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Chemistry IN NEW ZEALAND

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Conservation at Te Papa

Marine Biotoxins

2003 Nobel Prizes

Carbohydrate Chemistry at Industrial Research Ltd.

How Plants (and Cyanobacteria) Produce Oxygen

Carbonation of Cements and Mortars

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Chemistry
IN NEW ZEALAND

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On the cover ...

NZ Science Scene

LAKE TAUPO'S WATER QUALITY RESEARCH

The Foundation for Research, Science and Technology has approved $1.8 million over the next five years to address the declining status of New Zealand's lakes.

Scientists from the National Institute of Water & Atmospheric Research (NIWA) and the University of Otago will use the extra funds to focus on the wide range of issues currently affecting New Zealand lakes, including helping to halt the decline in Lake Taupo's water quality. Research on Lake Taupo will dovetail with work on its catchment already announced by the Foundation, and with a recent Cabinet decision to assist in funding the prevention of further deterioration of the lake.

TACKLING AIR POLLUTION FROM VEHICLE EMISSIONS

The Government has announced a range of new initiatives to reduce growing air pollution from motor vehicle emissions in New Zealand. These emissions contribute to serious health problems, including asthma, heart disease and bronchitis. A NIWA report commissioned by the Ministry of Transport and released last year estimates that around 400 people die prematurely each year due to exposure to vehicle emissions. Now the Government has decided to introduce the following initiatives:

- emissions screening of pre-used imported vehicles
- emissions screening of in-service vehicles
- education of vehicle users on the need for, and benefits of, regular vehicle maintenance and repair.

These build on earlier initiatives introduced to tackle vehicle pollution, such as:

- changing fuel standards to reduce the sulfur content of diesel and petrol fuels
- a new Land Transport Rule to ensure vehicles entering New Zealand have been built to a recognised emissions standard
- increasing transport funding to tackle severe traffic congestion in key areas
- undertaking further research on the health impacts of vehicle emissions.

2003 NZIC PRIZES AND FELLOWSHIP

At the NZIC AGM in Nelson the President, **Dr. David Bibby**, announced the 2003 awards and prizes:

Easterfield Award
Dr. Kate McGrath
(University of Otago).

SGS Prize
Professor Geoff Jameson
(Massey University).

Chemical Education Award
For 2003 this is jointly awarded to
Dr. Sheila Woodgate
(Senior Tutor, The University of Auckland).
Mr. Richard Rendle
(Foundation Studies Tutor, University of Canterbury).

FNZIC
Dr. Owen Curnow
(University of Canterbury) has been admittted as a Fellow of the Institute.

2004 TRANSIT OF VENUS EXPEDITION

The Royal Society of New Zealand, with sponsorship from the Freemasons of New Zealand, will send a party of nine students and three teachers to observe the first Transit of Venus for 120 years. This rare astronomical event is historically significant for New Zealand. It was the reason Captain Cook set sail into the southern ocean on his epic voyage. His mission was to observe the 1769 Transit from the newly discovered islands of Tahiti. Astronomer Edmond Halley had realized that observations of the Transit from different places on earth would enable astronomers to work out the distance to the Sun and, in turn, the Stars.

To win places on the 2004 Transit of Venus Expedition to Britain, teams comprising three students and one teacher from each school will be asked to produce a video and supporting material which may be viewed on the web. Entries will explore an aspect of Cook's first voyage, Polynesian or Maori culture at the time, or astronomy, including the Transit of Venus. The competition is open to all Year 9-13 students. Information will be sent to schools.

While in the UK, the students, who will be accompanied by the teacher from their school who led the project, will produce daily video reports for transmission back to New Zealand via a web stream. The website that will host the trip, developed by e-net Ltd of Auckland and funded by the government's Science and Technology Promotion Fund, will be a well-developed and publicised multimedia resource for all New Zealand schools to tune into.

The recent publication of Dame Anne Salmond's book, "The Trial of the Cannibal Dog", is a timely reexamination of Cook's South Pacific voyages and the cross cultural dynamics. These topics will be within the scope of the competition. Dame Anne's work was supported by the Marsden Fund, which is administered by the Royal Society of New Zealand.

Whilst the Tahiti observation of the Transit was not particularly successful because of the limitations of the instruments, Cook's first voyage added greatly to European understanding of the South Pacific, including New Zealand. Joseph Banks collected no less than 30,000 botanical specimens and Cook's circumnavigation of New Zealand

disproved that the land was part of the "Great Unknown Southern Continent" which was commonly believed to exist. His forays far south showed that there was no such continent.

The competition for schools will be one of a series of events the Royal Society intends to initiate and organise next year around the Transit of Venus.

For more information contact Glenda Lewis at (Glenda.lewis@rsnz.org), 04 470 5758 or 025 210 0997.

MATHEMATICS AND INFORMATION SCIENCES CAREERS POSTER

The Royal Society of New Zealand Committee on Mathematics and Information Sciences has produced a coloured A1 poster for secondary school/undergraduate students illustrating how Mathematics and Information Sciences underpin many different careers, and showcasing some young people who are successfully using these subjects in their careers.

The poster was launched at the New Zealand Association of Mathematics Teachers' (one of RSNZ's Constituent Organizations) Conference in Hamilton in mid-July. About 3000 posters have already been distributed from the Royal Society offices.

The posters are available at $10 per tube (holding up to five posters) from the Royal Society. The cost covers GST, postage and packaging.
Email: sales@rsnz.org

2004 ZONTA SCIENCE AWARD AND ZONTA/ BRANZ AWARD

The Zonta International Club of Wellington is inviting applications for two science awards. Applications for both awards close on 6 February 2004. Further information and application forms are available from Mandy Natush.
Email: mandy@businessporirua.co.nz

The biennial Zonta Science Award was first awarded in 1990 and aims to encourage women to pursue a science career, and to acknowledge the valuable contribution of women scientists. The Sponsors are BP Oil New Zealand Ltd and the John Illott Charitable Trust.

Criteria for applicants are an emerging woman scientist with a PhD who has already excelled in pure or applied science (excluding clinical medicine), a New Zealand resident studying for further qualifications or involved in research that benefits New Zealand, and someone who appreciates the role of women in science and is an advocate for these women.

The Award consists of $5,000 in cash and return air travel to Europe or the USA, to be used for further study or to attend a professionally related conference.

The biennial Zonta/BRANZ Award is being offered for the first time in 2004. BRANZ (the Building Research Association of New Zealand) is the principle sponsor, and the Award's aim is to encourage women to pursue a scientific career particularly in an area of science applicable to the building industry.

Criteria for applicants are a woman graduate intending to enroll for a PhD, a New Zealand resident planning to pursue research that benefits New Zealand, and an excellent communicator who appreciates the role of women in science and is an advocate for them. It would be an advantage to aspire to a career in a building related field.

The award consists of $25,000 per annum for a maximum of three years while studying for a PhD.

PLASTICS INDUSTRY WORKS WITH ERMA TO DECLARE POLYMERS NON HAZARDOUS

The Environmental Risk Management Authority has determined that seven commonly used groups of plastics are not hazardous. The seven applications to determine if these groups of plastics were hazardous were submitted by Plastics New Zealand (Inc). These decisions mark the first stage of an initiative by the industry group to formally confirm that the main groups of polymers, commonly used by the plastics industry in New Zealand, are not hazardous and therefore not subject to the Hazardous Substances and New Organisms Act.

The Authority decisions are the result of an initiative by Plastics New Zealand to work with ERMA New Zealand to identify which polymer groups could be determined non-hazardous. Joanna Wojnar, an organic chemist, was contracted by Plastics New Zealand to carry out the research. ERMA New Zealand in turn contributed by waiving the cost of processing the applications.

The polymer groups determined as non-hazardous include certain fluoropolymers, polyethers, polyamides, polyesters, polyolefins, polycarbonates and vinyl polymers, in their pure state without additives.

Plastics New Zealand, an association of plastics manufacturers and plastics raw materials suppliers, has a total of 166 members, representing more than three-quarters of the plastics industry in New Zealand. This technical work has benefited not only the Plastics New Zealand members but the plastics industry nationwide.

Carolyn Cox, Manager for Environmental Affairs with Plastics New Zealand said "The great news is that we have formal confirmation by ERMA New Zealand that the polymers we work with are not hazardous in their pure state. It's a win-win situation. For ERMA New Zealand having these polymers determined non hazardous means they do not need to be transferred as part of Notified Toxic substances. For the Plastics Industry, it demonstrates that we are able to comply with new legislation and we are pleased to be able to confirm to the public that the substances we work with are not hazardous."

GOOD PROGRESS WITH HAZARDOUS SUBSTANCES STRATEGY

Work is on track to implement the Hazardous Substances Strategy. The Strategy is aimed at reducing the cost of complying with hazardous substances legislation without compromising safety and the environment.

One of the early milestones has been the first transfer of a group of hazardous substances from their old controls to the Hazardous Substances and New Organisms (HSNO) regime. "Explosives came under the HSNO Act as of August and that has been a cause for celebration," says Ministry for the Environment Senior Operator Kay Baxter.

Extra funding has been approved for hazardous substances enforcement. Negotiations are underway on allocating it to local bodies to help support their enforcement capacity.

A new Bill amending the HSNO Act in line with the Strategy is due to be tabled in Parliament soon. "Speeding up the transfer process was a high priority in drawing up the Hazardous Substances Strategy so we are looking forward to the introduction of the Bill to do this."

Meanwhile, says Baxter, the next step is a discussion document, due out in December, on changes to the hazardous substances system.

"We're seeking public feedback on a range of issues, including how the compliance and enforcement regime might be improved, as well as improving the approvals process and the way controls are communicated."

If you're interested in receiving a copy of the discussion document, email premar.kumar@mfe.govt.nz and give us your details. The document will also be available on the Ministry's website.

SCHOLARSHIPS GIVE COMPANIES THE FIRST LOOK AT UP AND COMING ENGINEERING TALENT

A set of scholarships at the Department of Civil and Environmental Engineering at The University of Auckland are fostering young engineering talent by developing partnerships with engineering companies across Auckland. The Department's First Look Scholarships were first developed in 2001 to provide students with valuable work experience, as well as some financial assistance during their studies. The scholarships involve students working part-time for sponsoring companies in return for financial support during their studies.

Head of Department Professor Bruce Melville says the scholarships have been extremely beneficial for the students, the Department and members of industry alike. "The scholarships provide students with the opportunity to gain first-hand experience on the job, an important part of their degree, while also providing them the security of financial support and employment when they finish their studies," says Professor Melville.

"The sponsors are able to pick from the best of the applicants and we've had positive feedback from all the companies involved as to the calibre of students. Companies such as Maunsell, previously Meritec, see it not just as gaining the best students, but also supporting the profession in general.

"The scholarships have also proven successful in attracting greater numbers of students into the Civil and Environmental discipline, with enrolment numbers more than doubling in the past two years," says Professor Melville.

Maunsell New Zealand Human Resources Manager Sue Quinnell says the company has been involved with the scholarship since its inception and are pleased with its special nature.

"There are benefits to all involved. We have benefited from hand-picking the best students to work part-time in our company, while the students are able to work on real-life engineering projects and test their theories with practical examples that benefit our local community," says Ms Quinnell.

"We also see the scholarships as an opportunity to contribute to the ongoing development of the profession and society.

"Civil and Environmental Engineers are in demand worldwide, the First Look Scholarship enables us to share our knowledge and experience as well as encourage students to fulfil their potential and aspirations. Ultimately these students will be the ones responsible for driving change, developing and managing our environment and infrastructure in the future."

"We have two outstanding young students whom we are very proud to be supporting through their engineering studies and look forward to our ongoing relationship with them," says Ms Quinnell.

Third year environmental engineering student Fiona Cowan has been working for Maunsell for the past two years and says she has gained a wealth of knowledge and experience from such first-hand experience.

"Maunsell has been extremely supportive and I really feel like I'm part of the community," says Fiona.

"The first look scholarship has not only assisted me financially, but given me the opportunity to train and develop my skills on the job in preparation for the real world."

So far, Maunsell, Tonkin and Taylor, Fulton Hogan, Opus, Works Infrastructure, Vector Energy, Sinclair Knight Merz and Fraser Thomas are involved in the programme, however, the Department hopes to increase the number of partnerships in the future.

Companies interested in becoming a part of the first look scholarships should contact Professor Bruce Melville at the Department of Civil and Environmental Engineering, Phone: (09) 373 7599 xtn 88165

NEW JOURNALISM AWARD FOR AGRICULTURAL SCIENCE

The Foundation for Research, Science and Technology recently announced that it will sponsor an award for the New Zealand Young Agricultural Science Writer of the Year. The prize will consist of a $1,000 air travel grant that the winner can use to attend an agricultural event or conference of their choosing.

For further information contact
Peter Burke
Phone: (04) 917 7809

International News

HEINEKEN PRIZES 2004

Nominations are now being called for the 2004 Heineken Prizes. Candidates are nominated by other scientists or scientific institutions.

Nominations are restricted to individual, active scientists whose contributions to biochemistry and biophysics, medicine, history, environmental, and art research should be outstanding and a source of inspiration to others. Nominations must include a description of the research work and publications on which the nomination is based, a curriculum vitae, bibliography and one or two key publications.

The deadline for nominations is 1 January 2004.
Further information and nomination forms are available from <http://www.knaw.nl/heinekenprizes/>

HONOURARY FELLOW ELECTED TO CHILEAN ACADEMY OF SCIENCES

Professor Mary Therese Kalin Arroyo Hon. FRSNZ, Department of Biology, Faculty of Sciences of the University of Chile and Director of the Millenium Center of Advanced Studies in Ecology and Biodiversity has just been elected a new Corresponding Member of the Chilean Academy of Sciences.

Professor Kalin Arroyo received her primary and secondary education in Okato, New Zealand and gained a first class honours degree in botany from the University of Canterbury. Professor Kalin Arroyo was elected an Honourary Fellow of the Royal Society of New Zealand in 1998. In the late 1980s she participated in a multinational team of scientists that founded the Latin American Network of Botany. She is currently a member of the scientific committee of Diversitas, ICSU of Paris, and for seven years has been participating in the Program of Environmental Biodiversity of the United Nations.

UK R&D SUCCESS

UK companies are maintaining their R&D budgets even in the face of flat sales and falling profit margins. The pharmaceutical and biotechnology sector is the highest spender with a 12% compound growth rate over the past four years.

EU governments spent 0.75% of their GDP on R&D in 2002. Success rates in winning research funds are slightly but consistently higher for men than for women. A public commitment has been made by seven European companies to fund a "major programme" to create a strategic partnership with the education sector to encourage women in science and engineering.

Germany's main scientific organisations, including the Max Planck Society and Germany's main research-funding agency, the Deutsche Forschungsgemeinschaft, issued a joint statement backing initiatives to provide free scientific information over the Internet.

A mechanism for putting business in touch with scientists is being considered by the Confederation of British Industry (CBI). Rather than simply setting up a website with a database of contacts, CBI hopes to set up an intelligent service that can put business in touch with the appropriate research group for the work it wants to do.

STOP PRESS

New Royal Society Fellow

At the Fellows meeting on November 12 **Professor Geoff Jameson** (Massey University), our recent Royal Society of Chemistry Australasian Chemistry Lecturer, was elected to the Fellowship. Geoff is a highly acclaimed X-ray crystallographer, with special expertise in the elucidation of metal-containing proteins. He has also developed important methodology regarding structural elucidation in twinned crystals.

New Zealand Association of Scientists Shorland Medal

The 2003 medal has been awarded to **Ken MacKenzie** (Associate Professor Victoria University and Senior Scientist at Industrial Research Ltd.) in recognition of personal lifetime of research that has resulted in advances in knowledge or significant benefits to society. During his 37-year career in chemistry Ken MacKenzie has published some 240 research papers on the chemistry of ceramics and minerals, the development of new materials, and the application of new analytical techniques.

NZ Science & Technology Medal

Associate Professor John Ayers (Institute of Fundamental Sciences, Massey University has been awarded a Bronze Medal for his significant contribution to the development of novel cellulose-based ion exchangers that have led to the incorporation of new processes in the dairy industry, and innovative quality products being produced for the export market.

NEW DEVELOPMENTS IN THE ANALYSIS OF MARINE BIOTOXINS IN SHELLFISH

Patrick Holland, Paul McNabb, Andy Selwood, Lincoln Mackenzie and Veronica Beuzenberg

Biotoxin Laboratory, Cawthron Institute, Private Bag 2, Nelson
Email: patrick.holland@cawthron.org.nz

Introduction

The New Zealand coastline is a rich resource for shellfish production. Shellfish are an important traditional food source for Maori and many New Zealanders harvest food from natural populations of a variety of shellfish species. A range of shellfish species is also commercially harvested, mainly for export. Over the past 30 years aquaculture industries have been established using cultivation of native Greenshell™ mussel (*Perna canaliculus*), and the introduced Pacific oyster (*Crassostrea gigas*). Enhancement of natural populations of scallop (*Pecten novaezelandiae)* is also carried out in some areas by seeding with reared larvae. The cultivation of Greenshell™ mussel is now a $150 million export industry with the majority of production centred in the sheltered waters of the Marlborough Sounds.

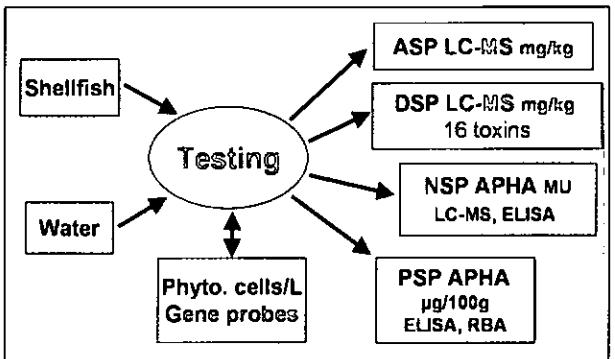

Figure 1. Test regime for marine biotoxin management in New Zealand. APHA refers to the standard mouse bioassay methods, the only authorised regulatory tests for NSP and PSP, published by the American Public Health Association.

Consumption of shellfish carries risks from contamination by microbes and marine biotoxins. The former is a low risk in New Zealand due to clean waters and controls on harvesting at risk periods, *e.g.* after heavy rain. The natural contamination arising from accumulation of toxins produced by phytoplankton is a more insidious and complex risk. Biotoxin risk for a particular area in which shellfish are grown is determined by the occurrence of potentially toxic phytoplankton species, the dynamics of phytoplankton growth and movement with their suite of toxins, and the rates of uptake, metabolism and elimination of toxins by different shellfish species. The New Zealand Food Standards Authority (NZFSA) has the primary responsibility for managing this risk through public health and commercial marine biotoxin programmes. The need to meet stringent export standards has led to devolvement to industry of the funding and routine management of the commercial quality assurance programmes under NZFSA audit. For example, the Marlborough Shellfish Quality Programme (MSQP) is a major cooperative venture that carries out sampling, collation of test data, and coordinating management decisions for shellfish production companies in the upper South Island.

