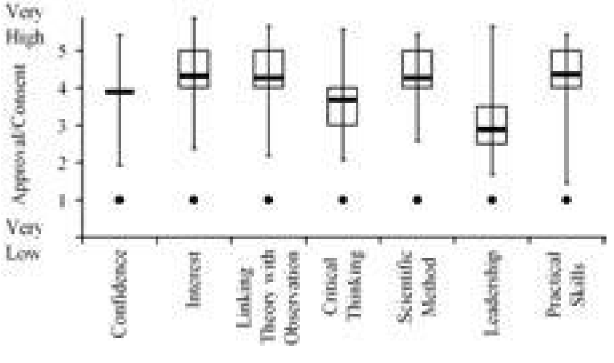

Fig. 3. Box plot showing spread of opinions of 300-level students regarding laboratory education assessed by independent indicators. (Key as for Fig. 1)

Seeing the improvement in opinion as the student advances through the levels leaves one question to be answered: Did student opinion improve or did the students with negative and neutral opinions move to other subject areas? A short follow-up survey of a sample of students indicated that over 95 % of the students' opinions improved as they progressed through the levels. This follow-up study included students moving to other subject areas; of the seventy-two 200-level students surveyed initially 52 (72.2 %) were included and replied to the follow-up study. Of these 52 students 38 were still pursuing a chemistry degree at Victoria University. The students commented that this improvement in opinion is due to better linkages between lectures and laboratories at 300-level than at the lower levels.

Laboratory Education Is Indispensable

Chemistry students appear to value highly laboratory education. As they progress through the levels, the linkages between lecture and laboratory materials increases and the appreciation of students for laboratory education grows as well. Several strategic aims, especially those regarding confidence, interest, linking theory with observation, scientific method and practical skills have been achieved quite well, with replies ranging between neutral and positive. Critical thinking and leadership are not realised well and laboratory personnel and academics should consider how to improve laboratory education in this regard.[5] Lectures and other forms of teaching and learning usually achieve better results in regards to critical thinking, but fall short in terms of inspiring confidence, interest, and linking theory with observation. In light of the achievements of laboratory education, and the way it compliments other forms of education, it remains important to keep it despite the (sometimes) high costs involved. Student opinion certainly appears to places a value on it, and teachers and academics are wise to consider the opinions of their students.

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Appendix 1. Questions from the survey

1. Please circle the most appropriate answer(s) for each question below

a) Are you currently enrolled in a chemistry *laboratory course*? Yes No

b) Are you currently enrolled in a chemistry lecture course? Yes No

c) How many university chemistry *lab courses* have you completed before this course?
0 1 2 3 4 or more

d) Are you currently taking part in chemistry *lab research project*? Yes No

e) What is your gender? Female Male

f) Your residency status?
NZ Citizen/Resident International Student

g) What is your current status at VUW?
__1st year undergraduate; __ 2nd year undergraduate;
__ 3rd year undergraduate; __ 4th year undergraduate;
__ postgraduate (MSc); __ postgraduate (PhD)

In response to each statement below, please circle the option(s) that most closely represent your views. Circle two responses to indicate an answer in between categories:

2. For me, to learn to understand and do chemistry well, *laboratory courses* are:

Absolutely necessary	Necessary	Very helpful, but not necessary	Somewhat helpful, but not necessary	Absolutely unnecessary

3. Considering the time and effort I have invested in chemistry *laboratory course(s)* overall, I would describe the value of what I have learned as

Very high	More than adequate	Adequate	Less than adequate	Very low

4. The contribution of *laboratory courses* to my achievements and progress in chemistry, is

Very high	More than adequate	Adequate	Less than adequate	Very low

5. *Laboratory work* has advanced my understanding of key concepts in chemistry:

A great deal	Quite a lot	Somewhat	Not much	Not at all

Chemistry *laboratory courses* are designed and taught to help you achieve specific learning outcomes. Please rate how well they have achieved those outcomes by circling the response that most closely represents your views:

6. *Laboratory work* has improved my confidence in performing well in chemistry

A great deal	Quite a lot	Somewhat	Not much	Not at all

7. *Laboratory work* has stimulated my interest in learning/doing more chemistry

A great deal	Quite a lot	Somewhat	Not much	Not at all

8. *Laboratory work* has helped me to link theory with observation

A great deal	Quite a lot	Somewhat	Not much	Not at all

9. *Laboratory work* has developed my ability to think critically

A great deal	Quite a lot	Somewhat	Not much	Not at all

10. *Laboratory work* has introduced me to scientific methods like analysis, observation and the deduction of results based on observations

A great deal	Quite a lot	Somewhat	Not much	Not at all

11. *Laboratory work* has helped me develop leadership skills

A great deal	Quite a lot	Somewhat	Not much	Not at all

12. *Laboratory work* has taught me valuable practical skills

A great deal	Quite a lot	Somewhat	Not much	Not at all

13. Please share 3-4 specific comments on the ways chemistry *Laboratory work* has helped you learn.
14. Please share 3-4 specific comments on the ways chemistry *Laboratory work* has hindered or interfered with your learning.
15. Please share 3-4 specific, practical suggestions for improving chemistry *laboratory courses*.
16. Other comments?

Chairing Scientific Meetings*

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*This article, originally published in *Chemistry International*, **2006**, *2*(5), 4-8, was brought to the editor's attention by Professor Sydnes during his recent visit to NZ. It is reproduced here with his permission.

Introduction

Chairpersons constitute an essential component of any major scientific meeting. It is, therefore, important that those selected for such a task understand that the role of the chairperson is to facilitate the execution of the meeting and function as a connection between the speaker and the audience. Surprisingly enough, this role is frequently not understood; in fact most scientists can testify that they have attended scientific sessions that were adversely affected by a chairperson belonging to one of the following groups:

- The *Oscar Winner*, who has spoken at conferences and chaired sessions for decades - speakers have to fit in with his/her performance, and *it is* a performance, developed and honed over many years.
- The *Know it All*, who is always ready to impose his/her stamp on any presentation and demonstrate brilliance by hogging question time.
- The *Unconstrained*, who is oblivious to the clock, frequently ready to stimulate irrelevant discussion and frustrate to speakers, especially the next one, and audience alike;
- The *Nervous*, who starts twitching 5 minutes into the lecture, shifting papers so as to be ready for the next presentation – s/he is capable of putting anyone off.
- The *Technophile*, who is looking forward to any breakdown in the presentation technology so that s/he can leap up to assist.
- The *Busy Professional*, who arrives a minute before the session starts – s/he is completely unaware of the session order or gender and presence of the speakers.

A collection of such experiences acquired over many years has inspired us to write this piece. Its purpose is to encourage chairpersons and conference organizers to work actively to achieve fluent and effective programming by identifying the key features of effective chairing and offering practical suggestions for organizers and prospective chairpersons. Although it is targeted especially at new chairpersons, it will, hopefully, be of interest also to more experienced colleagues.

Tips for organizers

It is a fact that *not all* experts make good lecturers. It is also true that good lecturers and brilliant scientists *do not necessarily* make good chairpersons. One reason is that the personality and verbal display that can carry a lecture may inhibit another's presentation by seeking the spotlight.

Photo Caption: Leiv Sydnes relaxing in the Akatarawa Valley

Very often members of the Scientific Committee are selected as session chairpersons. This may be appropriate, but *not* if there are linguistic or other limitations. This is especially true of Opening Sessions, where the audience's interest needs to be ensured. In order to reduce the probability of ending up with chairpersons that will jeopardize these sessions, the Organizing Committees should:

- *Identify session chairpersons early* – their role is at least on a par with that of the speakers.
- *Provide clear guidance of what level of activity is required* – for example, should there be a brief introduction to the session or a short summary of the presentations at the end.
- *Provide full details of the program of the sessions* – this may change at the last minute since speakers drop out or are replaced. Do not wait until the last moment to inform the chairperson of this (usually via a scribbled and often illegible note). Confusion in statements from the chairperson can readily undo months of planning.