The current management regimes rely on a combination of phytoplankton monitoring and testing of shellfish for toxins. The Cawthron Phytoplankton Laboratory checks water samples taken weekly from about 100 sites around

Table 1. Classes of marine biotoxins that can be significant contaminants in shellfish.

Class	Toxins	Mode of Action	Regulatory Limit	Test Methods
Amnesiac - ASP	Domoic acid and isomers	Brain glutamate receptor agonist	20 mg/kg	HPLC, LC-MS, ELISA
Paralytic - PSP	Saxitoxin and a wide range of analogues	Sodium channel agonist	0.8 mg/kg	Mouse assay, ELISA, HPLC, Receptor binding assay
Neurotoxic - NSP	Brevetoxins	Sodium channel antagonist	20 mouse units (ca 0.8 mg/kg)	Mouse assays, LC-MS, ELISA
Diarrhetic - DSP	Okadaic acid and analogues	Protein phosphatase inhibitor, tumour promotor	0.16 mg/kg	Mouse assays, LC-MS, PP2A
DSP 'other'	Pectenotoxins	?	0.16 mg/kg (with DSP)	LC-MS
DSP 'other'	Yessotoxins	?	0.16 mg/kg (with DSP)	LC-MS
Azaspiracid	Azaspiracids	?	0.16 mg/kg	LC-MS
Spiroimine	Gymnodimine, Spirolides	?	-	LC-MS

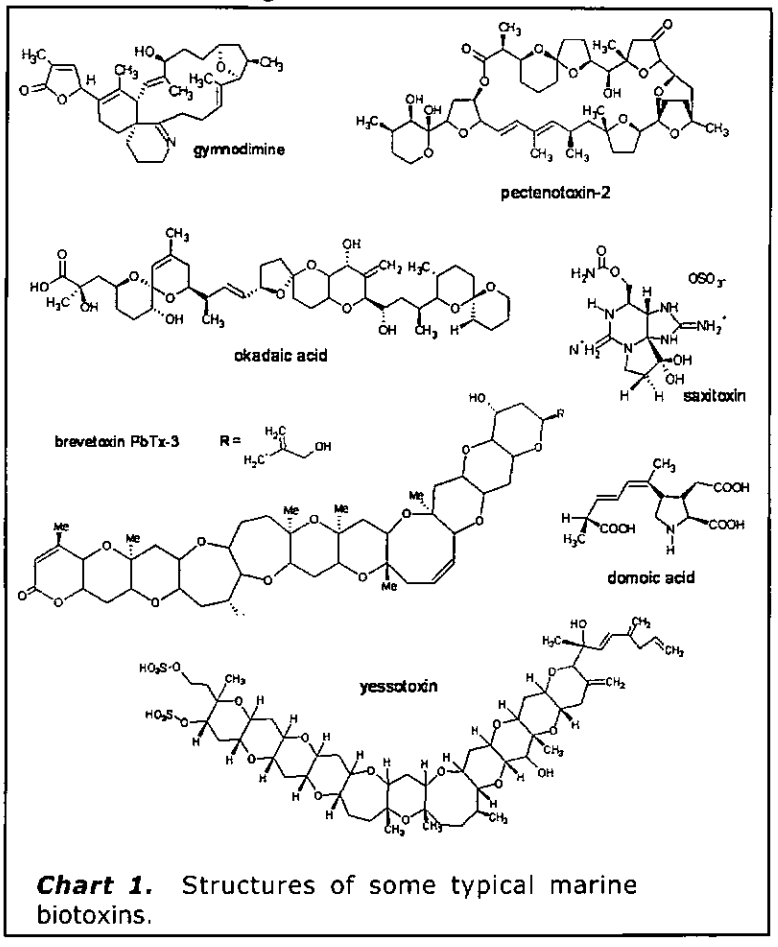

Chart 1. Structures of some typical marine biotoxins.

the New Zealand coastline to provide early warning for phytoplankton that are known toxin producers. Testing of shellfish samples from associated sites is carried out at intervals based on historical data or when triggers for numbers of toxic phytoplankton are exceeded. The Cawthron Biotoxin Laboratory carries out most of the biotoxin testing of shellfish for the New Zealand aquaculture industries and Australian shellfish industries. This regulatory testing is summarised in Figure 1.

Marine biotoxins and test methods

Table 1 lists the major biotoxin classes that can contaminate shellfish and gives their regulatory limits while Chart 1 provides the structures of some typical toxins. The compendium edited by Botana[1] details further information on toxin chemistry and physiological effects. Many marine dinoflagellates have a remarkable ability to synthesise diverse and highly complex polyethers through the polyketide pathway.[2] A range of new pectenotoxin and yessotoxin analogues and metabolites have recently been discovered by New Zealand researchers in collaboration with Canadian, Japanese, and Norwegian colleagues. The metabolites of some toxins in shellfish also have significant toxicity. For example, the toxic dinoflagellate *Karenia brevis* produces mainly brevetoxin PbTx-2 that is taken up by shellfish and transformed partially to PbTx-3 (aldehyde reduction) and other metabolites with sodium channel activity,[3] the type, and proportions depending on shellfish species.[4]

Mouse bioassays are the basis for traditional test methods for three major groups of toxins: diarrhetic shellfish poisons (DSP), neurotoxic shellfish toxins (NSP), and paralytic shellfish poisons (PSP). The mouse assays used for DSP also detect, with varying sensitivities, a range of other lipophylic toxins in addition to the okadaic acid group. The dependence on mouse bioassays for management of marine biotoxin risks has a number of drawbacks and there is currently a strong move in New Zealand to implement improved test methods that can provide the following "*Four-S*" benefits:

- *Speed* - to give higher sample throughput so results are available in hours rather than days.
- *Sensitivity* – to provide information on the build-up towards toxic events and subsequent depuration of toxins. The regulatory limits are at the limits of detection for bioassays, which also gives rise to risks of false negatives.
- *Selectivity* – to eliminate false positives from effects in bioassays of non-biotoxin components in shellfish extracts, and gain information on toxin compositions.
- *Sustainability* – to eliminate the sacrifice of small animals, which is ethically unacceptable for routine quality assurance of food.

Liquid chromatography–mass spectrometry (LC-MS) has become an essential research tool for advancing knowledge on new marine biotoxins.[5,6] LC-MS combines chromatographic separating power for complex mixtures with the sensitivity and high information content of mass spectrometry. Methods have been published for determination for some groups of toxins, for example ASP toxins[7] and DSP toxins.[8] Other approaches to analysis of marine biotoxins such as immunoassays and receptor binding assays also show promise.[9] However, the coherent combination and validation of several practical methods to provide results from comprehensive screening and high-throughput has not been achieved for any marine biotoxin monitoring programme. Recently, Cawthron has achieved some world-leading developments in application of LC-MS to marine biotoxin testing which have made significant progress toward the "*Four-S*" goal.

The LC-MS/MS method for ASP and DSP toxins in shellfish

The testing for DSP toxins by mouse bioassay is particularly unsatisfactory because of the range of lipophilic toxins and non-toxins that give responses via the intra-peritoneal injection route, and the lack of standardisation

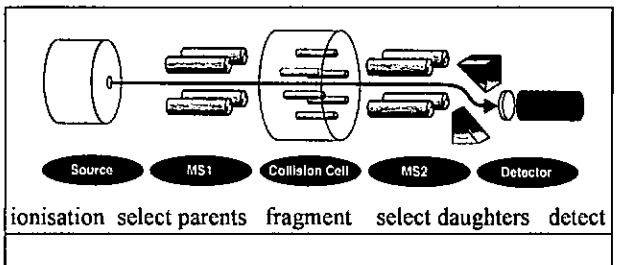

Figure 2. MS-MS in a triple quadrupole mass spectrometer (reproduced by courtesy of Waters-Micromass).

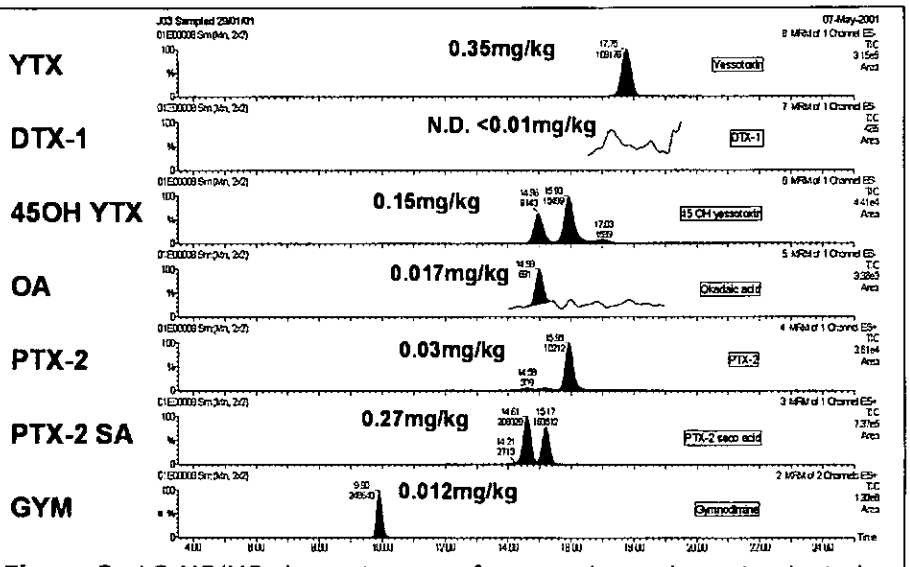

Figure 3. LC-MS/MS chromatogram of a mussel sample contaminated by DSP toxins.

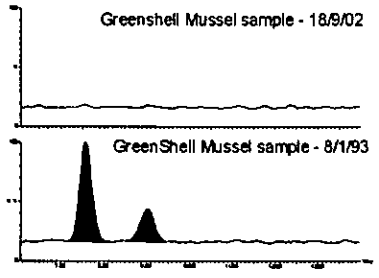

Figure 4. LC-MS/MS of shellfish extracts illustrating the presence of brevetoxins in a sample taken from the Hauraki Gulf following a *Karenia* bloom in 1993, and their absence in a sample taken following a similar bloom in 2002.

Table 2. Toxins determined by Cawthron LC-MS/MS method 40.105.

Toxin	Symbol	Quantitative?
Domoic acid	DA	Y
Okadiac acid	OA	Y
Dinophysis toxins (OA analogues)	DTX1, DTX2	N
OA esters (by hydrolysis)	DTX3	Y
Pectenotoxin-2	PTX2	Y
Pectenotoxin metabolites	PTX1, PTX6, PTX-seco acids	N
Yessotoxin	YTX	Y
Yessotoxin analogues and metabolites	Homo-YTX, 45OH-YTX, carboxy-YTX	N
Gymnodimine	GYM	Y
Azaspiracids	AZA-1 AZA-2, -3	Y N
Spirolides	SPX-A SPX-D, -desmethyl-C	Y N

of the assay protocols used in various countries. Cawthron has developed and fully validated a multi-toxin LC-MS test that can determine a very wide range of toxins in a single run (Table 2), including the ASP toxin domoic acid (for structure see Chart 1). Sample preparation is very simple with blending of a subsample of homogenate and 90% methanol followed by a hexane wash to remove non-polar lipids. An aliquot of the centrifuged extract is injected into the LC-MS. The use of a triple quadrupole instrument enables the multiple reaction-monitoring (MS-MS) mode of operation (Figure 2). LC separation (2 mm i.d. C18 column with acidic ammonium formate/acetonitrile gradient) is followed by electrospray ionisation (positive or negative ion mode depending upon the toxin). Within retention time windows, the mass for each toxin's predominant quasi-molecular ion, $[M-H]^-$, $[M+H]^+$ or $[M+NH_4]^+$, is selected in quadrupole-1, collisionally activated in quadrupole-2, and the masses of suitable daughter ions selected for detection in quadrupole-3. This multi-stage time/mass separation process of LC-MS/MS greatly enhances the selectivity of the method to give low detection limits with high confirmatory power. Figure 3 illustrates the typical pattern of peaks observed from LC-MS/MS analysis of shellfish contaminated by DSPs.

Linear calibration of the LC-MS responses to the toxins is based upon injection of mixtures of the toxins at five concentration levels (5-200 ng/mL). Certified reference standards produced by the NRC Institute of Marine Biosciences (Halifax, Novo Scotia) are now available for the toxins determined quantitatively by the method (Table 2). For the other toxins and metabolites only crude standards are available and semi-quantitative data are obtained using relative response factors to related quantitative standards, *e.g.* for YTX metabolites a RRF of 1.0 to YTX is taken. Collaboration between NRC-IMB, Cawthron Institute, and the Toxinology Group of, AgResearch has been important in improving the supply of reference materials for several key toxins.

The ASP/DSP method has been accepted by NZFSA for regulatory testing after an exhaustive validation process (see below) and has now been in routine use for two years with consequent "*Four-S*" benefits. Its value in managing shellfish for the benefit of public health and industry has been demonstrated during hazardous algal blooms, and the relationship has been clarified between toxic algae and contamination of shellfish with several new toxins having been identified.[10]

The LC-MS/MS method for brevetoxins in shellfish

The standard mouse tests used to regulate NSP toxins in shellfish have never been properly validated on New Zealand shellfish and there are doubts as to whether they

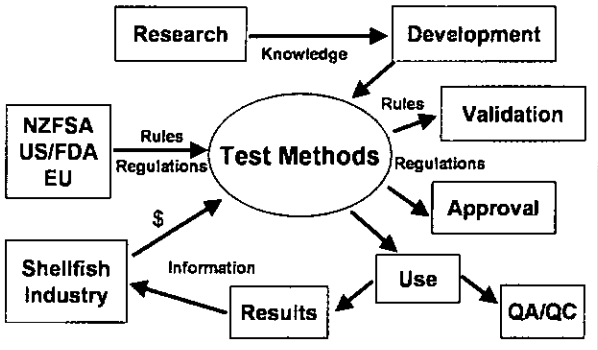

Figure 5. Processes for introduction of new methods to regulatory testing of shellfish.

are actually suitable for this purpose.[4] Fortunately, NSP appears to be rare in New Zealand with the last confirmed event in 1992. Thus, an effective screening assay that can prove shellfish are free of detectable brevetoxins would be suitable for most routine testing. Cawthron has developed such a method based on LC-MS/MS, which can provide very important "*Four-S*" benefits to biotoxin management. The NZ Food Standards Authority (NZFSA) is currently evaluating the Cawthron data in support of regulatory use of this method. Its utility was demonstrated during a bloom of a potential NSP producer *Karenia mikimotoi* in the Hauraki Gulf in 2002. Although there were some fish kills, these were shown as probably not to be due to NSP from testing of water and shellfish samples that were free of brevetoxins by LC-MS/MS to very low detection limits (Figure 4).

Introduction of new methods to regulatory testing

The process of introducing new methods to regulatory testing is a very lengthy one, from the development and validation of a new test to obtaining NZFSA authorisation for its use in the regulatory testing of shellfish (Figure 5). Because of the paramount needs for public safety and the acceptance of test data by regulators in countries to which shellfish are exported, NZFSA demands a very high standard of validation along with other supporting data before it will approve new methods. It has published guidelines for method validation covering areas such as precision, accuracy, limits of detection, comparability of results, and robustness.[11] Cawthron has conducted a complex series of within-lab validation experiments to establish the performance characteristics of its new LC-MS/MS methods. An inter-laboratory study of the ASP/DSP method was coordinated by Cawthron and involved 8 laboratories in 7 countries. Further QA/QC data have been generated during the use of approved methods, *e.g.* recovery data for the spiked control sample run with each batch. These exercises have provided many interesting insights into the routine operation of LC-MS/MS methods:

- The repeatability component has a large effect on overall precision of LC-MS methods probably due to the co-elution of shellfish extractives that do not generate interfering peaks but have subtle effects on electrospray ionisation of toxins.
- Precision for the majority of toxins falls within the bands expected from the AOAC Horwitz criteria for good to excellent methods.
- The precision data forms a good basis for estimation of the uncertainty of measurement for the methods,[7] an important parameter in regulatory testing.
- QA/QC data has proven the methods yield reliable data over long periods.
- The methods are straightforward to operate routinely, despite the complexity of the technology, due to the very simple procedures for sample extraction and cleanup, and the high degree of automation of the LC-MS equipment.

Conclusions

LC-MS methods have been developed, validated, and implemented showing that this powerful analytical tool is suitable for routine use in a marine biotoxin monitoring programme. High sample throughputs have been achieved for the primary analysis of a wide range of toxins in shellfish. These methods form the core for a new programme in New Zealand, centred on the laboratories of the Cawthron Institute, which has faster sample turn-around times and greatly reduced requirements for mouse bioassays. The greater information content and higher reliability of LC-MS results is leading to improved management of marine biotoxins in shellfish.

Acknowledgements

Dr. Chris Miles and colleagues of the Toxinology Group of AgResearch have supplied a range of reference materials containing pure or partially purified toxins. APEC made financial contributions to the production of crude toxin materials by Cawthron for use in preparation of standard materials by AgResearch and NRC-IMB, Halifax. The New Zealand shellfish industry, in particular MSQP, have given strong support to efforts by Cawthron to develop improved test methods.

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SCOPE/IUPAC REPORT ON ENDOCRINE ACTIVE SUBSTANCES

A report from the Scientific Committee on Problems of the Environment (SCOPE) and International Union of Pure and Applied Chemistry (IUPAC) project on Endocrine Active Substances, a major project looking at these potentially harmful substances from a world-wide perspective, will be published in a double issue of the IUPAC Journal, *Pure and Applied Chemistry*, **75** (11/12), 2003, edited by J. Miyamoto and J. Burger. An *Executive Summary* is available on the IUPAC website at http://www.iupac.org/publications/pac/2003/7511/. The *Executive Summary* will be sent to the IUPAC National Adhering Organizations, Associate National Adhering Organizations, and Company Associates, as well as major chemical societies and other interested organizations throughout the world.

The SCOPE/IUPAC project *Environmental implications of endocrine active substances: Present state-of-the-art and future research needs* was initiated during 2000 and culminated at a Symposium held 17–21 November 2002 in Yokohama, Japan, where 408 individuals from 31 countries gathered. Scientists, managers, and public policy-makers presented papers on human effects, wildlife effects, exposure assessment, and testing for Endocrine Active Substances and Endocrine Disruption effects. At the meeting, a range of needs was identified that applies to all aspects of the study of Endocrine Disruption and Endocrine Active Substances. The in-depth, comprehensive, authoritative review of Endocrine Active Substances and their environmental and health effects by this project will facilitate risk assessment and assist governmental and intergovernmental authorities, industry, and the wider public in framing policies and establishing research directions to address these issues.

We have learned during the past decade that the global effects attributed to Endocrine Active Substances are not as all pervading or fearsome as some have asserted. There are, however, sufficient examples and biological plausibility to leave little basis for complacency in the research community. Future well-designed research will elucidate the magnitude of the problem, identify target substances of concern, and advance our knowledge of human and wildlife health. In addition to overall conclusions regarding the present state of knowledge, a series of more than 40 specific research recommendations was developed to assist future efforts.

This is a SCOPE/IUPAC project. IUPAC was formed in 1919 by chemists from industry and academia. For over eight decades, the Union has succeeded in fostering worldwide communications in the chemical sciences and in uniting academic, industrial and public sector chemistry in a common language. IUPAC is recognized as the world authority on chemical nomenclature, terminology, standardized methods for measurement, atomic weights and many other critically evaluated data. More information about IUPAC and its activities is available at <http://www.iupac.org>. More information about SCOPE is available at <http://www.icsu-scope.org/>.

IUPAC IMPROVES LINKS WITH MEMBER COUNTRIES

A decision at the recent International Union for Pure and Applied Chemistry (IUPAC) Council meeting in Ottawa should significantly improve lines of communication between IUPAC and its member countries (National Adhering Organisations (NAO)). IUPAC will establish a Union Advisory Committee (UAC) that will have one member from each NAO. This Committee will advise the Executive Committee, and thus the Bureau, on matters of policy and will comment on future directions and initiatives. It is an expectation that the NAO representative on the UAC, being informed on IUPAC matters, will be one member of the country's delegation to the biennial Council meeting.

CHEMISTRY ENROLMENTS DOWN

Many countries are observing a decline in the number of students who choose chemistry as a major for tertiary education. This was discussed in depth at the World Chemistry Leadership meeting held in conjunction with the IUPAC General Assembly in Ottawa in August.

In response IUPAC has set up a Task Group that will 'embark on a global initiative to seek ways to reverse the decline in students studying chemistry and chemical technology'. The Task Group consists of the Chairs of IUPAC's Committee for Chemistry Education (CCE), Committee On Chemistry and Industry(COCI) and CHEMRAWN and representatives of chemical industry. It will consult with industrial stakeholders and try to identify common (worldwide) problems and regional variations. It will then prepare a strategy for IUPAC response and project funding. For the German response, see <http://www.year-of-chemistry.de>.

The Council meeting also set up a Task Group to evaluate the feasibility of establishing a website that chronicles innovations in chemistry that contribute to the quality of human life.

The objective is to educate the public about chemistry and its value to society and to bring balanced understanding about the benefits and risks of chemicals. Consistent with its goals, IUPAC will collate and integrate this array of information so that it is a more valuable resource for students, teachers, policy-makers, members of the chemical enterprise, columnists and the general public. If you have any views on this enterprise contact Professor Kip Powell who is a member of the Task Group at <k.powell@chem.canterbury.ac.nz>.

CONSERVATION AT TE PAPA

Gillian Andreae, Lesley Cobb, Joanna Morton and Phillipa Durkin
Te Papa Conservation Team
Te Papa Conservation Unit, 169, Tory Street, Wellington

As New Zealand's national museum, Te Papa cares for many thousands of collections and taonga that tell the stories of New Zealand's cultural and natural heritage. Te Papa looks after these treasures for all New Zealanders, including future generations. They are shown in Te Papa exhibitions, lent to others in New Zealand and around the world for exhibition and research, studied, and written about. Te Papa has a team of conservators with specialist knowledge on how best to care for these collections so they can be appreciated fully, and for as long as possible.

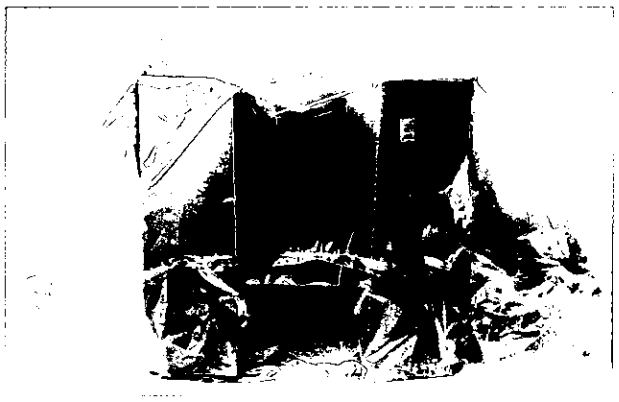
Conservators' expertise is based on the knowledge and understanding of the materials and composition of collection items. Te Papa's art, history, Maori, Pacific and natural history collections include a huge variety of materials so the conservation team covers a wide range, with each conservator specialising in particular areas. These different collections and materials all bring various challenges to the conservators' work.

Often the most effective and economical approach is preventive conservation. Te Papa exhibition spaces and collection stores are climate controlled to reduce the damage caused by physical expansion and contraction from changes in relative humidity, and to prevent mould growth. Storage systems are designed to physically protect collection items, but also allow them to be accessed safely with minimal handling risk. Storage materials are chosen for their long-term chemical stability. Insect and pest management programmes are operating and our quarantine facilities provide a range of ways to keep collections bug free. Conservators provide expert advice in developing exhibitions, assessing potential acquisitions and the care of collections in transit.

In other cases we need to intervene with the item itself. Conservators are skilled in the treatment of collection items to stabilise deterioration and repair damage. They are guided in this by ethical principles and an understanding of the cultural values, social history and aesthetics associated with the items. If we are to fully appreciate our cultural treasures, conservation treatment must respect their lives, history and culture, and not obscure or remove anything that can tell us more about a collection item's significance.

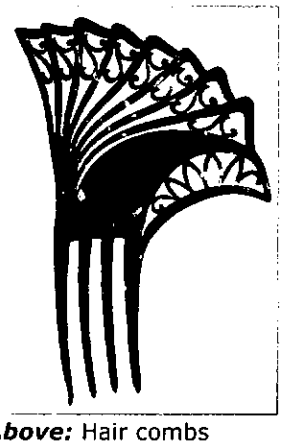
The Objects Laboratory works with both organic (wood, plant materials, bone, shell, horn, tortoiseshell, leather and skin) and inorganic materials (metals, ceramics, glass, stone). Frequently items consist of a number of different materials.

One of our current issues is the care and conservation of modern materials – plastics and rubbers. The amount of such material in the collections is steadily increasing. Recordings made from PVC, Rob Waddell's rowing skiff of epoxy laminate carbon fibre construction, a Xena: Warrior Princess action figure made from an unidentified plastic, and Fred Dagg's rubber gumboots are a few of our challenges. It is a particular problem because of the very varied composition and the rapid deterioration of many types of plastics and rubbers.



Above: Fred Daggs Gumboots.

Plastics are difficult to clearly identify without taking a sample from the object. Since this causes damage to the item, it is not something we can generally do. But identification is important: different materials can have widely differing requirements in terms of storage and care. The hair combs exhibited in Te Papa's *Masquèrade* exhibition were thought to be tortoiseshell, but have now been identified as cellulose nitrate. These were identified using binocular microscopy and ultraviolet light examination, together with research on the historic uses of cellulose nitrate.



Above: Hair combs exhibited in Te Papa's Masquerade exhibition.

Preventive conservation to slow deterioration is critical for these collections. For example, rubber deteriorates rapidly from oxidation. Industrial techniques for preserving rubber include applying antioxidants or impermeable coatings, but this approach alters the object. The approach chosen by Te Papa conservators is to control the environment, reducing light and reducing oxygen to very low levels so as to prevent rapid oxidation. Many rubber items in Te Papa's history collection are now being stored in low oxygen conditions. A microclimate with very low oxygen levels can be created for the collection item using heat-sealed oxygen barrier film bags and oxygen scavenger sachets, which contain finely divided iron that absorbs oxygen as

it oxidises. Light is a major initiator of oxidation so these collections are stored in the dark and exhibited only for limited periods of time under low light levels. Rubber can also cross-link and stiffen as it ages, or can become sticky as it deteriorates. Rubber items are given supports to hold their shape, with silicone-release Mylar film to prevent sticking.

Te Papa's collections continue to grow each year as items are acquired, and as they are acquired their condition and needs for treatment and care are assessed. Existing collections are gradually being surveyed so conservation and preservation needs are known and prioritised programmes can be developed.

Te Papa's paintings have all been surveyed. There are about 1700 works in this collection. The earliest is a 17th century Russian icon; the most recent are contemporary paintings purchased soon after completion by the artists. Paintings are complex structures. Ultraviolet light examination, microscopy, X-ray and analysis to identify pigments or binders are all important tools for the painting conservator in deciding on how best to ensure the ongoing wellbeing of a work.

One of the more frequent treatments considered for oil paintings is removal of varnish. Traditional varnishes for oil paintings are commonly spirit varnishes, usually triterpenoids such as dammar or mastic, dissolved in turpentine. Although these have good optical and handling properties when first applied, they do not fare so well on ageing and are prone to photo-oxidative breakdown causing yellowing, darkening and cracking. For this reason varnishes are removed and reapplied in a process that has become so common it is known as *the cleaning cycle*.

Extensive testing is carried out before varnish removal, to establish the range of solubility of the varnish and to establish the safety of the underlying paint layer during the treatment. On the face of it, varnish removal from an oil painting should be relatively straightforward because the varnish is composed of a soft resin with fairly high solubility whereas the paint layer consists of insoluble pigments in a hard dried oil film. Yet many paintings are not simple systems with such clear-cut, disparate layers, and at the paint-varnish interface the solubilities can be alarmingly similar.

If technical examination and other investigations, *e.g.* the painters technique or previous restorations, indicate varnish removal, preliminary surface cleaning will be carried out and then varnish removal tests performed. Testing is done cautiously and in areas such as around the edges that will later be covered by the frame. Tiny squares are swabbed over with the solvent or mixture to be tested. The swab is inspected for any signs of varnish pickup plus any colour coming off the paint layer, and the test area is constantly monitored for any visual changes that would indicate solubility other than in the varnish layer. The *feel* of the swab and the gelling varnish also provide useful information. Every single colour must be tested since some areas may have higher solubility than others. Use of glazes, additives, or adulteration of the paint, can all lower the paint solubility, and leave it vulnerable to damage by solvent action.

Once the test areas around the edges have established a certain safety to proceed, further tests can be carried out in the body of the picture. Through this testing the paintings conservator can establish the range of solubility of the varnish in relation to any vulnerability of the paint layer, and arrive at a solvent or solvent mixture that will remove the varnish with the least possible swelling action on the paint layer. As with any solvent/solute system, the general principle at work is *like dissolves like*. However, although the varnish was originally soluble in a mild non-polar solvent such as turpentine, after ageing it becomes less soluble and requires increasingly polar solvents to remove it. Because low volumes of solvent are used, rather than forming a true varnish/solvent solution the solvent is absorbed into the varnish layer enough to swell and soften it, allowing it to be picked up on the same swab that has delivered the solvent.

Only after all the testing has been done and the safety of the operation been assured will the conservator begin the varnish removal. Sometimes partial cleaning – varnish removal from selected areas, or thinning the varnish without total removal – is a safer option. Occasionally a picture will have to be put aside as being unsafe to clean. Although varnish removal is a common procedure for paintings conservators, it still carries a risk and can never be done as a matter of routine but rather as a carefully considered decision to recover, as far as is possible, the appearance intended by the artist.

Artworks on paper face very different challenges. A major cause of deterioration is acidity, producing overall darkening of the paper, brittleness and foxing (small brown stains) which can be seriously disfiguring to the artwork. A number of contributors can cause the cellulose molecule in paper to break down, releasing hydrogen ions and catalysing an ongoing reaction. In many cases this deterioration is caused by the artwork being in contact with acidic backing materials but the process is also exacerbated by light.

Preventing acidic deterioration is of course the ideal. Artworks are supported by acid-free folders and mats, and protected within acid-free storage boxes or permanent frames. Light exposure is monitored and in most Te Papa exhibitions the artworks on paper are changed regularly to limit cumulative light damage and ensure future generations also have a chance to appreciate these artworks.

Prevention is not an option for many artworks already affected by poor matting and framing or display conditions, so stabilisation is one of a paper conservator's key challenges. Von Tempsky's *Return of the War Party* was recently treated to stabilise its condition and make it ready for exhibition.

This watercolour was painted in the 1860s and was in relatively good condition for its age, but display and several re-framings had taken their toll, and a corner was missing. Acidic vapour from the window matt had flowed from the

cut edge to contaminate the artwork, causing staining around the edge. Poor quality backings glued on with animal glue had created overall discoloration.

Above: Removal of varnish in process on painting.

Removing the backing revealed two previous backings in varying stages of removal. The animal glue used to adhere many older works on paper to their backings can stain, but has the advantage of being readily soluble. With the backings removed the artwork could be placed over water and soluble acidity flushed from the paper by osmosis. This can be a lengthy process, but it is safer than more extreme aqueous treatments such as full immersion. The movement of discoloration was monitored and the process continued until no more came from the paper. Aqueous treatment also rehydrates the cellulose, strengthening the paper.

In this case the loss of a corner was visually distracting, so this was in-filled with a sympathetic paper, and the fill toned with watercolour to minimise drawing the viewer's attention to it. The work has now been matted and framed using archival materials. It will be stored and exhibited in environmentally controlled conditions and its display times negotiated to ensure it can be appreciated for many years to come.

This article provides a snapshot of just some aspects of the work done by Te Papa's conservation team and a few of the issues they face in helping our heritage treasures to last. Conservation is a dynamic area, drawing on current research from around the world and constantly developing new approaches and safer techniques. Good scientific research and analytical capability is essential in developing knowledge and understanding, and enabling conservators to make safe and effective decisions.

Above: Missing corner on Von Tempsky's *Return of the War Party.*

Update

HOW PLANTS (AND CYANOBACTERIA) PRODUCE OXYGEN

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Introduction

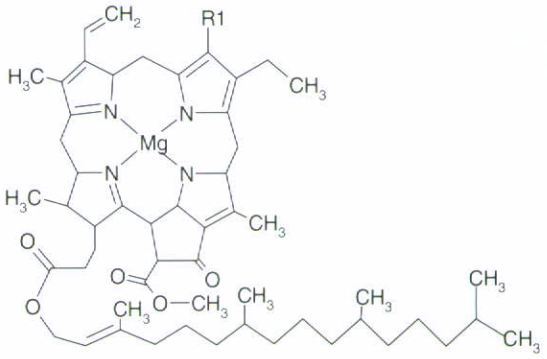
All of the oxygen in the earth's atmosphere is a result of chemical reactions occurring in plants and cyanobacteria (also known as blue-green algae). These organisms use the energy in sunlight to convert water into oxygen. This article describes the current state of our knowledge of the structure of the apparatus used to carry out this process. Our understanding is still incomplete but there have been very significant advances in our knowledge of this structure in the last five years including two crystal structure determinations. This is a very active area of research and this article will certainly be out of date by the end of next year.

Photosynthetic organisms (plants and cyanobacteria) contain *antennae* that collect solar energy and convert it into chemical energy. The photosynthetic apparatus and these antennae are located in the thylakoid membrane, an internal membrane in the chloroplast of the cell. The chemical energy is used to reduce CO_2 and form organic compounds. The overall photosynthetic reaction involves the oxidation of water and the reduction of nicotinamide adenine dinucleotide phosphate, NADP (Eq. 1):

$$2NADP^+ + 2H_2O \rightarrow 2NADPH + O_2 + 2H^+ \qquad (1)$$

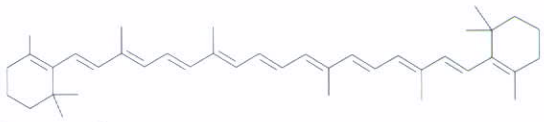
The net energy change for this reaction is 438 kJ mol^{-1}. This corresponds to the energy of a photon with a wavelength of 223 nm, *i.e.* light in the far ultraviolet. Even

Chart 1. Structures of some of the cofactors present in PSII.

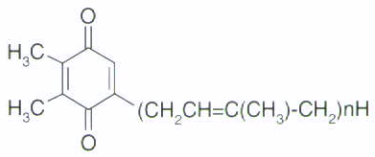


1 Chlorophyll a R1 = CH_3

2 Chlorophyll b R1 = -HC=O



3 ß-carotene



4 Plastoquinone

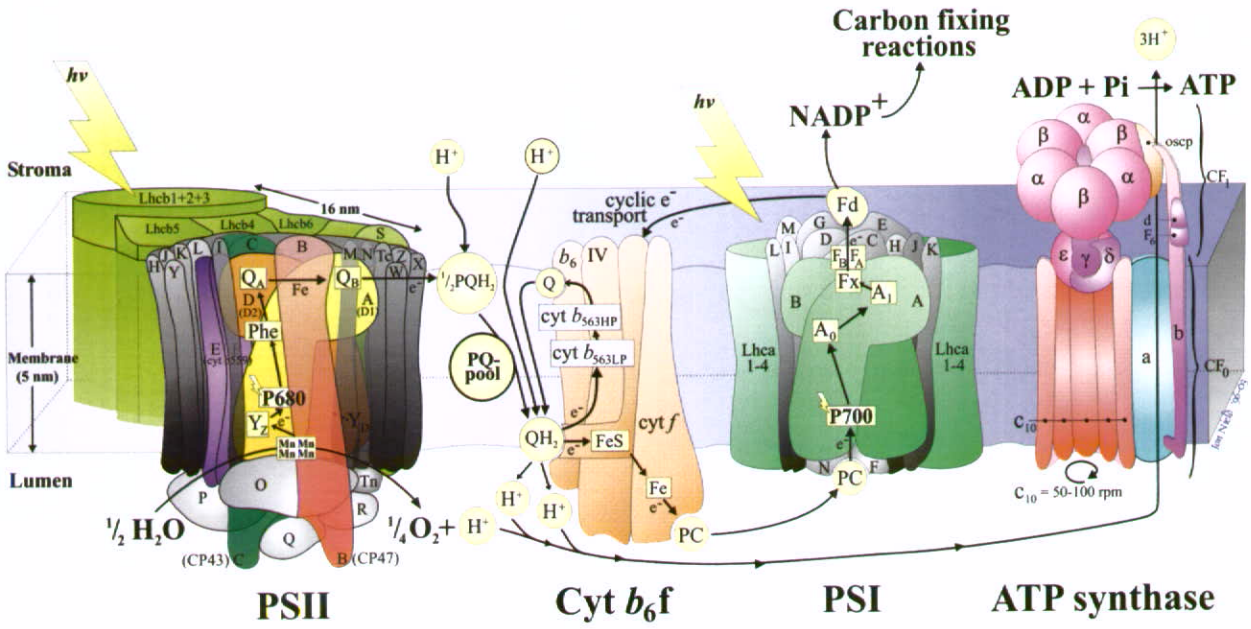


Figure 1. A possible arrangement of some of the proteins of the thylakoid membrane taken with permission from <http://www.bio.ic.ac.uk/research/nield>. For abbreviations see text. The arrows indicate the direction of electron flow.

if photosynthesis were 100% efficient (which it is not), more than one photon of lower-energy visible light would be necessary to generate one molecule of O_2. Experimentally it is known that about ten photons are required.