- *Ensure that water/soft drinks are available*. Do not forget bottle openers, if necessary – 90 minutes gazing at an unopened bottle can be torture in an airless room.

Tips for chairpersons

The chairpersons are in control, but the best chairpersons exercise the velvet glove rather than the iron fist. Pomposity and bluster are not qualities to display before an international audience, and are certainly not those to be passed on to younger colleagues. The activities of a successful chairperson may be divided into four sections.

Before the session

Ensure that the organizers have provided correct details of the session, its timing, the program, and the speakers. Check that audiovisual aids and microphones are available and working. If a plenary or keynote lecture is included, make sure that you have brief biographical details of the speaker, or seek the speaker out before the session to obtain these. If you do not know the speaker, ask one of the organizers to point him/her out. This can save hours of squinting at name badges of people that you imagine look like the speaker.

At the beginning of the session

Greet the speakers and seek any last minute information (see below). Inform them about the importance of keeping to the schedule, make it abundantly clear how you will inform them that time is coming to an end and how you are going to terminate the presentation before the next speaker is introduced. Calm any last minute nerves and try not to pass on yours to them, especially when less-experienced speakers are involved. Furthermore, make it clear that problems with the audiovisual equipment and the microphones are the responsibility of the organizers, not the speaker.

Ask the speakers to pronounce their names and, if necessary, make a note of these phonetically. It is not funny to mispronounce *foreign* names or organizations - it is, quite simply, *rude*. Remember, too, that the chairperson has precedence over the speaker, even if he or she is your old Professor or your present boss!

Ensure that the session begins on time. Five minutes before the stated start, invite people to take their seats. Good organizers will already have been ushering people through the doors (a bell may be a useful accessory here). Check that all speakers are in the room. Do not rely on the fact that you saw the first speaker 15 minutes ago. S/he may have retired to the washroom, or returned to their room. Ideally, arrange for all speakers to be in the front row.

Allow yourself 30 seconds to read through the names of the authors and the titles of presentations. Then start by speaking slowly and clearly. Welcome your audience. If you feel it appropriate, welcome the audience in the language of the venue (it is always much appreciated) – if you do this, ask a local colleague to repeat the words slowly and write them down phonetically. Briefly introduce yourself (and your co-chairperson if necessary). Make sure that the name on the table is in agreement! Do not give the audience the option of deciding whether you are Dr Rimsky or Professor Korsakov. Remember to remind members of the audience to switch off all mobile telephones (and ensure that your own is switched off!).

Introduce the session briefly and move to the first presentation. A typical introduction to a plenary/keynote paper should be no more that one minute, including maybe details of graduation, positions held, recent research interests and activities, awards – all to demonstrate the suitability of the speaker for the presentation to come. Conclude with something like: *It, therefore gives me great pleasure to invite Dr Knoblauch to present this plenary/keynote lecture on [title].*

For invited oral presentations, check that you have identified the right author and run through the pronunciations of the authors and their affiliations. A typical introduction could be: *The next paper is entitled [title] by Schwarz, Noir and Black from the Institute of Chemistry of the University of Innsbruck. This will be delivered by Dr Anni Schwarz.*

During the presentation

Be aware of any restlessness in the audience. Has the microphone has gone dead? Maybe the lighting needs adjusting.

The greatest challenge – and fear – of any chairperson is the *over-running speaker*. Sometimes s/he is apparent from the beginning (as, for example, when the introductory slide is still showing after 10 minutes), in other cases the presentation dribbles or gushes on and on. *The watchword in such cases is politeness*. It is possible to curb such speakers, but strangulation is really not an option. Some large conferences, often running parallel sessions, still adopt a green, orange (two minutes to go) and red (stop) light system, but this is not common and in any case may be ignored by those claiming to be colour-blind.

The chairperson must have a watch or clock watch and should note the exact time of commencement. Prior to the session the chairperson should have decided where to sit during the presentations since this can effect his/her actions. Make clear the nature of the signal you will send to the speaker (for example moving from front row to dais when 5 minutes remain). Alternatively, a hand signal may be used. Some presenters have, like some waiters, been known to lose their sight at such vital times, and so the signal should be significant. If a further indication is needed, then a firm: *Two minutes, please* through the microphone is very effective.

Incidentally, do remember to switch off the microphone between comments, since you are not likely to gain the speakers friendship if a comment *Isn't this ghastly.... Where did they find this cretin?* passes through the hall. If all else fails, walk to the podium and adopt a stance next to the speaker as your final signal. *Again, be polite.* Indicate that it is indeed an interesting topic, but there is a tight schedule, other speakers are waiting and further discussion and exchange of views can take place later during the tea/coffee break.

It is the unlikely prospect of the last scenario that causes the most stress amongst chairpersons simply because one is not totally in control. However, the audience is on your side. The only things to remember is to work through the signals in turn and stick to the conviction that *the conference is greater than the individual speaker*.

It is good to remember the names of speakers that do not comply with the time allotted, after all you will likely organize conferences yourself at some time and you can avoid these people. In any case you certainly do not want to experience a re-run the next time you take the chair.

After each lecture

Questions should only be allowed if the program is running according to or ahead of schedule. On the other hand, questions are an essential part of the scientific process and all lecturers, therefore, deserve at least one question. Thus, during the lecture it is important for the chairperson is to generate a couple of questions that can be asked if nobody else has one (if the topic is not in your area of expertise, a question can sometimes be prepared from the available abstract). This is especially important at the beginning of a conference when potential questioners may be rather shy or doubt their ability in English. Questions from the chair, therefore, provide a little more time for the audience and give the speaker a chance to move into less formal *answer mode*. If no further questions are forthcoming thank the speaker and perhaps comment that further discussion will be possible after the session or over lunch, *etc*.

Usually there are questions, sometimes too many. Ensure that the questioners have access to a traveling microphone, or speak up so that the whole audience can understand. Often questions addressed to the speaker are inaudible to those sitting behind the questioner so, if necessary, repeat the question (this also gives the speaker a few more seconds to prepare an answer).

Show that you have seen potential questioners so that they do not wave furiously. If there are a number of questioners, politely discourage the person who has three questions and a comment, by inviting him to ask one question to give others a chance. Do not be tempted to let questions continue to the detriment of the overall timing; it is far better to cut a discussion short and invite its continuation at coffee or during lunch.

Remember that every speaker deserves his/her full time. If the session is overrunning, do not put pressure on later speakers to speed up their presentations. It is not their fault. If necessary, ensure that a message is sent to the caterers alerting them to the fact that teas/coffees or lunches will be 10 or so minutes late. Remember that they are working to a schedule too. One memorable conference session managed to lose 90 minutes over a 3 hour period!

At the end of the session

If there is a link to the next session refer to it briefly, such as: *In this session we have heard about the methods developed to measure vitamin deficiency. After coffee/lunch we will see how these have been used in a clinical situation*. Thank all the speakers, the translators (if appropriate) and the lecture theatre staff and ask the audience to express this in the usual way. Announce the time at which the next session will begin.

Make a special point to informally thank the speakers in your session after the session has come to an end, especially those at the beginning of their careers. If you have constructive criticism to put forward, make it after some positive comments. A few words of support and encouragement at such a time will do wonders for their confidence.

Before leaving, look over the facilities and make sure you leave them as you would wish to find them. Hand the meeting over to your successor efficiently and on time, and make sure that your name plate has been removed.

Parallel Sessions

Concerns about smooth running and attention to timing obviously are particularly important when there are parallel sessions. Even if time for moving out/settling in seems to have been included in the program, most participants will probably, in practice, experience a time crunch when switching from one session to another. This is especially true if deviations from the lecture schedule are combined with complex logistics. Organizers can assist by briefing all chairpersons on the importance of timing (it just takes one laggard to cause chaos) and to ensure that the various lecture theatres are in reasonably close proximity.

Chairing the last session

The last session of the conference was coming to an end; the speaker and chairperson looked out across an audience of one. The speaker drew to a close and thanked the chairman, who thanked the speaker and congratulated the audience member for his perseverance and willingness to remain to the end. In reply the audience member informed the chairperson that he was, in fact, the last speaker.