The photosynthetic apparatus has three components, photosystem I (PSI), photosystem II (PSII) and the cytochrome b_6f complex. PSI is separated from PSII by at least 100 Å, and the cytochrome b_6f complex is apparently located between the two photosystems. Also present in the membrane is a very important enzyme, ATP synthase, which synthesizes ATP from ADP. A diagrammatic representation of the membrane and the photosynthetic apparatus is shown in Figure 1. The two photosystems function in series and are coupled by a pool of plastoquinone molecules, the cytochrome b_6f complex and the soluble electron carrier protein, plastocyanin. The reaction in which water is oxidized (Eq. 2) releases protons on the inside (lumenal side) of the thylakoid membrane:

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \quad (2)$$

Protons are also pumped across the membrane from the outside to the inside by the cytochrome b_6f complex. Protons are consumed on the outside (stromal side) of the membrane by the enzyme ferrodoxin-NADP$^+$-oxidoreductase. The proton gradient across the membrane is used to drive ATP synthesis.

The focus of this article is PSII as this is where oxygen evolution occurs. Twenty-five genes have been identified as encoding proteins for the PSII photosystem; these genes are referred to as *psb* (photosystem b) genes. Most of these genes are located in the chloroplast genome, but some are encoded on nuclear DNA. Most of the proteins are embedded in (intrinsic to) the thylakoid membrane but there are extrinsic proteins located on the lumenal side of the core complex. A summary of the proteins is included as Table 1. The intrinsic proteins have at least one, and up to six α helices spanning the membrane. The membrane is some 60-70 Å thick. Some of the intrinsic proteins have ends and loops that extend some 30 Å on both sides of the membrane. Also associated with PSII are light harvesting proteins with at least 250 chlorophyll molecules [both chlorophyll a (**1**) and chlorophyll b (**2**)-Chart 1], which collect the light. PSII has a number of other components or cofactors, a *special pair* of chlorophyll molecules called P_{680}, additional chlorophylls, carotenoids (**3**) and other light absorbing molecules, plastoquinones Q_A and Q_B (**4**), a cluster of four Mn^{n+} ions, Fe^{2+}, Cl^-, HCO_3^- and Ca^{2+} ions. Not all the proteins are necessary for O_2 evolution. Experiments in which some of the proteins are removed suggest that the CP47, CP43, D1, D2, cyt b559 and the extrinsic proteins PsbO, PsbP and PsbQ are necessary for O_2 evolution. The known functions of these proteins are given in Table 1.

The first step in the photochemistry of the photosynthetic reactions involves absorption of a photon by a chlorophyll molecule bound to a light-harvesting protein. The energy of this photon is then transferred via a linked network of chlorophyll molecules associated with CP47 and CP43 to

Table 1. Proteins of the PSII Apparatus.

Protein Name	Gene Name	Molecular Mass	Trans-Membrane Helices	Function
Membrane Bound Proteins				
D1	(PsbA)	38021	5	Y_Z, Q_B P_{680} pheo & Mn binding
D2	(PsbD)	39418	5	Y_D Q_A P_{680} & Fe^{2+} binding
CP47	(PsbB)	56278	6	Light harvesting, P_{680} binding
CP43	(PsbC)	50066	6	Light harvesting
cytochrome b_{559}				
α subunit	(PsbE)	9255	1	photoprotection
ß subunit	(PsbF)	4409	1	photoprotection.
H protein	(PsbH)	7697	1	Regulates Q_A & Q_B e^- transfer
I protein	(PsbI)	4195	1	Unknown
J protein	(PsbJ)	4116(P)	1	PSII assembly
K protein	(PsbK)	4283	1	PSII assembly & stability
L protein	(PsbL)	3755(P)	1	Normal functioning of Q_A site
M protein	(PsbM)	3700(T)	1	Unknown
N protein	(PsbN)	4722	1	Unknown
S protein	(PsbS)	21705	4	chl chaperonin
W protein	(PsbW)	5928	1	Plants only, Unknown function
X protein	(PsbX)	4225	1	Q_A functioning
Extrinsic membrane proteins				
33 kDa protein	(PsbO)	26539	0	Mn stabilising protein
23 kDa protein	(PsbP)	16523	0	Optimise Ca^{2+}, Cl^- levels Not present in cyanobacteria
16 kDa protein	(PsbQ)	10236	0	Optimise Ca^{2+}, Cl^- levels
R protein	(PsbR)	10236	0	Donor & acceptor side functions
T protein	(PbsT)	3283	0	Unknown
U protein	(PsbU)	15123(Sy)	0	Unknown; cyanobacteria only
Cyt c_{550}	(PsbV)	5928	0	H_2O oxid.; cyanobacteria only
ycf8 protein		3283	0	
5 kDa protein		~10000(Sy)	0	

the *special pair* of chlorophylls, P_{680}, bound to the D1 and D2 proteins of the PSII reaction centre. This excited form of P_{680} is a strong reducing agent; it transfers an electron to pheophytin, *viz.* a chlorophyll molecule that does not have a bound Mg^{2+}, producing the cation P_{680}^{+}. The electron is then transferred from pheophytin to plastoquinone Q_A (tightly bound to D2) and then to Q_B. Each plastoquinone associated with the Q_B site accepts two electrons from Q_A and two protons from the stroma. Q_B is then released into the lipid matrix of the membrane and diffuses to the cytochrome b_6f complex where it is oxidised. This complex then reduces plastocyanin (by one electron) and the electron is then transferred to the reaction centre P_{700} of PSI. In PSI, another photon is used to excite an electron from P_{700} to an acceptor A_0 (a 'chlorophyll a' monomer). The electron then transfers to a secondary acceptor A_1 (vitamin K_1) then to the terminal electron acceptors FX, FA and FB (three proteins containing clusters of four iron atoms and four sulfur atoms), and finally to NADP. Meanwhile, back in the PSII complex, the strongly oxidising P_{680}^{+} cation is reduced by the tyrosine-161 (Y_Z) residue on the D1 protein. The neutral tyrosine radical ($Y_Z^{\cdot}$) formed in this reaction (the OH proton is also lost), is in turn reduced by an electron from the cluster of manganese atoms located close to the lumenal surface of the membrane. This manganese cluster is believed to be the site of the water oxidation reaction. The electron flow is thus from water, to manganese, to $Y_Z^{\cdot}$, to P_{680}^{+}, to pheophytin, to Q_A, to Q_B, to the cytochrome b_6f complex, to plastocyanin, to P_{700}, A_0, A_1, FX, FA and FB, and then finally to NADP. The D2 protein in the PSII complex also contains a redox active tyrosine (Y_D) that is certainly not part of this electron chain and its function is obscure.

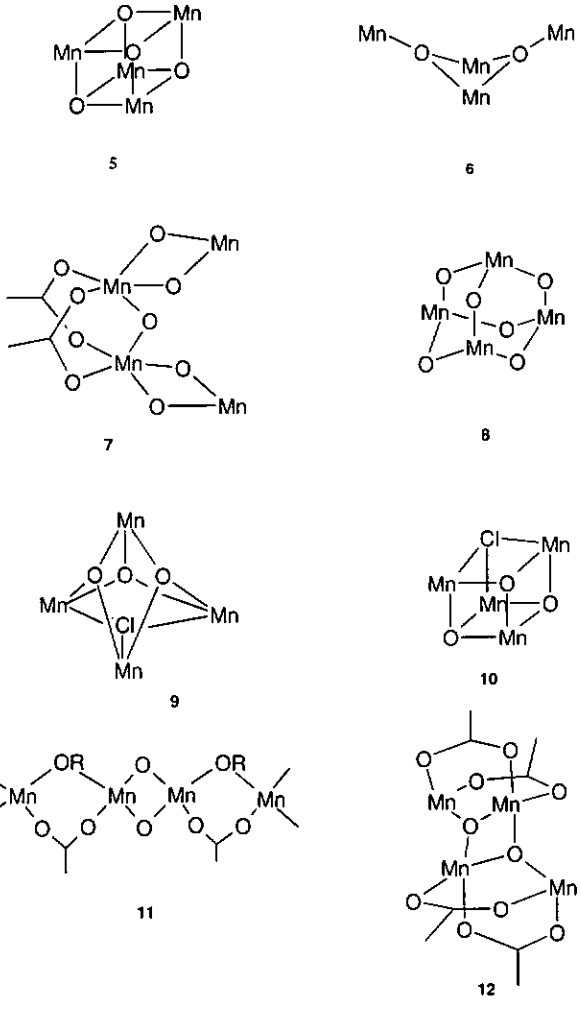


Chart 2. Structural arrangements in tetranuclear Mn complexes. For the sake of clarity only oxo, O^{2-}, chloride, and some carboxylate ligand atoms are shown. The Mn atoms are usually 6-coordinate.

The details of the functioning of the oxygen-evolving complex (OEC) part of PSII became clear from experiments, in which PSII preparations that had been held in the dark for some time were subjected to intense short flashes of light. O_2 evolution was not observed until the third flash and then peaks of oxygen evolution were observed every fourth flash. The accepted interpretation of these results is that the dark-adapted manganese cluster exists in a stable oxidation state called S_1. The first three flashes each result in the removal of one electron from the manganese cluster to produce new states S_2, S_3 and S_4 with increasing oxidising ability. S_4 oxidises water to O_2 gaining four electrons and forming the S_0 state. The fourth flash results in the oxidation of S_0 to the stable S_1 state. The manganese cluster thus stores electrons from the water oxidation reaction until they are required by the tyrosine radical. The $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transitions almost certainly involve oxidation of a manganese atom in the manganese cluster, but the $S_2 \rightarrow S_3$ transition may not. The S_4 state lasts for only a very short time so we have no information about the manganese oxidation state in the $S_3 \rightarrow S_4$ transition. If manganese is not oxidized in the $S_2 \rightarrow S_3$ transition then what is? No other redox species has been identified so we do not know the answer to this question. The half-lives for the reduction of $Y_Z^{\cdot}$ are in the range 30-1000 μs with each successive step being a factor of three slower than the previous one. The rate-determining step (with a half-life of ~1 ms) coincides with the release of O_2.

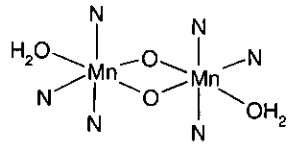
The Roles of Other Species

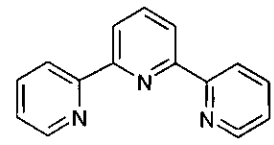
Overall four protons are released by the oxidation of two water molecules. Evidence suggests that each of the steps from S_0 to S_4 results in the liberation of one proton. There is not universal agreement on this point however. Such a scenario has an advantage: charge build-up is avoided, and one proton and one electron are each released in each change of S state. One Cl^- is essential for the oxidation of water. Chloride is apparently only required for the $S_2 \rightarrow S_3$ and $S_3 \rightarrow S_0$ transitions; Br^- can replace Cl^- but F^- inhibits the reaction. There is no evidence that the Cl^- is bound to either manganese or calcium and, while we do not know where it is bound, a recent suggestion is that it is part of the proton transfer process. Most of the current evidence suggests that intermediates such as peroxide are not formed during the S-state progression; O_2 is formed from water or manganese ligands in a single four-electron step. The oxidation states of the Mn atoms are also uncertain, but a consensus has emerged that the S_2 state contains one Mn(III) and three Mn(IV) species. Moreover, we cannot be sure about the oxidation states in the higher S states until we know whether Mn is oxidized in the $S_2 \rightarrow S_3$ transition.

Models for the Manganese Cluster

Since the discovery of the role of manganese in the photooxidation of water, inorganic chemists have endeavoured to make models of the manganese cluster. Ideally the model would have both the correct structure and be capable of oxidizing water to oxygen. Initially, efforts concentrated on the preparation of tetranuclear clusters of manganese ions in high oxidation states. This work has revealed a rich and fascinating facet of higher oxidation state manganese chemistry.[1] The different types of clusters isolated to date are shown in Chart 2. The formation of these clusters is dependent on the exact conditions employed in the preparation and the nature of the ligands used to occupy the coordination sites. From many such studies it is apparent that the compound isolated is that which is the most insoluble under the experimental conditions, and that in many cases there are species present in the solution that have different nuclearities and structures. Cubane structures, *e.g.* **5**, were prepared in 1985 by Professor Vickie McKee and her students when she was on the staff of the University of Canterbury. The "butterfly" arrangement of the manganese atoms in **6** was first prepared by Professor George Christou and coworkers from Indiana University, using acetate and 2,2´ -bipyridyl as ligands, but other bidentate ligands and carboxylates yield the same structure. The so-called "dimer-of-dimers" structure **7** was first isolated in 1995 by the group led by Bill Armstrong at Boston College. The adamantane structure **8**, first prepared in 1983 in Germany by Karl Wieghardt's group, was obtained using triazamacrocyclic ligands that occupy three coordination sites on the face of an octahedron. Monodentate imidazoles are the other ligands present in the pyramidal arrangement **9**. This compound and the distorted cubane **10**, prepared by Christou's group, are of particular interest because they contain coordinated chloride ion, an essential cofactor in the OEC. Compound **11**, formed with a tetradentate ligand *N,N,N´,N´*-tetrakis(2-pyridylmethyl)-1,3-diamino-2-propanol, has two Mn(II) species at the extremities of the linear array on Mn ions and Mn(III) in the center. Compound **12** is formed using the ligand 1,2-bis(2,2'-bipyridine-6-yl)ethane. Many of these clusters are known to exist in a number of different oxidation states.

The search for manganese complexes capable of oxidizing water to dioxygen has not yielded any tetranuclear complexes able to catalyze this reaction. However, Charles Dismukes' group at Princeton has prepared a Mn_4O_4 cuboidal complex with diphenylphosphinate ligands that decomposes with the formation of dioxygen when irradiated with UV light in the gas phase.[2] Two oxygen atoms from the corners of the cube form the O_2 molecule. One dinuclear complex, $[H_2O(terpy)Mn^{III}(O)_2Mn^{III}(terpy)OH_2]^{3+}$, can catalyze O_2 evolution from water using either $KHSO_5$ (potassium oxone) or NaOCl as oxidant. The structure of this complex and the terpyridine (terpy) ligand is indicated below. A mechanism for the oxidation reaction has been suggested that involves a preequilibrium between the complex and HSO_5^- or OCl^-. The rate-limiting step of O_2 evolution is proposed to be formation of a formally Mn(V)=O moiety which could then





terpy

competitively react with either oxone or water/hydroxide to produce O_2. This mechanism is supported by the isolation and structural characterization of the $[(terpy)(SO_4)Mn^{IV}(O)_2Mn^{IV}(O_4S)(terpy)]$ complex. Isotope-labeling studies using $H_2{}^{18}O$ and $KHS^{16}O_5$ show that O_2 evolution proceeds via an intermediate that can exchange with water, but more than one pathway for O-O bond formation is suggested by the labeling studies.[3]

Structural Determination of PSII

Given the complexity of the photosynthetic apparatus and the fact that most of the proteins are membrane bound, the determination of the overall structure of this complex was never going to be an easy task. The fact that we now have crystal structures of one of the light absorbing proteins,[4] of the PSI complex,[5] and most recently a crystal structure of a catalytically active PSII complex[6-8] is testament to the incredible advances that have been made in crystallising such proteins and solving their structures.

Electron Microscopy

Electron microscopy was the technique that revealed the overall structure of the thylakoid membrane. In the presence of divalent metal ions this membrane segregates into two structurally different components. Appressed membranes form stacks of several (up to dozens) membranes (the grana membranes). These stacks are connected by non-appressed membranes (stroma membranes). The major complexes of this membrane are not uniformly distributed over the membrane. About 85% of the PSII complexes are in the grana membranes while PSI and ATP synthase are largely localised in the stroma domains. The cytochrome b_6f complex preferentially populates the grana appressed regions. The PSII complexes are dimeric. Associated with the PSII complexes are proteins of the light-harvesting complex (LHCII) (which can be either monomeric or trimeric) but the association is quite heterogeneous. The basic unit is the so-called C_2S_2 supercomplex in which the central dimeric PSII core (C_2) is surrounded by two symmetry related structures that contain one LHCII trimer (abbreviated S for strongly attached), one CP26, and one CP29 monomer. This supercomplex can bind one additional monomeric LHCII complex and two additional LHCII trimers but these are not always present. The size of the dimeric PSII/light harvesting complex is about 175 x 250 Å in the plane of the membrane and it protrudes about 80 Å above the lumenal surface. Removal of the extrinsic proteins on this surface results in a height reduction to 60 Å.

A two-dimensional structure of PSII from spinach at 8 Å resolution was first obtained by electron cryomicroscopy

of 2-D crystals obtained from plants.[9] Subsequent work using this technique, notably from the group at Imperial College lead by Professor James Barber, resulted in three-dimensional images at lower resolution, about 17 Å. However, this resolution was sufficient to assign transmembrane helicies and locate the positions of many of the protein subunits. Thirty-four transmembrane helices were observed, twenty-two of which were assigned to the major subunits D1, D2, CP47 and CP43. Both CP47 and CP43 protrude above the lumenal surface of the membrane. The remaining twelve helices apparently belong to the low-molecular-weight proteins having single transmembrane helices. Comparison of the subunit organization of the higher plant photosystem II apparatus reported in these studies with the X-ray structures from thermophilic cyanobacteria discussed below shows significant similarities indicative of a common evolutionary origin.[10]

Spectroscopic Characterization

Prior to the work on the crystal structure of the PSII complex described below, a considerable body of structural evidence had been obtained spectroscopically. The manganese cluster and the tyrosine radicals have unpaired electrons that means that they are amenable to study by electron paramagnetic resonance (EPR) spectroscopy. EPR spectroscopy has also been used to determine the distances of the organic radicals from one another and the Mn cluster. Four of the five S states in the catalytic cycle have been characterized by EPR.[11] EPR spectra of the manganese cluster are complicated because clusters of manganese ions can have electronic excited states that are very close in energy to the ground state. These excited states can have different numbers of unpaired electrons from the ground state and may be thermally populated at quite low temperatures.