There is really no way of denying that the last session of any conference is equivalent to the speakers' *graveyard* after-lunch plenary. Some of the audience will have left, some will be leaving during the session, and those that remain will wish to get the earliest taxi or train to the airport. This is not to say that departees should not be quiet – the person who wanders around kissing friends *au revoir* is not doing a service to the speaker, nor is the person sitting in the middle of a row who decides to move. Departures between papers is usually possible; if not a seat should be taken at the end of a row.

No manner of wit or wisdom will delay those desperately wanting to avoid the traffic jams to the airport! The basic rule, therefore, remains the same: Stick to the timetable and do not prolong the session!

Selecting Young Co-chairpersons

In order to support and encourage the next generation of scientists in conference involvement it is a good idea to introduce co-chairing of sessions by younger (this being up to the organizers to define) and more-experienced (a euphemism for *older*) colleagues. We believe this will improve conference chairing in the long run and certainly

Photo Caption: Often the last session of a conference can be the speaker's graveyard

contribute to increasing the quality and knowledge transfer of conferences that seek to stimulate scientific discussion and generate new ideas. It also gives other young people in the audience the feeling that, in time, they could do the same. However, potential young chairpersons should be selected with care – not sleeping the night before and facing the audience rigid with fear is not what this experience is all about. In such circumstances, the responsibility is with the senior person to *look after* their more junior colleague. This is not, after all, a PhD viva.

Concluding remarks

It should be emphasized that it has not been our intention to outline *The Only Way* of chairing scientific meetings. On the contrary, each individual chairperson, like each presenter, should be encouraged to build on their own personality and develop their own style. However, there is no doubt that the overall quality of scientific meetings can be improved significantly by good and constructive chairing, characterized by clear leadership and the ability to catalyze scientific discussions during the sessions.

Good chairpersons will learn from their experiences and should not, knowingly, turn in a poor performance since this will reflect badly on themselves and on the organizers. So, before you accept that next invitation to Honolulu or Crete, ask yourselves what you can bring to the conference and prepare yourself.

Remember:

- The Chairperson is the servant of the meeting and the speaker, not the other way around
- Read through the programme in advance
- Identify the speakers and check the pronunciation of their names
- Explain how you will chair the session (timing, etc.)
- Speak clearly (and, if a native English speaker, do not speak too quickly)
- Keep to time
- Let questions flow
- Thank everyone
- Note the performance of other chairpersons, draw up a list of personal do's and don'ts
- Adapt good rules to your personality, don't try to change your personality
- Above all, enjoy the experience.

Good luck!

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The New Zealand Institute of Chemistry (NZIC) represents some 1000 members involved in the profession of chemistry. It is the only professional society for Chemists in New Zealand. Benefits of membership:

- four issues of *Chemistry in New Zealand* annually
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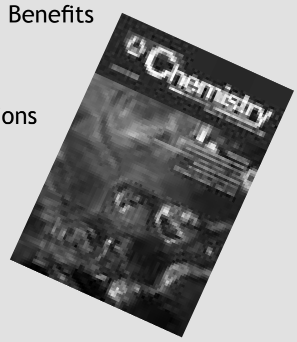

Chemistry in New Zealand *July 2008*

Education for Sustainability: What Does This Mean for Tertiary Chemistry?

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Education for sustainability is a responsibility for chemistry and every other discipline. The scale and urgency of the problems of unsustainability require critical examination of practice - research, teaching, and service. Population growth, increasing demand for commodities, waste accumulation and, most pressingly, climate change apply crippling pressure to the planet. The reports on the state of the planet, most significantly those of the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment,[1] give us from 10 to 15 years to check the acceleration in temperature rise. Human action is squarely in the frame. The reports look to education to enable better understanding and to encourage changes to the way we live.

Despite intensive media coverage when the first three Fourth Assessment Reports were released, one year on The *Dominion Post*[2] has a double page spread lauding the search for oil in ever more inaccessible sites and welcoming the prospect of millions more barrels to support NZ's economic growth. Fritjof Capra[3] points us away from the mechanistic thinking that spawned this industrial approach and towards systems thinking derived from ecology. The systems he describes are interrelated self-organizing systems, living, non-living, and technological. From this systemic perspective, economic and technological decision-making cannot be seen in isolation from the social and biophysical systems in which they are embedded. Some argue for technological solutions to improve *eco-efficiency*,[4] including a *service and flow economy* built on lease rather than purchase of goods. This already exists within some industries, *e.g.* photocopying, where manufacturer responsibility for recycling of parts and materials occurs in a biomimetic approach[5] to components as technical nutrients.

Others argue that deeper change is needed. The UK *Forum for the Future* maintains that it is global capitalism rather than capitalism *per se* that is the problem and supports an international perspective aimed at human dignity and social justice, promoting national integrity and self-sufficiency. The *five capitals* model of sustainable development[6] draws particularly on real cost accounting research.[7] The model conceptualizes a sustainable society as one that maintains or restores capital assets, including the stocks and flows of natural, manufactured, human and social capital, as well as the financial capital by which the forms of substantive capital are measured and traded. That the values driving consumerism are beginning to be questioned is evident in recent media attention to research on the sources of *happiness*.[8]

The UN has required member states to develop and implement a comprehensive National Sustainable Development Strategy by 2005. So far the NZ government has approved only a *Programme of Action* focusing on selected aspects.[9] Late last year the Prime Minister[10] introduced two new energy strategies and stated that government intended to work towards *a carbon neutral New Zealand*, claiming leadership in the field. It is difficult to see how the strategies will achieve sustainability, when renewable sources are only preferable and biofuels are promoted despite all the known consequences for living, human and social systems. Clearly there is a key role for chemists in this debate.

Sustainability Literacy

The UN has declared 2005–2014 a *Decade for Education for Sustainable Development* (UNDESD), which promotes a key role for tertiary education. In late 2007, the Commission for UNESCO signed a partnership agreement with Sustainable Aotearoa NZ (SANZ) giving SANZ the mandate to coordinate UNDESD activities for NZ.

As the goal for education for sustainable development, and education for sustainability, there is wide support for sustainability literacy at the tertiary level. However, there is a range of views in regard to its meaning, *e.g.* Murray[11] describes the acquisition of defined skills relevant to the built environment. Such an approach has been criticized as indoctrination and inappropriate to university study. Acquisition of a broader set of facts-based and process-based skills is described by Dale and Newman.[12] A definition arising from the Forum for the Future's Higher Education Partnership identifies a sustainability literate person as one who understands the need for change to a sustainable way of doing things, has sufficient knowledge and skills to act appropriately, and rewards others' behaviour that favours sustainable development.[13] These definitions, however, derive from a cognitive deficit view of literacy, where essential knowledge and skills are defined by *experts* without recognition of the contexts and perspectives of the individuals concerned.

A contemporary view of literacy as social practice recognizes that literacy is embedded in culture.[14] James Gee has articulated such literacy as evident in the *way of being* or *Discourse* of the relevant social group entailing communication via language, illustrations and icons, and includes appropriate behaviours, attitudes and values consistent with those of the group;[15] fluency in the Discourse allows members to communicate effectively. This cultural view suggests a range of sustainability literacies; professional (including those of the graduate chemist), citizenship, and everyday literacies. Individuals acquire a number of Discourses, not all consistent with each other, and these evolve as aspects of a given Discourse are challenged.

Parallel and conflicting Discourses of sustainability and sustainable development have developed despite common meanings for the terms when they were introduced in the

1980s. Both terms referred to a society that met its own needs without affecting the chances of future generations. Contradictions developed between the Discourses largely through narrow understandings of *development* as economic development. Currently, however, broader understandings of development and common recognition of the biophysical limits of the planet have resulted in these Discourses increasingly overlapping. No distinction is made between the terms in the present discussion.

Recognition of Sustainability in Chemistry Courses at NZ Universities

An investigation of the sustainability content of undergraduate and postgraduate courses (or papers) in chemistry for chemistry qualifications offered at NZ universities in 2008 was carried out through a survey of the web listings of six of NZ's eight universities; neither AUT nor Lincoln offered qualifications in chemistry. Despite the limitations, which include the quality of the website and the policy decision in respect of the detail of course content provided, the survey identified those courses the university wished to advertise to enrolling students as addressing sustainability. The results are given in Table 1.

Only taught courses are included and only courses for which content is identified, either through the course title and/or the course description. Where special topic courses offer choice from specific modules they are included. Courses with the same content offered under different course numbers are identified just once. Courses are not distinguished by credit value. Indication that a course addressed sustainability was taken to be evident where topics referred to included sustainability or sustainable development, *green chemistry*, ecosystems, the environment, human or social issues, hazards, pollution or toxicology.

Nearly all universities offered specialist courses in environmental chemistry, mostly at postgraduate level and commonly in association with analytical chemistry. Otago linked the environment with physical chemistry at most levels. Only two universities, however, came close to infusing consideration of a more comprehensive whole systems approach to sustainability across the range of undergraduate chemistry courses. Auckland and Waikato each offered several courses at first year that either indicated specialisation through the course title or included consideration of issues in the course description; Waikato University carried this consideration through into the second year. Waikato and Otago offered sustainability-related courses that included interdisciplinary approaches.

While the introductory web pages of the chemistry departments tended to claim a central role for chemistry in understanding the world, the survey suggests this understanding was unlikely to recognise a world degraded by human action. Where there was recognition, courses tended to indicate investigation of changes to cycles and systems of the natural environment. Few courses investigated interrelationships between environmental and human, social or economic systems. Green chemistry, focussing on safety in chemical design and processing, was identified at Auckland and Massey The notion of sustainability was used at Auckland University, but it was unclear.

A survey of students enrolling in universities and colleges in the UK[16] found nearly two thirds would like to learn more about sustainable development in their coursework and 42% believed that such learning would help them get the job they wanted. Although 25,000 students responded to this on-line survey, the respondents represented only 7% of the sample contacted. However, only 30% of respondents identified themselves as environmentalists. Students were aware of the challenges facing the planet and believed there were radical lifestyle changes ahead.

Strategies for Education for Sustainability in the Tertiary Sector

The tertiary sector identified through NZ's Tertiary Education Strategy includes all the professional development carried out in the workforce, all learning and teaching undertaken through tertiary education organizations (universities, polytechnics, wananga, and private training organizations) and education in the community.[17] Five broad strategies are described for developing education for sustainability through chemistry.

Developing Understanding

Understanding how the planet works is dependent on understanding of cycles and systems of the natural world, and thus on science. The ongoing unpopularity of science18 and perceived difficulty of chemistry, however, provides a significant challenge for extending fundamental understanding.

Table 1. Web-based university information on sustainability in chemistry courses

University	No. of taught chemistry courses with sustainability in title or content (cont) *vs* all taught														
	100-level			**200-level**			**300-level**			**Postgraduate**			**All levels**		
	Title	Cont.	All	Title	Cont.	All	Title	Cont.	All	Title	Cont.	All	Title	Cont.	All
Auckland	0	3	4	0	1	5	0	1	8	1	1	9	1	6	26
Waikato	2	1	4	1	4	9	1	0	5	1	0	5	5	5	23
Massey	0	0	3	0	0	5	0	1	5	1	0	4	1	1	17
Victoria	0	0	3	0	1	7	0	0	5	0	0	5	0	1	20
Canterbury	0	0	5	1	1	9	1	0	9	1	0	12	3	1	35
Otago	0	1	3	1	0	4	1	0	5	3	2	6	5	3	18
All	2	5	22	3	7	39	3	2	37	7	3	41	15	17	139

Tertiary education research over the last 30 years has identified the link between understanding and a deep, rather than surface, approach to learning, and learning for meaning, rather than reproduction. Learners successful in developing understanding relate new ideas to knowledge and experience, examine argument, and construct symbolic objects of understanding that represent the coherence of their ideas.[19] Despite understanding being a primary goal of the discipline, undergraduate science students are likely to adopt a surface approach to learning as they perceive the curriculum to be overloaded and to have little freedom of choice in regard to content or method.[20] Students' concern for the state of the planet provides an opportunity to develop learning tasks that will encourage their active and sustained engagement.

Critical Reflection on Practice

The distinctive Discourses of social groups, discussed above, are evident in the different *epistemic cultures* of practising scientists (Knorr-Cetina[21] identified the questions, theories and methods of high energy physics and molecular biology that lead to contrasting aims and practices) and the different disciplinary *ways of thinking and practising* of university teachers.[22] These characteristic ways of behaving, whether in research or teaching, are taken for granted and difficult to change. Individuals rationalize and maintain the social systems they create in a process that Anthony Giddens calls *practical consciousness*.[23] To change the social systems individuals need to develop discursive consciousness in discussion and critical examination of the systems with their peers.

In respect of sustainability, a collegial process to identify institutional stakeholders and a framework of underpinning values, including fairness and justice, would provide a context for examining policy and practice documents and identifying contradictions. Government research funding opportunities that conflict with sustainable practice, for example, provide dilemmas for researchers who may be under pressure from institutional managers to secure funding regardless of long-term goals for the planet. There is no escaping the political nature of discursive consciousness. Students would benefit from opportunities to collectively examine accepted ways of thinking and practising in the discipline through authentic problem-solving activities.

Promoting Interdisciplinarity

The complexity of industrial society means that a systemic approach to sustainability necessarily requires an interdisciplinary approach, with disciplines working together to address a single issue. While government is recognizing, through its Environment Research Roadmap, the need to consider whole systems, it is currently calling for a multidisciplinary approach, where disciplines work alongside each other.[24]

According to Good,[25] an interdisciplinary approach is difficult to achieve because it requires members of one discipline to see an issue from the perspective of another, but it provides insights not otherwise achievable. Historically, new research and development has occurred at the boundaries of disciplines where practice is least stable. Practitioners are most vulnerable at the boundary of their discipline and it is here their respect for practitioners of other disciplines is greatest.

Tertiary teachers wanting to develop interdisciplinary coursework would find it useful to work with one or two other enthusiastic staff through an integrated approach to a common problem. Incorporating the approach into an existing course establishes a model for addressing sustainability across the curriculum, and is likely to be more easily adopted than a new course. A series of required sequential interdisciplinary papers or modules on sustainability through the three years of an undergraduate programme is another option, but it can imply that sustainability is a topic for specialists and that the disciplines themselves do not need to change.

Collaborating in Community Projects

Community projects include collaborative research and development initiatives in which research institutes, tertiary education organizations, business and industry, local government, and not-for-profit organizations work together to develop sustainable practices, including carbon management. These projects, and student research and community placements, not only improve research connections and community linkages but enhance the sustainability literacy of all participants. Participants have the opportunity to experience the development of sustainability fully, through examination of interconnected environmental, human, social, technological, and economic systems in real-world contexts.

The establishment of Regional Centres of Expertise for Education for Sustainable Development (RCEs), under the auspices of the UN University, is an international initiative to meet the goals of the UNDESD.[26] The aim is to coordinate local partnerships of tertiary education organizations, local authorities, schools and not-for-profit organizations to conduct research and build capacity for education for sustainability. To date 55 RCEs have been established around the world, though none of these are in NZ.

Modelling Sustainable Behaviour

Probably the strategy most readily undertaken is modelling sustainable behaviour in everyday practice: in personal life, *e.g.*sustainable transport, fair-trade purchasing; professional life, *e.g.*recycled stationary, video conferencing; the laboratory, *e.g.*recycling, saving power; and by encouraging corporate responsibility, *e.g.*sustainable procurement, encouraging biodiversity. These all these serve to raise awareness, the need is to change the core assumption of the validity of material consumption and the current orthodoxy of economic growth.

Conclusion

There are encouraging signs of the infusion of sustainability in undergraduate chemistry courses in a few universities. Across the Universities surveyed, however, the pattern of environmental chemistry courses could be considered tokenism. Most chemistry students will continue to complete undergraduate study without ever formally examining sustainability issues. These students enter the workforce without the understanding of systems theory or the developed reflective thinking abilities that would allow them to address the sustainability issues that they will surely face.