A multiline EPR signal from the S_0 state has been observed. This signal, which is wider than the S_2 signal described below, has at least 20 peaks. The spectrum suggests that the S_0 state has a ground state with one unpaired electron and no thermally accessible excited states. EPR signals of the S_1 state of the spinach oxygen-evolving-complex (OEC) arise from a low lying excited state with two unpaired electrons. Three EPR signals can arise from the S_2 state of the OEC, a multiline signal due to the ground state, which has one unpaired electron, a signal from an excited state with five unpaired electrons, and a signal from a different excited state with five or possibly more unpaired electrons. The stability of these states differs between plants and cyanobacteria. The multiline signals are reminiscent of the signals measured with dinuclear Mn(III)-Mn(IV) metal complexes and suggest that these oxidation states may be present in the cluster. Different EPR signals from the S_3 state are observed depending on the conditions. In PSII samples in which the oxygen evolving activity has been inhibited, the observed signals are thought to arise from interactions between the manganese cluster in an oxidation state equivalent to S_2 and $Y_Z^{\cdot}$. EPR spectra due to the S_3 state itself can be observed and apparently come from a low lying excited state with two unpaired electrons. EPR studies of the tyrosine radicals suggested that Y_Z is about 5 Å from the manganese cluster and about 10-15 Å from P_{680}, and that Y_D is ~27 Å from the manganese cluster and ~30 Å from Y_Z.

Vibrational spectroscopy, particularly Raman and low frequency infrared spectroscopy, has been used to investigate hydrogen bonding to the Y_Z radical, structural changes in the different S states, and Mn-ligand and Ca-ligand vibrational bands. Of particular importance in the study of the manganese cluster has been the use of Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. This technique measures the absorption of X-rays by an atom when an inner core electron is ionised by an intense beam of X-rays. The fine structure on the absorption bands is due to the interaction of the emitted electron with the electrons of the nearest neighbours of the ionised atom. The fine structure thus provides structural information (bond distances and angles) about the immediate coordination environment of the ionised atom. The technique is specific for a particular element which has advantages in systems as complicated as the OEC. Three major well-resolved peaks are observed in the manganese EXAFS spectrum of the S_1 state of PSII. These peaks have been interpreted (with considerable controversy) as suggesting the presence of two oxygen or nitrogen atoms per Mn (EXAFS is unable to differentiate between C, N or O) at ~1.85 Å, between 2 and four O or N atoms located 1.95-2.15 Å from the Mn centres, ~1.25 Mn atoms at 2.74 Å and 0.5 Mn or a Ca^{2+} at ~3.30 Å from the Mn atoms.[12,13] Studies of the other S states using EXAFS suggest that S_0 and S_2 have very similar structures to S_1 but the S_3 state is different. The 2.74 Å vector splits into two vectors at 2.8 Å and 3.0 Å as does the 3.3 Å vector which was resolved as two vectors at 3.4 Å and 3.6 Å.[14] These changes have been interpreted as resulting from changes in the internuclear distances due to the formation of a bridging oxyl radical. Oxyl radical formation has never been observed, however, in any Mn-oxo model system. EXAFS investigations of the Ca^{2+} ions have generated some controversy but the measurements from unperturbed samples give a Mn^{2+}-Ca^{2+} distance of 3.5 Å that is consistent with the results from the Sr^{2+}-substituted enzyme. Comparison of the EXAFS spectra from the OEC and that of the model complexes shown in Chart 2 suggested that the "dimer-of dimers" complex **7** provided the best description of the structure of the manganese core of the OEC.

EXAFS spectra, polarography, and EPR spectra have recently been used to investigate the time course of the disassembly of the Mn complex. Three distinct phases of the disassembly process were identified. Loss of the oxygen-evolution activity and reduction of Y_D occur simultaneously (k_1 = 1.0 min^{-1}). EXAFS spectra reveal the concomitant loss of a heavy atom separated by ~ 3.3 Å from the manganese cluster and possibly related to Ca^{2+} release. Subsequently, two Mn(III) or Mn(IV) ions separated by ~2.7 Å in the native complex are reduced to Mn(II) and released (k_2 = 0.18 min^{-1}). These X-ray absorption data are highly suggestive of the two unreleased Mn ions forming a di-μ-oxo bridged Mn^{III}_2 complex. Finally, a tightly bound $Mn_2(\mu\text{-}O)_2$ unit is reduced and released (k_3 = 0.014 min^{-1}).[15]

X-ray crystallographic studies

The structures of proteins are now almost routinely determined by X-ray crystallography provided suitable crystals can be grown. The crystal structure of the reaction center of a photosynthetic purple bacterium that does not evolve oxygen was determined more than 15 years ago and resulted in the award of the 1988 Nobel Prize in Chemistry to J. Deisenhofer, H. Michel and R. Huber. There are protein sequence similarities of the proteins in this reaction center to the proteins of the PSII complex so there was reason to believe that the structures might be similar. Crystal structures have also been determined for the most abundant light harvesting complex protein of PSII,[4] the PSI complex[5] and ATP synthase from spinach,[16] but until recently suitable crystals of the PSII complex had not been prepared. This situation has now changed and crystal structures of the intact PSII complex and some of the component parts have now been determined. In addition, a recent report has described the crystallization of the extrinsic 23 kDa protein from tobacco, and the structure of the extrinsic 16 kDa protein Psbq from spinach has been deposited in the Protein Data Base.[17,18]

The structure of PSII from the thermophilic bacterium *Synechococcus elongatus* has been determined at a resolution of 3.6 Å.[6,7] The crystals used in this structural study were competent in oxygen evolution and contained 17 protein subunits, PsbA to PsbO as well as PsbU, PsbV, and PsbX. More recently, the structure from another thermophilic cyanobacterium *Thermosynechococcus vulcanus* at 3.7 Å resolution has been reported.[7] These resolutions are insufficient for the determination of atomic positions, but with knowledge of the protein sequences it is possible to build a reasonably accurate model of the complex. The amino acid sequences of the photosynthetic proteins of these two organisms are almost identical and the structures are very similar. The latter structure seems to be of better quality because the 12 kDa protein (PsbP) was located in this structure and large parts of the loops on the lumenal side of the D1, D2, CP43, and CP47 proteins, which have not yet been identified in the *Synechococcus elongatus* structure, were characterized in the *Thermosynechococcus vulcanus* structure. Real sequences of the CP47, CP43, D1, D2, cytb559, and PsbK proteins, and the extrinsic cytochrome c550 were used in the modeling of the latter structure. PsbI, PsbH, PsbX, and the 33 and 12 kDa-extrinsic proteins were modeled as polyalanines. The lower mass subunits have been modeled as amino acids without sidechains. The *Synechococcus elongatus* structure has to date only been modeled as amino acids without sidechains. The enormity of the task involved in working with these crystal structures is evident from the fact that if atomic resolution is ever to be achieved the location of more than 45,000 atoms has to be determined!

Both structures contain 36 *trans*-membrane α-helices. The extrinsic proteins PsbO, PsbP, PsbV, and PsbX do not contain *trans*-membrane helices and are located on the lumenal side of the complex. A cluster of ten *trans*-membrane helices assigned to the D1 and D2 proteins forms

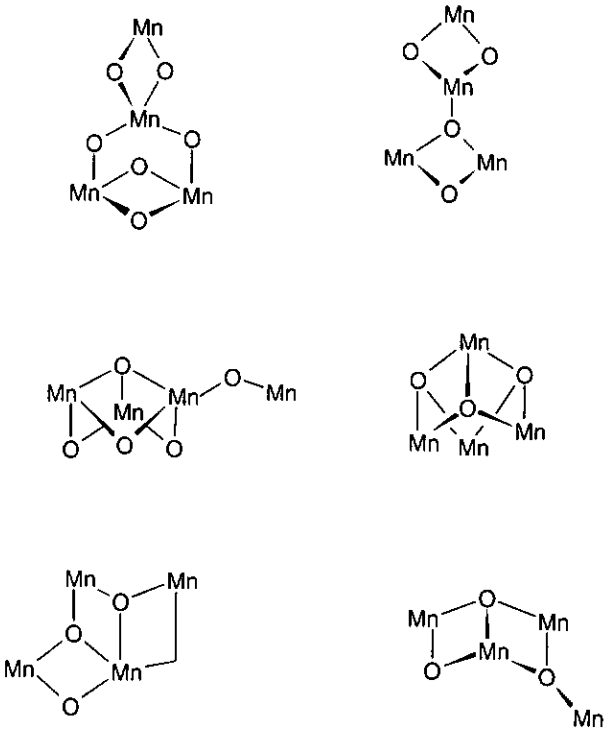


Chart 3. Possible arrangements of the manganese atoms in the PSII OEC.

the central core of PSII. The arrangement of these helices resembles the arrangement of the L and M subunits of the reaction center of purple bacteria and to a lesser extent the central domain of PSI.[8] The D1 and D2 proteins are flanked by the CP47 and CP43 proteins. Each of the CP47 and CP43 subunits has six *trans*-membrane α-helices. Two other helices in close proximity to D2 were assigned to cytochrome b559. The remaining 12 helices have not yet been assigned unambiguously. More than forty cofactors have been identified in the structures at this resolution but the exact number varies in the two structures. Twenty nine (30 in *Thermosynechococcus vulcanus*) antenna chlorophyll molecules bound to CP47/43, 6 chlorophylls and 2 pheophytin bound to D1/D2, the four manganese atom cluster, a non-heme iron located at the D1/D2 interface on the stromal side of the complex, and the 2 heme groups of cyt b559 and cyt c550, respectively, have been identified. Two ß-carotene molecules (one *cis* and the other all *trans*) have been identified in the *Thermosynechococcus vulcanus* structure close to the reaction centre.

One surprise from the structural study was the arrangement of what was thought to be the special pair of chlorophylls that comprise P_{680}. There are four chlorophylls located at the center of the D1/D2 core, two symmetry related pairs. Two molecules are oriented parallel to the membrane with a center to center distance of 10 Å, the other two are tilted at about 30° to the membrane plane and are located about 10 Å from a member of the first pair. It is now thought that all four of these chlorophylls are involved in the energy transfer and that, at least at room temperature, the excited state of P_{680}^{+} may be delocalized over all four chlorophylls. The reason why these chlorophyll molecules have such a high redox potential (between 1.0 and 1.3 V) is not known.

One pleasing feature of the crystal structure determination was confirmation of the distances determined spectroscopically with those present in the crystal. The manganese cluster is 7 Å from Y_Z and the latter is 14 Å from the P_{680} chlorophylls. The pheophytin molecule is 11 Å from one of the chlorophylls of P_{680} and 12 Å from the Q_A binding site. Y_D is 30 Å from the manganese cluster and 14 Å from the P_{680}. The cluster of manganese atoms in PSII is assumed to be in a region of high electron density with dimensions of approximately 6.8 Å x 4.9 Å x 3.3 Å. This cluster is deeply buried within the protein and shielded from the aqueous phase by loops of the intrinsic and the extrinsic subunits. Individual manganese atoms have not been resolved and they have been placed somewhat arbitrarily in this region so that the arrangement of the Mn atoms resembles a Y. Combining this knowledge with the results from the EXFAS studies has resulted in a number of new proposals for the arrangement of the manganese atoms; these are shown in Chart 3. The internal structure of this region of electron density has not been resolved, and Cl^- and Ca^{2+} ions might be present in this region.

Protein sidechains bound to the manganese cluster have not been positively identified in the *Synechococcus elongates* structure. The C-terminal end of the D1 protein, the A/B loops, and the loop between the end of helix C and the lumenal CD helix of the D1 protein are in close proximity to the manganese cluster, as is a loop from CP43. Site-directed mutagenesis studies (reviewed by Diner[19]) suggested that the residues on the D1 protein, Asp170, His190, His332, Glu333, His337, Asp342, and the C-terminal carboxylate Ala344 could function as manganese ligands. In the *Thermosynechococcus vulcanus* structure four or five connections between the polypeptide backbone and the manganese cluster have been identified. The C-terminal carboxylate Ala344, Asp170, Glu333 (or His332) are probable ligands, and His337 and Asp189 (or His190) possible ligands. Asp342 seems to be excluded by the X-ray studies but a new candidate Tyr73 of the D1 protein is close to the Mn cluster.

One of the puzzles of these structures is that to date no Ca^{2+} ion has been located in either of the structures. Ca^{2+} is essential for the proper functioning of the OEC. It seems likely that a Ca^{2+} is in the same region of high electron density occupied by the manganese ions. The volume of this region is large enough to accommodate a Ca^{2+} ion and a tetranuclear cluster of Mn atoms. This suggestion is in agreement with the EXFAS studies that suggest the Ca^{2+} is within 3.5 Å of a Mn atom.

Certainly we can expect that the resolution of the crystal structures of the OEC will be improved in the future as techniques for the growth of the crystals are improved. Determination of the structures of the individual protein subunits will also help in understanding the overall structure and functioning of this huge apparatus. The challenge for the manganese chemist still is to make tetranuclear complexes (with or without Ca^{2+}) that have structures similar to those shown in Chart 3 and to react them with water to produce oxygen.

Acknowledgements

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CHEM ED 2003

Every second year since the end of the 1980s enthusiastic and dedicated secondary school chemistry teachers in various centres have, with the help of NZIC and the local University and/or College of Education, organized conferences for secondary teachers of chemistry, alternating with the scientifically broader biennial SCICON, organized by the NZ Association of Science Educators. Wellington hosted about 145 registrants to Chem Ed 2003 - *Bringing Chemistry to Life* - at Victoria University of Wellington from July 6-9. A hard working committee chaired by Dr. Suzanne Boniface of Queen Margaret College planned and organized the conference with the goals of:

- expanding teacher knowledge of what is happening in chemistry research and industry today
- providing stories and ideas to take back to the classroom
- discovering more about how students learn and perceive the chemistry ideas taught
- providing workshops and talks that are relevant to the classroom.

Above: Hon. Steve Maharey, Associate Minister for Education addresses the conference.

The first goal was achieved by having a number of speakers from the Wellington area giving an overview of their research in the context of its relevance to New Zealand's future–*Cutting Edge Chemistry*–and then a field trip to a manufacturing plant or to a CRI laboratory. Three invited overseas participants, Vanessa Kind from Norway, Roy Tasker from Sydney, and Deborah Corrigan from Melbourne contributed to the other three themes by each giving a keynote lecture and running workshops.

The conference actually started on the Sunday evening as planned, despite severe snow storms which blanked all of the eastern South Island and blocked all the main roads from Auckland to Wellington except through Taranaki, and even closed the main road from Napier to the Wairarapa. This latter rare occurrence caused Vanessa Kind to experience a drive few New Zealanders would have done!

The conference was given a flying start with two talks, Norman Cates on *The Chemistry of the Lord of the Rings*, and Professor Jeffery Tallon on *Oxygen - in several flavours*.

Norman discussed the role of chemistry and the experimentation that was necessary to get the right properties of polymers and adhesives in making the enormous numbers of prostheses used (he personally made every ear in the trilogy!) and displayed many of these. His most useful reference was Ben Selinger's classic text, *Chemistry in the Market* Place. The chain mail that was passed around was not as heavy as it looked–it was electroplated plastic.

Jeffery looked at oxygen from many angles and in doing so ventured into theoretical physics, superconductivity, allotropes and abundance, and its discovery as highlighted by Djerassi and Hoffmann's recent play. The use of liquid oxygen to separate physically two different structures of a superconductor material as its boiling point fell between their critical temperatures, clearing the way for acceptance of a patent, was fascinating.

Other Wellington-based chemists who gave talks during the following three days were Professor Jim Johnston on *Nanophase silicas and silicates – New Materials and their Applications*, Gerald Smith on *The Chemistry of Maori Dyes and Paints*, Ian Brown on *New Materials for the Hydrogen Economy*, Professor Paul Callaghan on *Deforming molecules: the surprising mechanics of complex fluids and soft matter*, Paul Benjes on *Industrial Research Limited – drug development capabilities with a special focus on the development of a new class of potent anti-cancer drugs*, and Tony Clemens on *Production of High Purity Hydrogen from Coal for use in Fuel Cells.*

At most conferences the wine and cheese session is purely social. Not so here; it was a symposium – *Chemistry just gets better with age.* Justin Bendall from the Fonterra Research Centre (previously NZDRI) dismissed some myths about flavour (sweet/sour/salty/bitter) and discussed a variety of compounds responsible for flavour and our appreciation of wine and cheese, and the chemical reactions by which these compounds develop over time. Practical work–careful sampling and analysis of the cheese and wines whose time-resolved flavours were discussed–was compulsory.

Professor David Bibby, (NZIC President) closed the conference with some thoughts and visions on where chemistry was going to be of great importance in the future. He comments were presented under four headings; demographic change (by 2030 there will be more people over 80 years than in any younger age decade), mankind global impact, future energy issues, and information and communications technology.

At a time when preoccupation with the introduction of NCEA, and the assessment involved, appears to dominate the secondary education scene, and the time demanded of teachers to carry out this assessment threatens the very quality of the teaching of chemistry, it was heartening to find, other than in a forum to discuss matters of concern to teachers, assessment played no part in the formal programme. However, it was certainly a dominant topic for individual discussion, and the forum allowed for teacher concerns to be aired. Two government organizations are involved. The Ministry of Education is responsible for curriculum, writing of standards to be attained and for training teachers in this area. NZQA manages the assessment. Many teachers expressed views that it was difficult or impossible to get questions on concerns answered by these bodies, and a message articulating these concerns was constructed. Another concern was of the limitations placed on practical work, and particularly on

practical demonstrations, by safety regulations. There seems to be no recognition that teachers are professionals and can make judgements. There is an over reaction to labelling of chemicals. Teachers were fully cognizant of the importance of safety, but when regulations prevent the fun of chemistry being conveyed these regulations are over zealous.