Helping students understand fundamental processes is familiar territory to chemistry academics. However, in order to allow such understanding to contribute to the development of sustainability literacy, students need the opportunity to explore the relationships between these processes and the processes and systems accessible through other disciplines. Moreover, new perspectives critically reflecting upon taken-for-granted practice are needed. Such interdisciplinary innovations provide opportunity and challenge to traditional undergraduate teaching practice, not least in terms of large classes and full courses. They require reduced content, critically reflective investigation, collaborative project work, and greater opportunity for discussion and debate. The changes also have the potential to provide deeper understanding in general and to address the ongoing issue of the perceived difficulty of chemistry, which continues to discourage so many potential students.

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Correction to Article

Protecting Cultural Heritage: Reflections on the Position of Science in Multidisciplinary Approaches *This Journal*, (**2008**, *72*, 75-77) ran with incorrection captions under each Figure. The images and correct captions are shown below. The publishers apologise unreservedly.

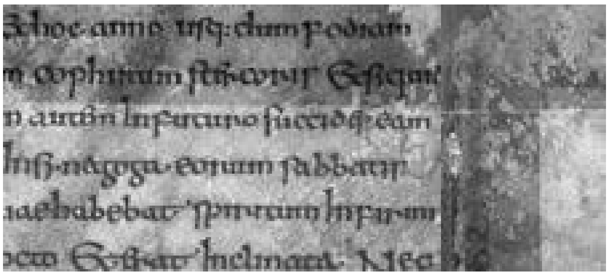

Fig. 1. Dyes in Preolumbian Peruvian textiles (reproduced with permission from the Royal Institute for Cultural Heritage, Brussels): A combination of medium destructiveness and high resolving power allowed for the identification of biological sources used for dyeing, and revealed changes in use as a function of cultural periods - see ref. 12.

Fig. 2. High-level destructiveness analysis of synthetic membranes without touching the 8th century parchment of the Codex Eyckensis (reproduced with permission from the Royal Institute for Cultural Heritage, Brussels). This revealed a polyvinylchloride polymer with 30 % (w/w) monomeric plasticizer; after removal of the membranes, the Codex could be conserved by the application of an innovative parchment leafcasting technique – see ref. 13.

Patent Rights Bombshell Dropped on Australian University: The Implications for New Zealand

Case law long ago established that any intellectual property developed by an employee in the course of his or her employment belongs to the employer. If the employee applies for intellectual property protection himself by obtaining a patent, for example, the patent is deemed to be held in trust for the employer. However, a recent decision of the Federal Court of Australia in the case of *University of Western Australia v Gray*[1] has potentially modified this principle.

The Circumstances

Dr Bruce Gray was a Professor of Surgery at the University of Western Australia during the 1980s and 1990s. In the course of his tenure he developed a method of targeting treatments for liver cancer using microspheres of radioactive yttrium-90. The patents that resulted from this line of research and other inventions were held in Dr Gray's name and were subsequently acquired in 2000 by Sirtex Medical Ltd., an Australian public company of which Dr Gray was a director and major shareholder. In 2004 the University of Western Australia sued Sirtex on the basis that the patents were held in trust for the University by Sirtex.

The Decision

Given the well established case law, shockwaves travelled through Australian universities upon the release of Justice French's 17 April 2008 judgment, which holds that the University never had any rights in the intellectual property developed by Dr Gray. Justice French not only considered the development of the case law surrounding intellectual property and employment in Australia, he also considered the relevant case law in the US, the UK and Canada. He ruled that Dr Gray was employed to undertake and stimulate research, *not* to create new inventions.

Whilst Dr Gray could possibly have produced a patentable invention in the course of his normal research activities, Justice French inferred that creating inventions was not an expected outcome of his employment. In particular, it was considered that Dr Gray's obligations to the University as an employee were not the same as those of a researcher employed by a private commercial entity. Justice French considered that a private commercial entity would expect an employee to advance the commercial interests of the employer, whereas a university, a not-for-profit entity, was likely to only have an academic research requirement, with no commercial imperative.

One of the arguments made by the University was that it owned the rights to any patents developed by Dr Gray during his employment because his contract incorporated the University's intellectual property regulations. Justice French did not find this argument persuasive because the University regulations are limited to the management of University property only. Because Justice French had already established that the patent rights were the personal property of Dr Gray, the University regulations could not, therefore, be held to support an ownership claim for the patents.

So how will this decision affect researchers in New Zealand?

Given the increasing interest in commercialisation of intellectual property by New Zealand universities, it would not be surprising if the universities are not already reviewing their employee intellectual property policies. This decision could be persuasive in a New Zealand court, especially if the decision is appealed, and subsequently upheld by the Australian Court of Appeal. The importance of this judgment in New Zealand cannot be overlooked. It has far reaching implications. Academic institutions in New Zealand, and indeed around the world, will be keeping a close eye on any further developments with this case.

A reminder: if you have any queries regarding patents or patent ownership, or indeed any form of intellectual property, please direct them to:

Patent Proze

Baldwins

PO Box 852, Wellington

Email: email@baldwins.com

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[1] University of Western Australia v Gray (No 20) [2008] FCA 498

Blair Hesp and Jarrod Ward of Baldwins specialise in chemistry and biotechnology patents. Blair joined Baldwins in 2006, and has a PhD in pharmacology from the University of Otago as well as a NZDipBus with a management focus. Jarrod joined Baldwins in 2007, and has completed the requirements for his PhD thesis in chemistry at the University of Auckland. Blair and Jarrod are currently studying towards law degrees and registration as patent attorneys.

Letter to the Editor

Re : The standard of climate change debate

Most members of the public, if they were asked what science should be, would (hopefully) state that it is the application of logical analysis to observation, in order to provide statements regarding the nature of nature. Logical analysis was invented by Aristotle over 2000 years ago, and a scientific debate should follow its rules. If it does not, the public will recognize the deficiency, even if they cannot analyse for themselves, and the net result is that science falls into disrepute.

The response by Mackie and Hunter[1] to Gray[2] is not encouraging. Paragraph 1 is a put-down: Gray is accused of making statements *so lacking in clarity and substance that it would be uncharitable to respond in detail*. One example from Gray: *Atmospheric carbon dioxide concentration is not well-mixed but variable*. Following Aristotle, that is a correct statement in the formal sense, and it is true, not true, or we cannot tell. What is unclear?

Paragraph 3 attacks the journal, but not the issue. The validity of a series of statements should depend on observational data, the validity of an analysis should depend on the logic employed, and neither depends on somebody else's assessment of the place where it was published.

Paragraph 4 commences with a logic error. For example, the underlying argument is of the form *if B, then C*. There is nothing illogical whatsoever for Gray to assert that A is not an element of the set B, and then add: even if it were, A does not support C and would therefore falsify the if-then statement. Then there is a further problem. Gray asserts through a reference to Beck that: *Some 90,000 previous measurements have been suppressed and unwanted figures are not published*…. That is either true or not true. That Gray's reference is considered unreliable by most climate scientists is simply an example of the fallacy *ad verecundiam*. The fact that something else Beck wrote is wrong is irrelevant; Gray made a statement and it should either be accepted or refuted. The average unbiased spectator, seeing the refusal to refute the statement, will believe it to be true, for if it is untrue, why not simply refute it?

So, what is the truth? Personally, I am unsure, but I do not find this type of debate particularly enlightening. What particularly bothers me is my memory of the non-classical carbenium ion: about 600 theses emerged on this topic from two opposing camps, and no camp *ever* published any fact refuting their position. Not only that, but it is debatable that no conclusion was ever reached that satisfied the unbiased but interested spectator. (I would argue the real mechanism was never stated.) The only plausible explanation is that each camp *understood* what was going on sufficiently well to design experiments to support their position. Accordingly, in any debate, the volume of data is not important; what is important is the determination of which clear statements are true or untrue, and the problem of climate change is no different.

References

1. Mackie, D. S.; Hunter, K. A. *Chem in NZ* **2008**, *72*, 35.
2. Gray, V. R. *Chem in NZ* **2008**, *72*, 34.

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Editor's Note:

This letter adds a philosophical note to the debate, and perhaps justifiably criticizes the perception of a scientist's credibility on the basis of the inferred reputation of the journal in which the work is published as a proxy for the truth of the data or idea. It is timely in this debate to recall that the history of science contains many examples of the majority view of scientists of the day later being proved incorrect. Examples include phlogiston theory, evolution,and plate tectonics. The problem with global warming is that the stakes are higher than for these other theories: if it turns out not to be true money will be lost, and we will feel that resources could have been used more prudently (a bit like the Y2K drama), if it turns out to be true, we can at least feel we did something about it.

No doubt the debate will continue, but not in these pages for with this issue of the journal correspondence on the global warming debate is now closed.

Have a story in your head?

The Royal Society of New Zealand are again running their creative writing competition. There are two categories for the Manhire Prize; fiction and non-fiction. Winners in each category receive $2,500.

The topic this year is evolution.

"'The Universe makes rather an indifferent parent, I'm afraid,' said Dickens' kindly Mr Jarndyce. Humans have evolved to understand and intervene in the unsentimental processes of nature. With some unfortunate and unintended consequences. Back to nature or on to the future?"

Closing date is 15 August 2008.

For more details see the website: *http://www.rsnz.org/education/manhire/index.php*

Conference Calendar

17th International conference on photochemical conversion and storage of solar energy, Sydney, Australia, 27 July - 1 August 2008.

Further details available at the website: www.ips17.com/

XXII IUPAC Symposium on Photochemistry, Goteborg, Sweden, 28 July - 1 August 2008.

Further details available at the website: http://photoscience.la.asu.edu/Goteborg2008/

20th International Conference on Chemical Thermodynamics, Warsaw Poland, 3-9 August 2008.

Further details available at the website: www.icct2008.org/

5th SETAC World Congress, The Society of Environmental Toxicology and Chemistry, Sydney, Australia, 3-7 August 2008.

Further details available at the website: www.setac2008.com/

XXth International Symposium on Medicinal Chemistry, Vienna, Austria, 31 August - 4 September 2008.

Further details available at the website: www.ismc2008.org

PSA2008, Particulate Systems Analysis 2008, Stratford Upon Avon, United Kingdom, 2-4 September 2008.

Further details available at the website: www.psa2008.co.uk/

Praha 2008, The 20th International Conference on High Resolution Molecular Spectroscopy, Prague, Czech Republic, 2-6 September 2008.

Further details available at the website: www.chem.uni-wuppertal.de/conference/

International Conference on Organometallic and Co-ordination Chemistry, Onboard a ship – Volga & Sheksna Rivers, Russia, 2-8 September 2008.

Further details available at the website: http://iomc.ras.ru/node/2

MAM08 The 4th IUPAC-Sponsored International Symposium on Macro- and Supramolecular Architectures and Materials: Synthesis, Properties and Applications, Dusseldorf, Germany, 7-11 September 2008.

Further details available at the website: www.chemie.uni-duesseldorf.de/Faecher/Organische_Chemie/OC2/ritter/MAM_08

Technical Chemistry, From Theory to Praxis, Perm, Russia 8-12 September 2008.

Download a notice about the conference at: www.itch.perm.ru/

23rd European Colloquium on Heterocyclic Chemistry, Antwerp, Belgium, 9-13 September 2008.

Further details available at the website: www.echc08.org/

WATOC 2008, World Association of Theoretical and Computational Chemists, Sydney, Australia, 14-19 September 2008.

Further details available at the website: www.watoc2008.com/

AACB 46th Annual Scientific Conference "Laboratory Medicine: Promoting Population Health", Adelaide, Australia, 15-18 September 2008.

Further details available at the website: www.aacb.asn.au/web/Meetings/Annual_Scientific_Conference/

Chemistry in the New World of Bioengineering and Synthetic Biology, Oxford, United Kingdom, 22-24 September 2008.

Further details available at the website: www.rsc.org/ConferencesAndEvents/RSCConferences/chembio08/index.asp

Chemeca 2008, Towards a Sustainable Australasia, Newcastle, Australia, 28 September – 1 October 2008.

Further details available at the website: www.chemeca2008.com/

Mathematical and Algorithmic Challenges in Electronic Structure Theory, Minneapolis, Minnesota, USA, 29 September – 3 October 2008.

Further details available at the website: www.ima.umn.edu/2008-2009/W9.29-10.3.08/

ICCBE, International Conference on Chemical and Biomolecular Engineering, Venice, Italy, 1-3 October 2008.

Further details available at the website: www.waset.org/iccbe08/

XIV European Seminar on Computational Methods in Quantum Chemistry, Isola d'Elba, Italy, 2-6 October 2008.

Further details available at the website: http://h2.ipcf.cnr.it/rizzo/XIV_ESCMQC.html

MIPTEC Conference, the leading European event for Drug Discovery, Basel, Switzerland, 14-16 October 2008.

Further details available at the website: www.miptec.com/

30APS, 30th Australasian Polymer Symposium, Melbourne, Australia, 30 November - 4 December 2008.

Further details available at the website: www.30aps.org.au/

RACI ChemEd08, Fremantle, Australia, 29 November – 3 December 2008.

Further details available at the website: www.raci-chemed08.org/

NZIC Conference, Chemistry and the Biosphere, Dunedin, 30 November – 4 December 2008.

Joint conference with NZSBMB & NZSPB. Further details available at the website: www.otago.ac.nz/nzic

RACI Organic 08, Wrest Point, Hobart, Tasmania, Australia, 7-12 December 2008.

Further details available at the website: www.organic08.org/

Inorganic Chemistry Conference IC08, Christchurch, New Zealand, 14-18 December 2008.

Further details available at the website: www.chem.canterbury.ac.nz/ic08/

ANZSMS22, The 22nd biennial Australia & New Zealand Society for Mass Spectrometry Conference, Sydney, Australia, 27-30 January 2009

Further details available at the website: www.mmb.usyd.edu.au/ANZSMS22/

AMN4, 4th MacDiarmid Institute for Advanced Materials and Nanotechnology Conference, University of Otago, 8-12 February 2009

Further details available at the website: http://macdiarmid.ac.nz/events/amn-4.php

Grants and Scholarships

Grants, scholarships and funding currently available for your application.

International Conference Fund

This fund is provided by the Minister of Research, Science and Technology and administered by the Royal Society of New Zealand. It is funding to assist organizations and institutions to host major international conferences in New Zealand.

There is no closing date for applications.

For further information see the website: http://www.rsnz.org/funding/int_conf/

Conference Assistance Programme

This programme is to provide assistance for bidding to host an international conference in New Zealand. This can include discounted airfares to travel to present a bid, help to write bid documents and accompanying marketing material, as well as other assistance.

For further details see the website: http://www.conventionsnz.com/cap.aspx

Technology Fellowships

This scheme is to encourage innovative companies to involve postgraduate students in their research and development programmes. The scheme provides a taxfree payment and travel allowance to the student.

There is no closing date for applications.

For further details, criteria and an application form see the website: http://www.frst.govt.nz/funding/business/techfellow

Technology Expert Fund

This is funding to pay partial costs of an expert for a technically challenging research and development project that will result in new products, processes or services being commercialised by the company.

There is no closing date for applications.

For further details, criteria and an application form see the website: http://www.frst.govt.nz/funding/business/TechExpert

SmartStart

This scheme can provide funds for a company to overcome issues to successfully complete research and development projects. This includes determining commercial feasibility, developing an R & D strategy, intellectual property strategy or investigating a range of solutions to a technical problem. Up to $5000 can be approved within a week and maximum funding is $25,000.

There is no closing date for applications.

For further details, criteria and an application form see the website: http://www.frst.govt.nz/funding/business/TechExpert

Growth Services Fund

This fund is intended to assist new initiatives that will have a significant impact on a business that will lead to substantial and sustained growth. Co-funding of up to 50% is offered.