Above: Vanessa Kind - *Bringing Chemistry to Life.*

Bringing Chemistry to Life was the title of Vanessa Kind's keynote talk, with a major theme of the importance of making chemistry alive in society and schools. Students must experience relevant chemistry and learn chemistry in contextual settings if the perception held by many that it is boring, never understood and too complicated is to be dispelled. Experts in chemistry, *i.e.* professional chemists and chemistry teachers sense or see things through "molecular spectacles", but those learning the subject are not yet in this position. Their experiences to date are concrete and macroscopic, and this must be appreciated by the teacher in developing rational explanations of chemical matters. Vanessa discussed the problems and mistakes all too prevalent in classrooms. She considered the three ideas that give chemistry its uniqueness: the formation of new substances through chemical reactions, matter is conserved, and matter is made up from tiny particles. Students have misconceptions in these areas and they matter and are a block to further learning. Great care is needed with language, *e.g.* matter has been used in different senses in the previous two sentences. Excess detail can obliterate the basics. Deborah Corrigan's talk *What is real world chemistry?* took up issues raised by Vanessa and added real synergism into the conference. What is real chemistry and what is of interest to students is not a static question with the continuous rapid developments, and the answers will keep changing with successive generations. Thus, while I have heard discussion on this for 30 years of chemical education conferences it is as pertinent today as ever, and enthusiasts such as Vanessa and Deborah do chemical education a service by keeping it in front of new generations of teachers. Many of the workshops presented gave teachers examples and ideas for making chemistry alive and exciting: *Fat to Bust, Fuelling the Future", Chemistry of the Chocolate Cake* and *How Green is New Zealand Chemistry.*

What has changed more recently and continues to change rapidly is information technology. IT creates great opportunities for the teaching and presentation of chemistry, and a constant challenge to teachers to make the most of it for the benefit of both themselves and their students. Aspects of this were the subject of the third overseas keynote lecture and of many workshops.

Roy Tasker has been a pioneer in developing animations for the visualization of chemistry at the molecular level. I vividly remember a presentation in Auckland some years ago in which animation of the dissolution of sodium chloride in water was being developed. His keynote address *The VisChem Learning Design: Bringing Chemistry to Life by Visualising the Molecular Level* showed what great development there has been since then. Roy discussed the importance of testing whether these animations do in fact improve understanding, and of the dangers of poor animations (of which there plenty available) leading to new misconceptions. The way teachers use the animations is more important than the resources themselves. Older teachers had to make do with stick and ball models, then space filling models came on the scene for those who could afford them. With computers stick and ball models of molecules overlaid with electron cloud pictures can be constructed, with colouring of electron clouds to show areas of high electron density. Roy commented that these were the best and they appear in new chemistry text books. For anyone interested in the VisChem Learning Design go to <http://www.learningdesigns.uow.edu.au/beta6/examplars/info/LD9/index.htm> and see <http://www.vea.com.au> for the animations available.

Teaching is a very personal thing, and teachers like to write their own course material, but this can be very time consuming and involves much reinventing of the wheel. Writing exercises and problems can be very time consuming. Systematic use of a textbook, which allows the teacher some import, is one way round this and there was a huge offering of textbooks on display, along with guidebooks, revision books, problem books, *etc.* The main changes one sees in new textbooks seems to be increasing size, a CD in the back cover, more sophisticated graphics and asides (boxes) on applications, stories, and historical information. While many of these are very attractive, the basic material is essentially not new and one feels authors are themselves reinventing the wheel. There is the risk that the sheer size and amount of information could have an adverse effect on students. Two workshops provided information on available material, which is the reverse of this trend, and helps students by providing precise information on basic topics and on the language of chemistry, both of these coming from The University of Auckland. The first was on The University of Auckland's *Best Choice* (see: <www.che.auckland.ac.nz/bestchoice>). The philosophy of *Best Choice* is (i) Read a little and then answer lots of questions on what you have read, and (ii) Learn even more from the feedback given with every response. There are now 1500 screen pages providing a mixture of information (reviews of common topics, bonding, acid-base, redox, *etc.*) and interactive question pages (10 of these to one review page). More topics are being written and added and it covers material of years 12, 13 and first year university. It can be accessed by any student anywhere in the world for no cost. The second was on a small commercial CD, *Let's Talk Chemistry*,

Above: One of the Chem Ed 2003 Workshops in progress.

from which The University of Auckland's *Manual on the Basic Vocabulary and Language of Chemistry* can be printed, and a more user-friendly electronic html version can be down-loaded on to an individual computer, or a school or university network <see http://www.members.optushome.com.au/scottsoft>. One would hope that courses, well thought out and developed from years of experience, will become available on the Internet.

Historically New Zealand university chemistry departments have actively supported and helped secondary teachers, and played official roles in the areas of curriculum and examinations. In recent years their official roles have diminished or gone and the teachers are filling the roles required by the Ministry of Education and NZQA. It would be to the detriment of school chemistry if cutbacks in resources and staff that the universities are now experiencing were to further weaken tertiary-secondary interactions. Fortunately there was no sign of this at this conference. Staff from four universities were there and presented workshops on a range of topics, and we had a description of the way Lincoln University Regional Education subjects in chemistry and biochemistry have been run as an after school programme at a Christchurch school. Of course Victoria was central to the running of the conference.

The printed conference programme was excellent and in addition to programme details, abstracts, *etc.* there was useful information on NZIC, the VUW School of Chemical and Physical Sciences and the MacDiarmid Institute for Materials and Nanotechnology, RSNZ, and The NZ Association of Science Educators.

Rumour has it that it is Dunedin's turn to host the next biennial Chem Ed conference. Let's hope Otago's teachers and professional chemists will accept the challenge. One question in the end-of-conference questionnaire was 'Should Chem Ed be combined with the NZIC conference?' No doubt it would be good if teachers could mix more with New Zealand's professional chemists, attend the plenary lectures and experience the atmosphere of a research oriented conference. Chemical Education would be one of the symposia. Would teachers want to attend a conference immediately after breaking up at the end of the school year? Could the smaller centres, which now seem to be favoured as conference venues cope with the extra numbers and demand of rooms and computer facilities to run the numerous workshops essential for Chem Ed? Whatever happens, it is essential for the health of chemistry teaching in this country that the biennial Chem Ed conferences continue so that teachers can come together to make new contacts and share experiences and ideas. Two things that would help in communication but were not done at Chem Ed 2003 would be to have e-mail addresses on the list of participants and the attendees affiliation (school, university *etc.*) on their lapel labels.

I believe that the committee plans to produce the proceedings of the conference on a CD.

In summary, Chem Ed 2003 was a stimulating conference and a great success; thanks and congratulations are extended to Suzanne Bomface and her committee – Margaret Dick (Sacred Heart College), Elizabeth Douch (Tawa College), Penny Kinsella (Newlands College), Stuart Mason (Scots College), Matt Morris (St. Patrick's College, Kilbirnie), Jennifer Stacey (Samuel Marsden Collegiate School), Peter Spratt (Royal Society of New Zealand), Ray Vowles (The Correspondence School), and also to the Wellington-based scientists who took time out to talk about their current work and its relevance to New Zealand.

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NEW ZEALAND AND THE HYDROGEN ECONOMY*

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**Based upon an invited lecture presented at Chem Ed 2003, July 2003*

New Zealand is rapidly moving to a future where environmental and infrastructural drivers are forcing change to our accepted pattern of energy supply. These drivers include meeting our obligations to reduce CO_2 emissions under the Kyoto protocol and ensuring viable energy solutions to meet the future needs of our transport and distributed electrical energy sectors. The concept of a hydrogen economy is rapidly gaining international momentum and offers New Zealand and the world a clear solution. However, existing hydrogen production from hydrocarbon sources will neither meet CO_2 emission criteria nor provide a fuel cell feedstock of sufficient purity. To implement a future hydrogen economy, New Zealand must develop advanced technology solutions for the *manufacture and storage of clean hydrogen.*

What is the Hydrogen Economy?

Many commentators have written essays and even books[1] on this subject but the essentials can be reduced to a simple but clear model in which future transportation and stationary energy needs can be met through the operation of three closely linked technologies, namely the generation, storage and utilisation of hydrogen. The latter component has received immense commercial investment for many years from a range of international corporates, specifically in the field of fuel cell technology. New Zealand cannot compete with such investment, so the challenge for New Zealand becomes one of providing viable front-end hydrogen generation and storage solutions in order to take up the economic advantages that fuel cells will deliver.

However, current commercial fuel cell technologies are critically dependent on high purity hydrogen for their operation as they employ precious metal catalysts that are at risk of being poisoned with exposure to even ppm levels of CO/CO_2. International economies have been dominated for many years by provision of non-renewable coal, oil and gas solutions to hydrogen generation, so the concept of generating clean hydrogen, *e.g.* from water, has been of low priority. Very recently, national and international oil and gas shortfalls and supply risks, and increasing environmental concerns of greenhouse gas build-up have forced a review of this priority. Further, the concept of large-scale hydrogen storage or *banking* has only recently been focused away from physical solutions (compressed gas storage) towards chemical solutions. Industrial Research Limited and its research partners have recently proposed technology solutions to the first two of these key components, namely the manufacture and storage of clean hydrogen.[2] This article reviews the current international state of technology in these two areas and how the hydrogen economy will impact upon New Zealand's future.

National and International Hydrogen Futures

International decision-makers have identified hydrogen and fuel cells as key technologies to contribute to energy supply security and environmental protection in the mid to long term. Their words have been backed by action and investment. Some selected snapshots are:

- In late 2002 the European Union announced a long-term, £2.1 billion programme on hydrogen and renewable technologies.
- In his January 2003 State of the Union Address, President Bush announced: *"Tonight I'm proposing $1.2 billion in research funding so that America can lead the world in developing clean, hydrogen-powered automobiles. A single chemical reaction between hydrogen and oxygen generates energy, which can be used to power a car - producing only water, not exhaust fumes. With a new national commitment, our scientists and engineers will overcome obstacles to taking these cars from laboratory to showroom, so that the first car driven by a child born today could be powered by hydrogen, and pollution-free. Join me in this important innovation to make our air significantly cleaner, and our country much less dependent on foreign sources of energy."*
- The Japanese R&D budget for fuel cells and hydrogen has tripled since 1995, reaching US$200 million per year in 2002.
- Other OECD and non-OECD countries (Canada, Italy, UK, China) either have R&D programmes in place, or are expanding their investments.
- Small countries such as Iceland and Singapore are already committed to introducing hydrogen and fuel cells in their electricity and end-use sectors.
- General Motors Corp. aims to launch commercial sales of *f*uel *c*ell *e*lectric *v*ehicles (FCEV) by 2010, with total sales of 1 million by 2020. GM currently spends 25% of its R&D budget on FCEV development.

In response to this rapidly changing funding environment, international energy technology and economic forecasters are becoming more bullish in their predictions:

- Price Waterhouse Coopers projects the global demand for fuel cell products to reach $46 billion per year by 2011 and grow to $2.5 trillion per year by 2021.[3] Their report states *"the impact fuel cells will have on the world is comparable to other global "change technologies" such as electricity, the telephone, television, personal computers and the Internet"*.
- The Boston Consulting Group has predicted that FCEV will capture some 20 percent of markets in North America and Europe by 2020.[4]
- Frost & Sullivan report No. 7834-18 appears even more optimistic, predicting that at some point in the 2015-2020 period, sales of FCEV will exceed sales of conventional vehicles and that sale of conventional vehicles will cease at some point between 2025 –2035.[5]

So what is New Zealand's position in times of such escalating international investment? Firstly, the NZ Energy Efficiency and Conservation Authority, in its September 2001 position statement, clearly urged the Government to adopt strategies for implementing renewable and efficient energy systems in support of the Kyoto protocol.[6] The Government responded in 2002 by ratifying the Kyoto protocol and has subsequently embarked on a process of negotiating specific greenhouse agreements with major national corporates.[7]

New Zealand energy forecaster Jonathan Leaver (Director, Centre for Sustainable Engineering Initiatives, Unitec) has recently advanced a clear strategy to show the progressive uptake of hydrogen as a transport fuel in New Zealand over the next few decades.[8] His energy modelling predicts a 2020 introduction of fuel cell technology into New Zealand's vehicle fleet, with 30-50% market penetration by 2030. This would require 150 PJ of conventional fuel to be displaced by hydrogen, equivalent to 1 million tonnes of hydrogen p.a. and equating to a NZ$4.5 billion industry p.a. (2003 dollar terms) for *transport fuel costs alone*. This value may rise further should there be a negative impact of carbon tax on the conventional fuel price. Thus the Kyoto obligations will impose severe cost penalties on those energy companies whose production portfolio includes coal, *e.g.* Genesis Energy, unless they can provide *clean* coal energy generation technologies.

For New Zealand to move forward from here requires an understanding of the drivers we face as a country and how these drivers can lead to specific opportunities and benefits.

Drivers, Outcomes and Benefits for New Zealand

New Zealand is exposed to essentially the same drivers for a hydrogen economy as many international countries: the Kyoto protocol; the environment; and security of fuel supply. In the context of a future New Zealand hydrogen economy these drivers highlight research opportunities that will lead directly to a suite of high value business opportunities based on the development of IP in clean hydrogen technologies. These drivers are of substantial environmental and infrastructural importance and include:

- Managing energy supply demands and costs for rural communities and industries. Many networks and lines currently need replacement or upgrade in areas such as

the East Cape.

- Reducing the magnitude of CO_2, SO_x and NO_x emissions. Road transport contributes around 16% to New Zealand greenhouse emissions.[9] This will halve by 2030 as the hydrogen economy grows, saving $60 M p.a. in carbon tax penalties.
- The tangible (carbon tax) and intangible (environment quality) costs of future use of non-renewable energy in the manufacturing sector.
- The opportunity for energy companies to manage capacity through *banking* or *time shifting* energy as stored hydrogen. This will become particularly important as we endeavour to capture maximum efficiency from fledgling renewable energy technologies such as wind and wave power, whose output may not coincide with daily or even seasonal demand cycles.
- Increased energy security and reduction of the import-export imbalance through indigenous renewable supply of transport fuel. New Zealand producers meet only 30% of current oil requirements.[10]

Securing these infrastructural and environmental benefits will lead to new advanced technology manufacturing opportunities of considerable economic value to New Zealand, such as:

- A *new industry sector to* design and develop manufacturing plant to supply export and domestic markets with products based on hydrogen generation and storage technologies, *e.g.* from specialist components such as conducting ceramic membranes through to turnkey hydrogen production plants.
- A *new transport fuel industry base* to supply a future fuel cell powered vehicle fleet (NZ $4.5 billion p.a. by 2030).
- A *new chemicals industry base* to manufacture and use high purity hydrogen as a feedstock for new chemical technologies, such as hydrogenation processes and the manufacture of chemical hydride storage media.
- A *new energy industry base* to use high purity hydrogen in current and future energy applications, including electricity generation.
- A *new service industry* to support the international maintenance and operation of hydrogen technologies.
- Financial returns through wider international IP licensing and technology transfer.

It is clear that the drivers for change to a hydrogen energy future for New Zealand are primarily environmental and infrastructural, but it is equally clear that these will deliver major economic and technology growth benefits. These same drivers lead us to seek to develop a strong IP base in hydrogen technologies in New Zealand to support new export-focused manufacturing industries.

Overview of Hydrogen Manufacturing Technologies and Opportunities

The manufacture of high purity hydrogen suitable for direct supply to current fuel cell systems is technically and economically challenging:

- Routes involving reformation from hydrocarbon sources have been active for many decades, but carry the cost and technology overhead of separation of the hydrogen from CO_2 and other contaminant gases as well as the increasing challenges, penalties and costs associated with the *non-renewable* tag.
- Direct electrolysis of water is capable of generating hydrogen of the highest purity but at a high cost that is uneconomic for all but the highest value-added uses for the gas.

To implement a future hydrogen economy New Zealand will need a high purity, reliable and economic supply of hydrogen, capable of being generated and/or distributed nationally. From most environmental and processing perspectives, the source of this hydrogen should be water rather than hydrocarbons. Two technology options stand out as offering considerable promise. These are:

Hydrogen manufacture from water using new thermochemical cycles

Numerous thermochemical cycles have been proposed for the manufacture of hydrogen from water.[11] Even the simplest cycles must have at least two steps, for hydrogen generation and reagent regeneration, but many cycles require four or more steps with escalating degrees of engineering difficulty. Calcium-bromine and sulfur-iodine cycles have been proposed by *nuclear* nations (US, France, Japan) to take advantage of excess heat from nuclear power generation.[12] The University of Tokyo (UT-3) calcium-bromine cycle has four steps:

[1] Water splitting with HBr formation at 1000 K:

$CaBr_2 + H_2O \rightarrow CaO + 2HBr$

[2] Oxygen formation and $CaBr_2$ regeneration at 823 K:

$CaO + Br_2 \rightarrow CaBr_2 + 0.5O_2$

[3] Hydrogen formation at 923 K:

$3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2$

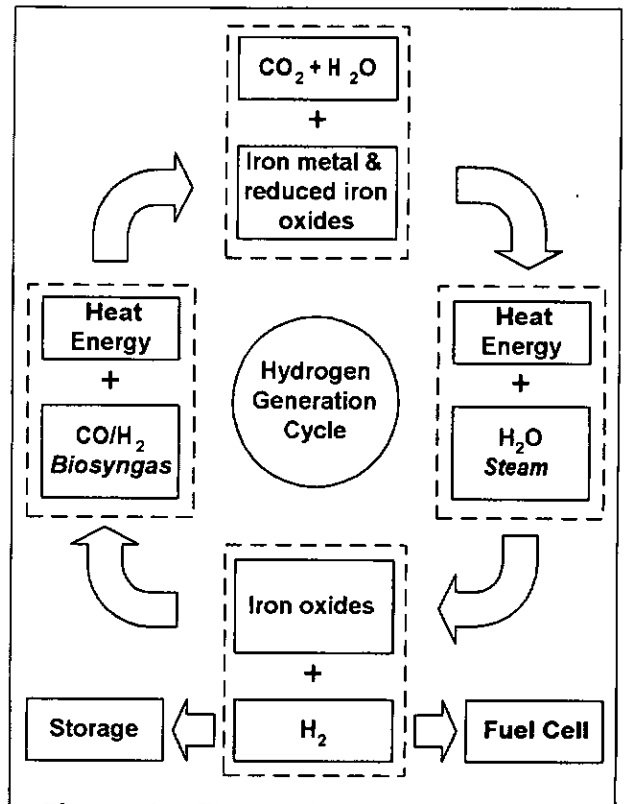

Figure 1. Thermochemical cycle for the manufacture of hydrogen from water using iron oxide as an intermediate.

[4] Bromine regeneration at 493 K:
$Fe_3O_4 + 8HBr \rightarrow 3\,FeBr_2 + 4H_2O + Br_2$
A variation proposed and modelled by the Argonne National Laboratory[12] would combine steps [3] and [4] as:
[3*] Bromine regeneration using non-thermal plasma:
$2HBr + \text{plasma} \leftrightarrow H_2 + Br_2$
Practical economic application of these concepts remains a major technical hurdle.

By contrast, the well-known steam-iron cycle has been a practical, if inefficient, production technology for many years. In essence, high temperature steam is exposed to iron metal or reduced iron oxides, liberating pure hydrogen and forming higher iron oxides. To complete the cycle, these iron oxides are gas reduced at elevated temperature. Schematically, this cycle can be represented as in Figure 1.

Industrial Research has proposed a new metal-oxide-based thermochemical cycle for hydrogen production.[2] While earlier technologies have used coal and coal gas as the reductant there is the potential in New Zealand to use a CO/H_2 *syngas* generated from wood biomass. A thermodynamic assessment of the cycle chemistry indicates that the generation and regeneration steps are thermodynamically permitted over a wide range of temperatures below 700°C. These process conditions are readily achieved using wood biomass-derived heat energy and CO/H_2 biosyngas reductants, giving a process that is *carbon-neutral* in terms of CO_2 emission legislation. The clear separation of generation and regeneration legs eliminates risk of CO/CO_2 contamination in the hydrogen gas stream. IRL's research partners at CRL Energy contribute considerable expertise in both coal-derived and biomass-derived engineering and gasification technologies. Industrial Research has a primary patented IP position from which to launch this science and technology development.

Hydrogen manufacture through thermally assisted electrolysis of water

The benefits of thermo-electrolysis of water have been recognised for several decades, yet no system has been commercialised, mainly due to demanding materials requirements. The total energy required to split water into H_2 and O_2 at a given temperature has both electrical and thermal energy components, with the electrical component becoming less dominant as the cell temperature and/or pressure is increased. Calculations demonstrate the efficiency to be gained through undertaking electrolysis at elevated temperature and pressure: at 1000 °C and 1 bar H_2O pressure the reversible potential requirement drops to 75% of its room temperature value, whereas at 1000 °C and 500 bar the reversible potential drops to 47% of its room temperature value (both for H_2 at 1 bar).[13]

To capture the immediate benefit of electrolysis under high pressure-temperature conditions, there is a need to design and develop a very high surface area, low electrical resistance conductor that will reduce the power loss caused through heat dissipation in the electrode/electrolyte assembly. Industrial Research has proposed a research strategy involving both high temperature ceramic conductors and high pressure-temperature technologies that together provide the basis for a unique solution for this goal by a process equivalent to designing a high temperature fuel cell operating in reverse.[2]

Overview of Hydrogen Storage Technologies and Opportunities

The search for viable hydrogen storage systems for transportation and stationary applications is accelerating. *Viable* implies safe, fuel efficient, weight efficient, and cost effective. The international focus has been set by the US Department of Energy who have established benchmark storage targets for transportation applications. An initial Department of Energy target for *onboard* hydrogen storage systems of 6.5 wt% has more recently been upgraded into a developing series of targets:[14]

- 1.5 kWh/kg (4.5 wt%), 1.2 kWh/L, and US$6/kWh by 2005
- 2 kWh/kg (6 wt%), 1.5 kWh/L, and US$4/kWh by 2010
- 3 kWh/kg (9 wt%), 2.7 kWh/L, and US$2/kWh by 2015

In parallel with these transportation targets, low cost, *off-board* hydrogen storage systems will be required for hydrogen infrastructure needs to support the transportation, stationary and portable power markets by 2015.

Three strategies for hydrogen storage can be envisaged.

1. Physical storage - tanks for either compressed hydrogen gas or liquid hydrogen.
2. Reversible chemical storage – storage of hydrogen in solid materials so it can be released and refilled without physically removing the storage medium from the vehicle.
3. Irreversible chemical storage - releasing hydrogen via an on-board chemical reaction with the storage material and replenishing the hydrogen off-board.

The established physical storage technologies using high gas compression or liquefaction cannot meet the energy density targets with existing metal alloy containment vessels. Typically, hydrogen stored at 200 bar in a steel cylinder represents only ~1 wt% of the total stored mass. Potentially, lightweight composite storage vessels with improved performance may be developed over time, although these will still incur high cost overheads associated with the gas compression. A simple illustration highlights the infrastructure challenge that must be faced: a good size filling station may sell 25 tonnes of fuel each day. One 40 tonne tanker can deliver this fuel, but it would need 21 hydrogen tankers to deliver the same amount of energy to the filling station as compressed gas.

To achieve the Department of Energy targets new approaches to hydrogen storage are needed, specifically the identification of chemical solutions. There are excellent recent reviews on this subject that will give readers more detailed information and extensive references beyond this brief survey.[15,16] Some of the families of materials for chemical storage of hydrogen are briefly described below:

Metal Hydrides

For the best part of 30 years there has been active international research in metal hydrides, focused mainly on the IIIB, IVB, and VB transition metal groups, including

the lanthanide and actinide series. Hydrogen is stored interstitially in vacancies or defects in the metal structure, leading to the potential for relatively fast adsorption-desorption kinetics but with a storage capacity that is only rarely above 2 wt%. Metals are classified according to their ability to bind hydrogen strongly (A type) or weakly (B type), with control of the A-B balance and the introduction of other doping metals used to design suitable adsorption-desorption rates in windows of pressure-composition-temperature near ambient pressure and temperature. The result is an alloy classification system into families such as AB_5, *e.g.* $LaNi_5$, AB_2, *e.g.* $TiCr_{1.2}V_{0.8}$, and AB, *e.g.* $TiFe_{0.85}Mn_{0.15}$. A key reference tool for all metal hydride researchers is the US Department of Energy sponsored Sandia Hydride Database.[17,18] Metal hydride storage systems for small or stationary applications are already commercially available through companies such as ChevronTexaco or Hera.[19,20]

Complex Hydrides

Whereas metal hydride storage systems are dominated by transition metals which limit gravimetric hydrogen storage to a few percent, the Group 1-3 light metals (Li, Na, Mg, B, Al) can form complex hydride systems having high theoretical hydrogen storage capacity. These light metal hydrides have high-energy ionic or covalent bonding so the pressure-temperature conditions required to achieve hydrogen reversibility are demanding. For example, lithium borohydride ($LiBH_4$) contains 18.4 wt% H_2, but how are we to release and recharge hydrogen from this material.

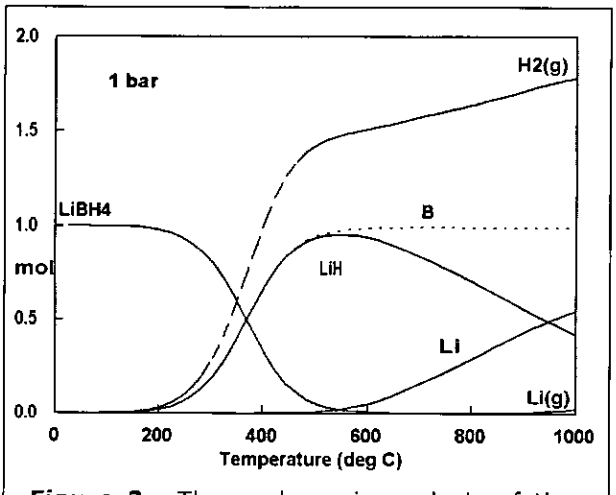

Figure 2. Thermodynamic analysis of the thermal decomposition of $LiBH_4$ at 1 bar pressure.

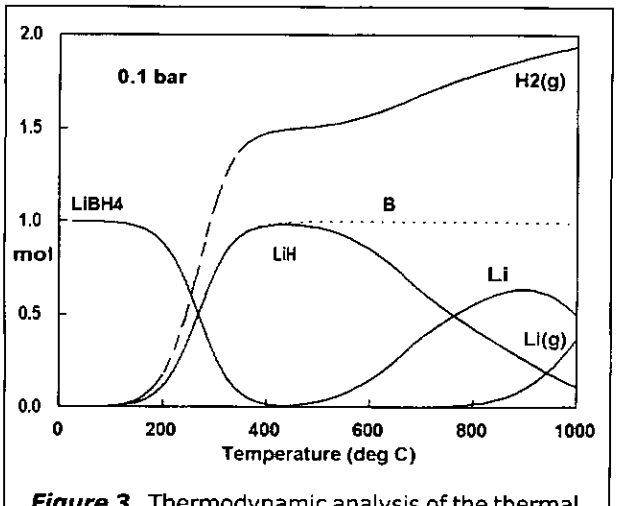

Figure 3. Thermodynamic analysis of the thermal decomposition of $LiBH_4$ at 0.1 bar pressure.

Figure 2 shows the thermodynamic equilibrium achieved by simply heating $LiBH_4$ to maintain 1 bar total gas pressure in an inert gas environment. Decomposition commences above 200 °C and is complete by 600 °C, but some hydrogen is retained in the stable lithium hydride phase until much higher temperatures. The reaction equation can be summarised as:

$$LiBH_4 \rightarrow B + LiH + 1.5H_2(g) \quad (1)$$

Continuous removal of the H_2 gas (lowering the partial pressure of H_2) will force the reaction to the right. This effect can be simulated using a reduced pressure calculation (Figure 3), which demonstrates at least 100 °C reduction of the decomposition temperature when the total gas pressure is reduced to 0.1 bar.

An alternative strategy for hydrogen recovery from $LiBH_4$ is through hydrolysis. In this case the reacting water can be split to contribute additional hydrogen beyond that available from the lithium borohydride.

$$LiBH_4 + 4H_2O \rightarrow LiOH + H_3BO_3 + 4H_2(g) \quad (2)$$

However, no viable regeneration process for the reformation of lithium borohydride from the products of equations 1 or 2 has yet been developed.

The most studied complex hydride system in recent years has been sodium alanate ($NaAlH_4$) which undergoes a two stage dissociation process on heating:[21]

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2(g) \quad (3)$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + 1.5H_2(g) \quad (4)$$

This system has been shown to reversibly adsorb and desorb up to 4.2 wt% hydrogen when catalysed by Ti-doping and subjected to pressure-temperature schedule, but this falls short of the Department of Energy transport targets.

A complex metal hydride system showing immense potential is sodium borohydride, $NaBH_4$. This material contains 10.6 wt % H_2 and is a well-known reducing agent in organic and organometallic chemistry. Once stabilised by the addition of a small quantity of sodium hydroxide, aqueous solutions of $NaBH_4$ are non-flammable and form a stable and safe means to store hydrogen. On exposure to a suitably configured ruthenium catalyst, hydrogen is released from both the sodium borohydride *and* the water.

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2(g) \quad (5)$$

Patents to this process are held by the Millenium Cell Corporation, but no viable sodium borohydride regeneration process has been demonstrated.[22] Very recently however, Industrial Research and the University Canterbury have designed and patent protected a novel

process for the reformation of sodium borohydride from sodium metaborate, which may provide the key for serious exploitation of $NaBH_4$ as a hydrogen storage material.[2]

Physisorbed Hydrogen

Materials with large specific surface areas such as zeolites, nanostructured carbon species or carbon nanotubes are potential substrates for physisorption of hydrogen. The interactions between hydrogen and such substrates are weak, so significant physisorption is generally only observed at low temperatures (77 K). A flurry of excitement regarding spectacular claims for hydrogen storage in carbon nanotubes has recently become more muted as numerous research groups have failed to duplicate the original results.[16,23] Current indications are that hydrogen is physisorbed in proportion to the specific surface area of the carbon nanotubes and is limited to about 2 wt% for carbon materials.

One of the newest areas of interest for hydrogen storage is in organic and metal-organic framework structures. Yaghi and co-workers have recently synthesised microporous metal-organic frameworks (MOFs) in which Zn_4O-based entities are connected via naphthalene or benzocyclobutene linkers to form a cubic three-dimensional structure capable of physisorbing a variety of gases, but most notably hydrogen.[24] Some 2 wt % H_2 was stored in the pore structure at 78 K and 10 bar pressure and was reversibly released on exposure of the material to ambient pressure and temperature. The quantity of hydrogen stored was shown to be closely related to the cage dimensions, which were in turn controlled by the selection of the organic linker. Neutron scattering spectroscopy indicated two discrete hydrogen binding sites associated with the Zn and the organic linker group. This area represents an outstanding opportunity for innovative metal-organic materials design and synthesis, where New Zealand chemists could make a strong contribution of international value. Industrial Research together with partners at the Universities of Canterbury and Otago, have proposed a new initiative in this field.[2]

Summary

New Zealand's ability to implement a future hydrogen economy will be greatly accelerated if local researchers can design and develop advanced technology solutions for the manufacture and storage of clean hydrogen. This will not only enable New Zealand to participate in the new technologies that fuel cells will deliver internationally but will seed a suite of new commercial opportunities while providing environmentally sustainable solutions to meet our future energy needs.

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PRODUCTION OF HIGH PURITY HYDROGEN FROM COAL FOR USE IN FUEL CELLS

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**Based upon an invited lecture presented at Chem Ed 2003, July 2003.*

Introduction

In the past financial year, CRL Energy Limited (CRL) and Industrial Research Limited (IRL) were granted funding from the Foundation for Research Science and Technology for a joint project to develop a technology platform for moving New Zealand towards a hydrogen-based energy economy.

The move toward hydrogen energy is a global one and is rapidly gaining momentum.[1-8] It is driven by factors such as the need to meet increased energy demand using clean - ideally *zero-emissions* – technologies, the need for increased energy security, and advances in hydrogen utilisation technologies of which fuel cells are probably the most well known example.

What is a Hydrogen Energy Economy?

There are several definitions including *a future where hydrogen is the accepted means of storing and transporting energy* and the US Department of Energy definition that sees hydrogen as *a secure and clean energy future.* These are undoubtedly true but we would also add that a hydrogen energy economy is a future, which offers flexibility and opportunity within the energy sector.

The reasoning behind this thinking is illustrated in Figures 1 and 2. All energy systems may be regarded as a chain of events comprised of five links.[9] The two end links are the services that people require and the energy sources that nature provides. In between are the three essential links – a transformer technology, an energy carrier, and a service technology – needed to convert what nature provides into what people require. The region extending from sources through transformer technology to energy carrier may be regarded as the energy sector.

Figure 1 shows two common existing examples. In one case the requirement is to gain liquid refreshment. The service technology is a refrigerator, the energy carrier is electricity and, in most cases in New Zealand, this will have been generated by water falling through a hydraulic generator. The other requirement in Figure 1 is to get from point A to B at a fairly rapid rate. The service technology is a car, the energy carrier is petrol (gasoline) and this will have come from an oil refinery.

Figure 2 shows the impact of introducing hydrogen. It will be seen that the energy sector becomes much more expansive (opportunity and flexibility), a range of energy sources now come into the mix (opportunity and flexibility), petrol is no longer required as an energy carrier, and the two energy carriers that remain (hydrogen and electricity) are readily inter-convertible (flexibility).

It should also be noted that since arguably every nation has at least one of the energy sources in abundance, the basic promise offered by hydrogen energy is that of clean, reliable energy for all, forever. Hence the global interest in developing it and the massive research effort being made to make that promise a reality.

Some highlights to date include the opening of the world's first hydrogen energy centre in Las Vegas (Nevada) in November 2002. Here natural gas is converted to hydrogen by steam reformation and the hydrogen used both to power a small fleet of cars and to provide heat and power for the

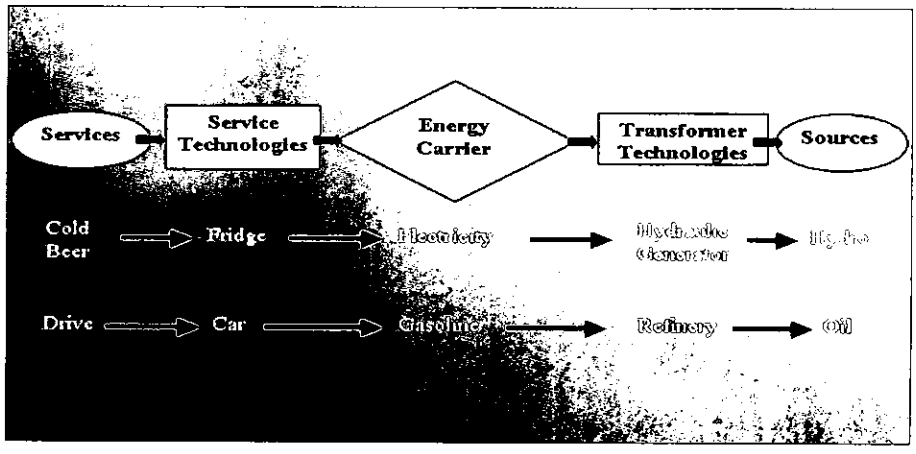

Figure 1: Current energy system example.

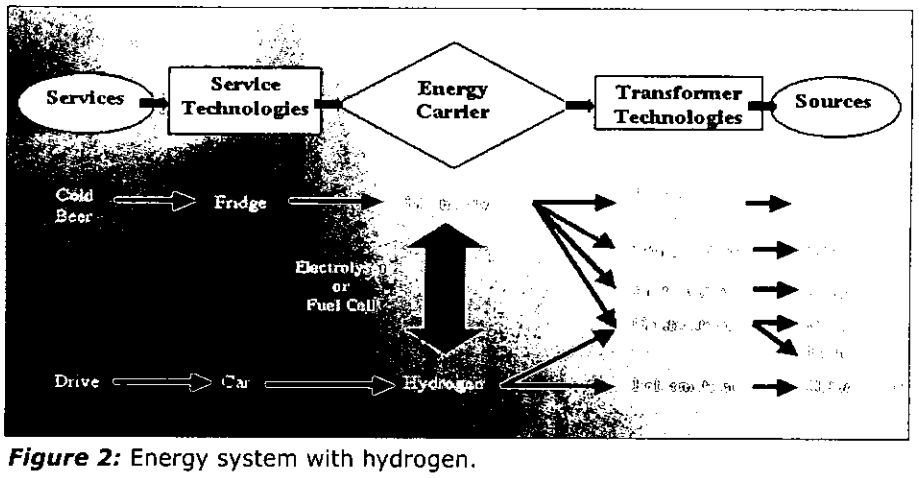

Figure 2: Energy system with hydrogen.

facility. Orange County (California) is also trialling a fleet of cars powered by hydrogen fuel cells and has installed five refuelling sites within the greater Los Angeles area. Major car manufacturers Honda, Mitsubishi, Toyota, Ford, General Motors, and Daimler Benz are producing their first commercial fuel cell powered vehicles, and Iceland is on track to become the world's first country to run on hydrogen energy. Government and industry investment into hydrogen energy is also increasing rapidly; big oil companies are investing heavily in hydrogen energy.