For further details see the website: http://www.nzte.govt.nz/section/11964.aspx#acc

Claude McCarthy Fellowship

This fellowship has four categories for graduates of science, medicine and literature from a New Zealand university. The first one provides for up to $5,000 for a graduate who is registered or enrolled for doctoral degree to travel overseas to present at a conference or do a short period of research towards their doctoral degree. Category B provides for up to $30,000 to enable a graduate whose normal occupation does not allow them to undertake research to carry out research at a New Zealand university. Category C provides for up to $40,000 for any university staff member who is a graduate, to carry out original research outside their organization. Category D provides for not more than $10,000 for any university staff member who is a graduate, to take leave to travel overseas to do up to three months research.

Closing date for applications is 1 August 2008.

For further details see the website: http://www.nzvcc.ac.nz

Woolf Fisher Scholarships

This scholarship is for three or four years of postgraduate research leading to a doctoral degree or equivalent at the University of Cambridge or the University of Oxford.

A Woolf Fisher Scholar receives a maintenance allowance of £12,000 per year as well as an approved college fee, university composition fee and an annual return economy airfare from London.

Closing date for applications is 1 August 2008.

For further details see the website: http://www.nzvcc.ac.nz

New Zealand Science and Technology Postdoctoral Fellowship Scheme

These fellowships are for those with a doctoral degree. Funding is $58,000 per annum for up to three years and up to $29,000 per annum for research related costs.

Closing date for applications is 4 September 2008.

For further details see the website: http://www.frst.govt.nz/funding/students/postdoc

Te Tipu Putaiao Fellowships

These fellowships are for students completing masters, doctorate or postdoctoral work in a science, engineering or technology discipline. Funding depends on the qualification ranging from $10,000 stipend for a masters to $58,000 for a post doctorate.

Closing date for applications is 4 September 2008.

For further details see the website: http://www.frst.govt.nz/funding/students/TTP

The Todd Foundation Awards for Excellence

These awards are for projects, which have a practical application that is likely to be of direct benefit to New Zealand and its people. They include the category of science and technology. A candidate must have a degree or equivalent. The value of the award depends on the nature of the research project.

Closing date for applications is 1 October 2008.

For further details see the website: http://www.nzvcc.ac.nz

New Zealand Postgraduate Study Abroad Award

This award is available to postgraduate students enrolled in either Doctoral or Master’s degree programmes at a New Zealand institution, whose research would benefit from up to six months of study or research overseas. The value of the award is up to $10,000 depending on the proposed project.

Closing date for application is 1 November 2008.

For further details see the website: http://www.newzealandeducated.com/int/en/institutions_courses/scholarships/outgoing/new_zealand_postgraduate_study_abroad_award

Grants and Scholarships continued on page 116

Science, BPA and Baby bottles

Type Bisphenol A (BPA) and baby bottles into Google and you get 411,000 results.

More than enough information to blow the mind of any parent who half heard a news story that baby bottles containing BPA were not good for their baby.

Baby bottles containing Bisphenol A have been in and out of the media over the past few years. In 2003 a number of newspaper articles in the New Zealand Herald followed the report of Ohio researchers finding birth defects in mice, that had low exposure to BPA.

In February 2008 a report called "Baby's Toxic Bottle" was released by a group of American and Canadian Non Governmental Organisations that showed bottles leached BPA when heated. In May 2008 Canada's national public agency, Health Canada, became the first regulator in the world to label BPA toxic.

BPA is a polycarbonate that was originally used because it was considered safe, and had the useful attributes of being hard, shatterproof, lightweight and transparent.

BPA is also an oestrogen mimic in the mammalian body and thus can affect cellular activity. In New Zealand plastics containing Bisphenol A are marked with a 7 or the letters PC.

There is much debate over whether the BPA levels that leach out of the plastic are dangerous. While BPA is used in many everyday products, the possible ingestion of BPA by babies from their bottles has received the most attention.

Trying to establish whether baby BPA consumption is something we all should be worried about is difficult. It may seem rather than trying to track down papers and reports to read, it is easier just to avoid products containing BPA. But then one comes across the site with a report about BPA used to coat the inside of metal tins and thus it has leached into the baby formula as well (*http://www.ewg.org/reports/bpaformula*). Before mothers, who exclusively breastfeed can feel too smug, Isitinus.org says BPA is already in the urine of 95% Americans, according to an Alaskan Community Action on Toxics Fact Sheet.

To limit the amount of reading required it might seem a good idea to just look at the peer reviewed papers but this information is not freely available. The "Baby's Toxic Bottle" report and others claiming BPA is unsafe, can be instantly downloaded by a parent panicking about their choice of bottle. It is a different matter to probe further and check the research the report's findings are based on. Try to check many of the papers cited and one instantly hits a locked off wall of pay-to-view scientific papers. The "Baby's Toxic Bottle" report is fully referenced but only about half appear to be papers printed in scientific journals and a casual reader has no easy way of checking most of these papers. Therefore it is difficult to tell how much weight should be given what science.

It is understandable for many journals to want payment for viewing papers online, however in the information war this may not be a winning strategy.

Another option is to find out more about the groups and writers involved in the headline grabbing "Baby's Toxic Bottle" report and get an understanding of their background and areas of expertise. One of the groups listed as supporting the reports release is MOMS (Making Our Milk Safe). Their website says "MOMS was founded in the spring of 2005 by four nursing mothers". Their backgrounds are a writer, urban planner, communications expert and international development expert. An attorney founded another group, Clean Water Action.

Trying to find out the writers' backgrounds is difficult, and time consuming, especially if you are mother with small children vying for your attention. It was reassuring to find an academic, Dr Fred vom Saal from the University of Missouri who studies foetal exposure to low dose natural oestrogen levels but the two main contacts for the report were Mia Davis, who I have been unable to establish her background and Michael Schade, who has a degree in Environmental Studies. As far as I am aware this report was not published in any peer-reviewed journal.

Truth is becoming democratically decided by the size of easily accessible information. For BPA this is looking likely to mean its demise in many uses.

Scientists need to seriously think what they are going to do about this as it can ramifications for funding and future research. What product, process or drug will be called into question next?

On a more positive note, The Royal Society of Chemistry had a well put together article by freelance science writer, Fiona Case in the 2008 April edition of Chemistry World and this article was freely available online, unfortunately on my Google search for Bisphenol A it was listed on page four.

Here is the link:

http://www.rsc.org/chemistryworld/Issues/2008/April/BisphenolABabyBottleDebate.asp

Grants and Scholarships continued...

Post Graduate Field Research Awards

This award is for a maximum of $5,000 for a Doctoral student and $3,500 for a Masters student to carry out field research in developing countries for at least four weeks.

Closing date for applications is November 2008.

For further details see the website: http://www.nzaid.govt.nz/scholarships/postgraduate-awards.html

Wool Research Organisation of New Zealand Inc and New Zealand Wool Industry Charitable Trust Post Doctorate Fellowships

These fellowships are for holders of PhDs for study and research in topics related to wool including protein chemistry and process chemistry. Successful applicants receive a stipend of between $50,000-$65,000 per year for up to three years.

Applications close 30 November 2008.

For further details and the research topics given priority see the website: http://www.meatandwoolnz.com/main.cfm?id=233

Merck’s High Performance Liquid Chromatography Solvents

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Chemistry Competition a Great Success

Fifteen schools from Christchurch and North Canterbury sent 26 teams of three students to compete in the NZIC/CPIT Chemistry Competition for Year 12 students. The focus was on organic qualitative analysis. Since few schools have covered any organic chemistry at this time of the year, the key skills were problem solving and teamwork, along with basic qualitative analysis skills. The top three teams were particularly close, 1st place going to a team from Rangi Ruru Girls’ School, 2nd to Cashmere High School, and 3rd to Hagley Community College. The competition is one of four organised each year by CPIT, with the next being in September for Year 11 students.

Certainty in Small Molecule Identification by Applying SmartFormula 3D on a UHR-TOF Mass Spectrometer

Break through the limitations of formula elucidation with new dimensions of accurate mass data

Catherine Stacey, Sebastian Goetz, Carsten Baessmann, Clive Seymour
Bruker Daltonics.

Introduction

Characterization of compounds is daily work in all laboratories working with products from synthetic chemistry, combinatorial libraries or targeted structural modifications in medicinal chemistry. Electrospray ionization time-of-flight (ESI-TOF) mass spectrometry has become an integral part of this process to determine accurate masses of the compounds. Finding the correct molecular formula of an unknown compound requires more information than mass accuracy alone. The number of possible molecular formulae increases exponentially with increasing m/z values, even when using small mass error tolerances of <2 ppm, defining the minimum carbon content, and using normal chemical rules for C/H ratios. [1] The presence of additional elements, beyond C,H,N,O, further adds to the formulae list.

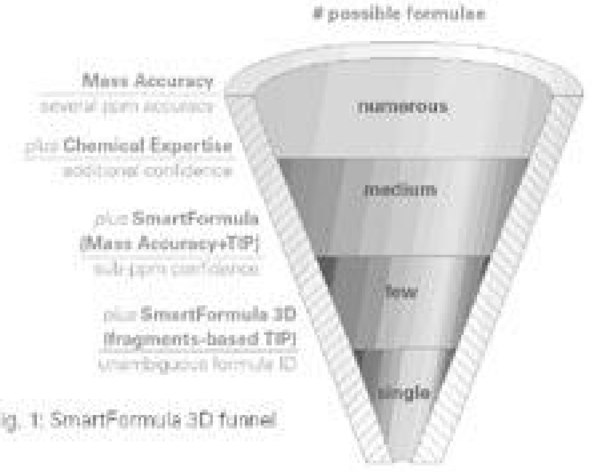

Fig. 1: SmartFormula 3D funnel

How SmartFormula works

The number of candidate formulae is greatly reduced if the isotopic pattern is used as an additional, orthogonal criterion. The theoretical isotopic pattern of each potential accurate mass formula is compared with the experimental determined pattern using the SmartFormula algorithm, which examines the isotopic ratios and spacing of the complete isotopic pattern.

The result is a short list of consistent formulae ranked in order of the fit. True isotopic pattern information over a wide dynamic range with fast spectral acquisition, together with accurate mass, are absolute necessities for this concept to work reliably. Bruker ESI-TOF mass spectrometers are superbly designed to meet these requirements.

Now, an extra dimension of information: SmartFormula 3D

For larger molecules, or those with many elements, a unique formula may not be possible within the mass spectral dimension. Adding MS/MS fragment information brings a whole new dimension of information into play (Fig. 1). Candidate formulae for fragment ions are used as small subunits of the parent ion. SmartFormula 3D iterates through the possible formulae that could be formed from these subunit candidates. As with SmartFormula, user input includes additional elements (or C,H,N,O by default), optional upper and lower limits for elements, number of rings and double bonds, C/H ratios, and whether to allow odd-electron fragment ions. Many potential formulae derived from the parent ion alone are eliminated, to leave only the candidate formulae that fit to the SmartFormula results for both the parent and matched fragment ions. The formulae for these ions, together with neutral losses, are displayed for review. SmartFormula 3D considers either all detected fragment ions, or only user selected ions, and candidates may be filtered to show only those with required neutral losses.

High mass formula determination

For compounds at higher mass, many hundreds of formulae are consistent with a mass accuracy of even 1 ppm or less. Even with prior knowledge of the compound, so that elemental formulae limits and chemistry rules may be applied, there are still many possible candidates. A confident determination of a compound such as erythromycin at m/z 734 (Fig. 2) is not possible. In fact, the SmartFormula pattern fitting gives the correct formula as the second best fit of 4 candidates within 2 ppm, using normal chemical rules (Fig. 3, 4). The fragment ion spectrum of erythromycin (Fig. 5) has 2 prominent fragment ions. The SmartFormula 3D interpretation of the spectrum considers the masses and isotopic patterns for all the fragment ions.

The candidate formula list is reduced to only one possible formula; the correct formula for erythromycin ($C_{37}H_{68}NO_{13}$) (Fig 6). In addition, SmartFormula 3D shows that for the incorrect candidate formulae, prominent fragment ions in the spectrum do not match to that formula.

This unique formula assignment is only possible with accurate mass of < 2 ppm in both MS and MS/MS, True Isotopic Pattern (TIP_{TM}), and a low neutral loss mass tolerance. If the tolerances are broadened, then other candidate formulae are still possible.

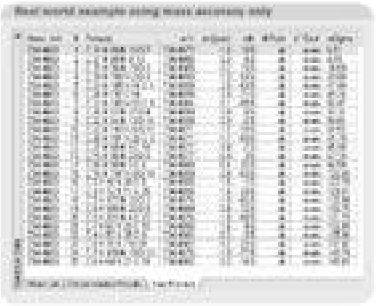
Real world example using mass accuracy only

Fig. 2: 4.2 ppm window without additional filtering gives a list of 29 candidates.


Four candidates left using SmartFormula

Fig. 3: After applying chemical rules 4 hits remain in a 2 ppm tolerance window.

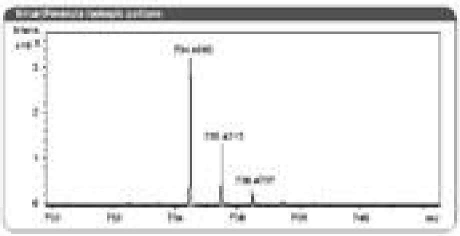
Fig. 4: SmartFormula isotopic pattern of erythromycin.

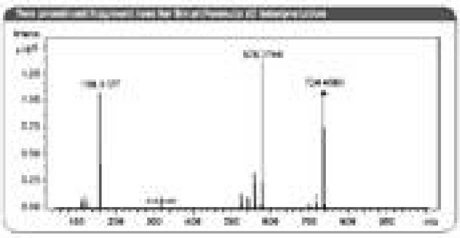
Fig. 5: MS/MS spectrum of erythromycin.

Confirmation of unexpected impurities

In a different experiment, metabolites and impurities of alprenolol ($C_{15}H_{23}NO_2$) were detected in an LC/MS analysis, including an unexpected compound with m/z 188.0930 [2]. Only 1 candidate, $C_9H_{10}N_5$, was possible from SmartFormula, but chemically unlikely. To confirm the formula, MS/MS analysis was used. SmartFormula 3D confirms that the fragment ions at m/z 104.04 and 146.07 fit only to the formulae C_7H_6N and $C_8H_8N_3$, so the parent ion formula is correct (Fig. 7). This unexpected formula was searched against a chemical database; the most probable compound is benzoguanamine, used in thermosetting resins, which is an unexpected contaminant in this sample.


SmartFormula 3D defines the correct formula

Fig. 6: Only the correct sum formula of erythromycin remains after SmartFormula 3D processing.


Detection of impurity after chemical synthesis

Fig. 7: Only the correct sum formula of the impurity in the sample after SmartFormula 3D processing.

Conclusion

SmartFormula and SmartFormula 3D are standard, integral modules of the Bruker Daltonics DataAnalysis data processing software, part of the Compass 1.3 suite. SmartFormula automates formula generation for all the detected peaks in an LC/MS analysis and results are included in reports. SmartFormula 3D is intended for investigation and interpretation of individual MS/MS spectra, ideal for the user who is investigating structural elucidation challenges. With these advanced capabilities, instrument accuracy plays a less dominant role in formula determination than the isotopic pattern. However, for large and complex molecules, a small mass tolerance helps to reduce possibilities. Typical mass errors are < 2 ppm for our **micrOTOF** series products and < 1 ppm for the **maXis**.

Acknowledgement

SmartFormula 3D was developed from an original concept by Don Richards, Pfizer.

References

[1] Kind, Fiehn: Metabolomic database annotations via query of elemental composition: Mass accuracy is insufficient even at less than 1 ppm, BMC Bioinformatics 2006, 7:234.

[2] Personal communication with Don Richards, Pfizer UK

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Professor Chris Hunter
Professor Mårten Wikström
Dr Sami Damak
Professor Max Coleman

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