It should be noted that while the ultimate aim is to produce hydrogen from renewable energy sources (wind, solar, biomass) it is generally accepted that there will be a transitional phase during which significant quantities of hydrogen will be produced from fossil fuels (natural gas and coal). To achieve the goal of *zero-emissions* energy requires management of the CO_2 produced with the hydrogen. Research investment into CO_2 capture and sequestration (geological or ocean) is the single largest item on the energy research investment budget of most of the world's developed countries.

The CRL/IRL programme

A major part of the CRL/IRL research programme is to develop and demonstrate the *coal* to *high purity hydrogen* to *electricity* package at the 50 kW scale. This is a suitable scale for distributed electricity generation and is likely to find initial application in remote rural areas that may be targeted for removal from the grid. Development of the package is also extremely challenging and requires building a significant pool of expertise in hydrogen energy. In terms of Figure 2, it corresponds to the pathway leading from coal via gasification to hydrogen via a fuel cell to electricity.

The Gasification Step

New Zealand has an estimated 8.6 billion tonnes of economically recoverable coal[10] reserves with an energy equivalent of at least 50 Maui gas fields. This has the potential to reliably meet energy needs for over 700 years if required.

Previous research at CRL[11] has shown that 90% of New Zealand coal reserves are well suited towards a particular type of technology known as *fluidised bed gasification*. The construction, commissioning and operation of a fluidised bed gasifier is therefore the first step in the project.

There are a range of coal gasifiers available but all of them are, in essence, containers into which is fed coal, air or oxygen, and steam and then devolatilisation, combustion and gasification occurs inside the container.

In the devolatilisation zone, the coal is heated to release volatiles and form a char.

Coal + heat → C (char) + volatiles

It is necessary to combust a portion of the fuel in order to provide the heat needed to devolatilise the coal and to drive the endothermic gasification reaction. For this reason a sub-stoichiometric quantity of air (or oxygen) is fed in with the coal:

$$C + O_2 \rightarrow CO_2$$

In the gasification zone, a large number of reactions may occur but the one that initiates the gasification process and on which all subsequent reactions depend is the endothermic reaction between char and steam:

$$C + H_2O \rightarrow H_2 + CO$$

One of the most important subsequent reactions is the water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Depending upon temperature and pressure, the Boudouard reaction,

$$C + CO_2 \leftrightarrow 2CO,$$

methane formation,

$$C + 2H_2 \leftrightarrow CH_4$$

and the steam reforming reaction

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$

may also take place, among others, within the gasifier zone.

Despite its importance and the amount of research investment aimed at understanding it, there appears to be no consensus regarding the mechanism of the gasification reaction. However, for our purposes the important criterion is that it occurs at a sufficiently rapid rate.

A fluidised bed coal gasifier (Figure 3) consists of a bed of fine refractory particles (sand or ceramic is commonly used) positioned above a dispersion plate. This is a metal disc containing a large number of small holes. Air is fed in

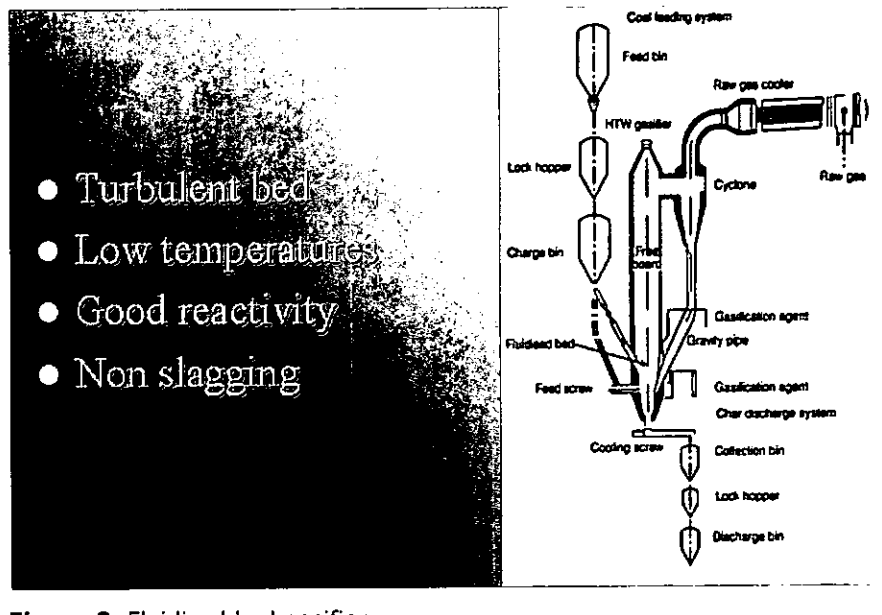

Figure 3: Fluidised bed gasifier.

from beneath the plate at a sufficient rate to lift the bed particles off the plate and induce a turbulent motion in the bed, *i.e.* to fluidise it. The coal particles (typically 6 mm topsize) are fed into this turbulent bed, as is a separate flow of steam. Because of the fine particle size, good mixing and long residence time in the bed it is possible to carry out the gasification process at low temperatures (800 to 1000 °C) compared to other gasification processes.

An essential feature of fluidised bed gasification is that the char derived from the devolatilisation process must be sufficiently reactive at these low temperatures. It is also important that the mineral matter in the coal does not form a low melting ash because the presence of oversize agglomerations in the bed is generally unfavourable towards good fluidisation. It is also evident that the walls of the gasifier are constantly subjected to bombardment by fine, hard particulates and it is wise to construct the gasifier of erosion resistant material. A large database of ash melting temperatures is available on New Zealand coals. The data strongly suggest that formation of bed agglomerates will not be a major issue.

Previous research carried out by CRL[11-13] clearly established that chars derived from a wide range of our lignite and sub-bituminous coals readily meet the reactivity requirement. In these experiments, samples of coal were charred in a small bench top-scale devolatiliser while fluidising under a nitrogen flow. The char was transferred under nitrogen flow into a small scale fluidised bed assembly and after stabilising at 800 °C, degassed, distilled water was injected through a syringe pump into the heated nitrogen gas stream. The product gas flowed through a condenser assembly, drying tower and particulate removal device to an MTI M200 gas chromatographic gas analyser. The concentrations of product gases (H_2, CO, CO_2, CH_4) and N_2 were measured every 90 seconds. Gasification was continued until at least 20% by weight of the carbon originally present had been consumed, by which time the gas composition had become steady. The reaction rate at the point of 20% consumption was calculated and compared with that obtained for Australian and German brown coals for which fluidised bed gasification was originally designed and developed.

The results clearly showed that the New Zealand coal-derived chars were anywhere from 1.1 to 1.7 times as reactive as their Australian and German counterparts. In addition, it was found that the syngas product was significantly richer in hydrogen than those typically obtained from the German and Australian coals.

The reason for the high reactivity and high hydrogen yields was found[11-13] to be due to ion-exchanged calcium attached to carboxylate sites within the coal. When charring occurs, the carboxylate sites are destroyed and the calcium ends up as microcrystalline deposits of calcium oxide spread throughout the char. These are responsible for catalysis of the gasification reaction and for pushing the equilibrium of the water gas shift reaction towards the right hand side thereby increasing the yield of hydrogen in the syngas.

Again, there is a degree of debate over the exact nature of the catalysis mechanism.[3,14,16] The following sequence is commonly cited:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO \rightarrow CaCO_3 + H_2$$

$$CaCO_3 + C \rightarrow CaO + 2CO$$

Overall $C + H_2O \rightarrow CO + H_2$

Similarly, there is still debate over the ability of calcium to influence the water-gas shift equilibrium.[17,18] Often cited is:

$$CO_3^{2-} + H_2O \leftrightarrow 2OH^- + CO_2$$

$$2OH^- + 2CO \leftrightarrow 2HCO_2^-$$

$$2HCO_2^- \leftrightarrow CO_3^{2-} + HCHO$$

$$HCHO \leftrightarrow H_2 + CO$$

Overall $CO + H_2O \leftrightarrow CO_2 + H_2$

The main consideration for our project is to design the gasifier and the gasification operation so as to enable the naturally occurring calcium to fully display its catalytic abilities. Our initial prototype uses air rather than oxygen and runs at or slightly above atmospheric pressure. It is, therefore, an example of an air blown, atmospheric, non-agglomerating, fluidised bed coal gasifier.

The syngas clean-up line

The syngas emerging from the gasifier contains a range of components besides hydrogen. These include particulates carried over from the bed, condensables, and tars from incomplete cracking of the volatiles released in the devolatilisation stage, H_2S, COS, CO, CO_2, CH_4, N_2, HCN, NH_3, and volatile trace metals. All must be removed in order to produce a hydrogen stream of sufficient purity to be utilised in the alkaline fuel cell of IRL.

The first stage of the clean-up line consists of an inertial cyclone designed to remove most of the particulates from the gas stream. A Venturi scrubber device where the remaining particulates, condensibles, tars, volatile trace metals, HCN and NH_3 are removed, follows this. The scrubber is in essence a fine water spray and although effective in removing the target species it does generate a waste stream. The bulk of the waste is recovered condensables and tars that may be recycled to extinction or, possibly, used for feedstock for value added processes. It may be noted that at this stage of the clean-up process we have produced a high hydrogen component syngas free of particulates. It is highly probable that this gas stream could be used in internal combustion engines or possibly micro turbine systems and it is envisaged that, contingent on obtaining suitable funding, these alternatives also will be evaluated.

Following the Venturi scrubber the syngas passes to an H_2S removal tower. A range of possibilities is available but the most suited for our purposes consists of a highly H_2S-selective tertiary amine in a packed column:

$$H_2S + R_3N \leftrightarrow R_3NH^+ + HS^- \text{ (fast)}$$

$$CO_2 + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \text{ (slow)}$$

$$2H_2S + SO_2 \leftrightarrow 3S + 2H_2O \text{ (Claus Process)}$$

Although the affinity of the amine for CO_2 is very much less than for H_2S, the concentration of CO_2 in the syngas is considerably greater and this can lead to less than desired removal levels of H_2S. Our targeted concentration in the emerging syngas is <5 ppm. Again this process produces a waste stream but it is possible to release the captured H_2S into a Claus oven and convert it to elemental sulfur plus steam. This not only cleans up the waste stream, it also produces a saleable commodity.

By this stage of the process the syngas is comprised of hydrogen, CO, CO_2, CH_4 and N_2. Again this may be used by technologies less demanding of hydrogen purity than the alkaline fuel cell.

The next stage in the clean-up line is a water gas shift reactor to complete the conversion of CO to CO_2 plus H_2O. This is normally carried out over a Cu-Zn/oxide catalyst and initial designs include this option. For the final clean-up stage, a Pressure Swing Adsorption (PSA) unit may be employed. This will generate a hydrogen stream of sufficient purity for the alkaline fuel cell and divert a waste stream comprised mainly of CO_2, N_2 with a little CH_4. At the small scale needed for 50 kW, the PSA unit will not perform optimally and some H_2 will also be diverted with the waste stream. This waste stream will also need to be managed and one objective of the programme is to model its behaviour under geological sequestration in a deep aquifer.

A range of options are currently being identified for the final stages of the clean up with a view to trialling them. These include membranes being developed internationally for high efficiency H_2 separation at volumes and flow rates better suited to our needs and combined water gas shift /H_2 separation membranes. Part of the IRL involvement in the programme focuses on membrane development. Hydrogen filters are also available and may be used – at least in the early stages of our development of the clean-up line.

The alkaline fuel cell

As for all fuel cells, this consists of an anode section where the high purity hydrogen is ionised,

$$2H_2 \rightarrow 4H^+ + 4e^-$$

a cathode where the hydrogen ions react over a catalyst to regenerate water,

$$O_2 + 4H^+ + 4e^- \rightarrow 2\ H_2O$$

and an electrolyte, in this case a solution of potassium hydroxide, to allow the positively charged ions to flow from anode to cathode.

One issue with fuel cells is that the catalyst is usually platinum-based and this can add significantly to their costs. However, a very vigorous research programme is being undertaken worldwide to identify cheaper alternatives and the US Department of Energy has set itself the target of reducing fuel cell prices from present levels (around $US1,000/kW output) to levels comparable with existing internal combustion engines (around $US20/kW) by 2015.

Other issues

Hydrogen production and utilisation technologies are just two of the issues associated with the move towards a hydrogen energy economy. Hydrogen storage and distribution also represent considerable technological challenges. Equally important is the need for education and public outreach and the drawing up of a set of safety protocols for operating a hydrogen energy economy.[6]

At a recent hydrogen investment roundtable held in Denver, the Director of the National Renewable Energy Laboratories, himself a former Apollo astronaut, remarked that the Apollo programme was *complex, but nothing like this* (the transition to a hydrogen energy economy). Clearly the transition to a hydrogen energy economy will not be easy but the rewards - a clean, secure supply of energy for all forever – are great. The implications for society generally are greater still.

Acknowledgments

We wish to thank the Foundation for Research, Science and Technology for their investment in this programme and to acknowledge the role of Solid Energy New Zealand Ltd, Meridian Energy Ltd, and BP New Zealand Ltd for their involvement in the governance of this programme.

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Chemistry at the Interface

2003 Conference, Nelson
30 November – 4 December

NZIC Conference venue:
The Rutherford Hotel

Foyer Rutherford Hotel

Scope

This year's New Zealand Institute of Chemistry (NZIC) international conference focuses on 'Chemistry at the Interface'. It will explore a variety of the interfaces associated with chemistry, including:

- Synergy with materials science
- Commercial development
- Biology and drug discovery
- Interdisciplinary methodologies

On the following page you will find the conference programme (may be subject to late changes).

Venue

The Nelson region is an outstanding centre for recreation with beaches set in an area of native bush and sheltering mountain ranges, which give it a Mediterranean climate.

Registration

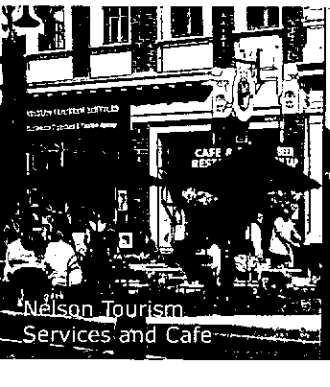
The conference registration fee for NZIC members and students are NZ$450 and NZ$190.

Details for the conference are available from:
www.chem.canterbury.ac.nz/nzicconf03.htm

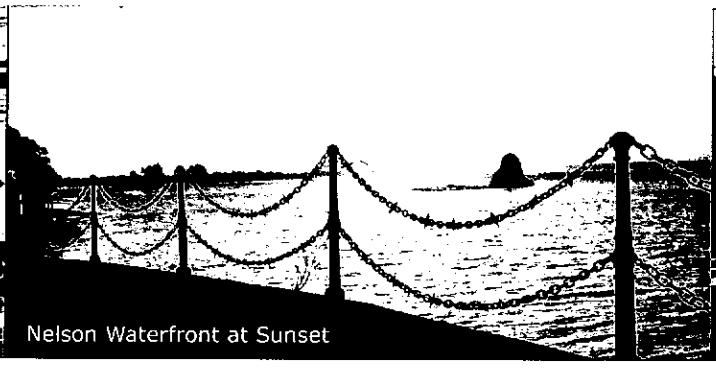
Invited Speakers

Chris Abell (Cambridge)
Paul Clemons (Harvard)
Terry Collins (Carnegie Mellon University)
David Fairlie (Queensland)
Craig Hawker (IBM)
Cameron Kepert (Sydney)
Andy Phillips (Colorado)
Vickie McKee (Loughborough)
Dieter Seebach (ETH, Zürich)
John Tallarico (Harvard)

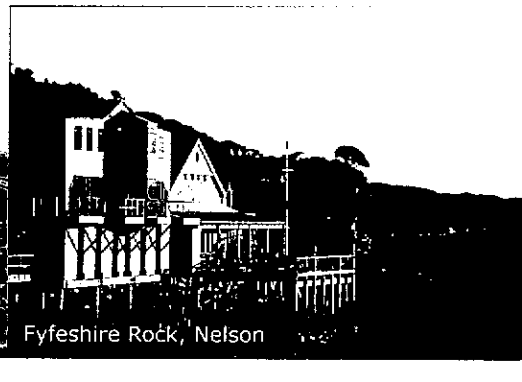
Ted Baker (Auckland)
Mike Boland (Fonterra)
Margaret Brimble (Auckland)
Paul Callaghan (Victoria)
Bill Denny (Auckland)
Gary Evans (Industrial Research Ltd)
Shaun Hendy (Industrial Research Ltd)
Murray McEwan (Canterbury)
Kathryn McGrath (Otago)
Brian Nicholson (Waikato)
Warren Roper (Auckland)
Ian Shaw (ESR)
Rob Smith (Otago)
Peter Steel (Canterbury)
Carol Taylor (Massey)
Selwyn York (NZ Pharmaceuticals Ltd)



Nelson Tourism Services and Cafe



Nelson Waterfront at Sunset



Fyfeshire Rock, Nelson

TIME	SUNDAY 30th Nov, 2003	MONDAY 1st Dec, 2002	TUESDAY 2nd Dec, 2003	WEDNESDAY 3rd Dec July, 2003	THURSDAY 4th Dec, 2003
08.30		Plenary Lecture 2 **COLLINS**	Plenary Lecture 5 **BAKER**	Plenary Lecture 9 **CALLAGHAN**	**Workshop** Rochfort Gordon Simpson Williams Hodgkinson
09.30		Plenary Lecture 3 **MCKEE**	Plenary Lecture 6 **FAIRLIE**	Plenary Lecture 10 **KEPERT**	
10.30		**Coffee Break**	**Coffee Break**	**Coffee Break**	**Coffee Break**
11.00		*Sympos. A* Brimble Newman *Organometallic* Roper Nicholson	*Sympos. B* McDonald McEwan *Sympos. C* McKinnon C. Abell	*Sympos. D* Steel Vos *Materials* McGrath Hendy	Henshaw S Johnson Long Zuelicke
12.00		Parker de Raadt Stocker (S) *Industrial* P. Shaw Dunningham Dawson Spencer Curnow Wright	Holroyd D. Smith Miskelly Easterfield Lecture **TAYLOR** Yorke Franich Boland	Bubendorfer M Johnston Fleming (S) *Nat Prod* Munro Holland van Klink *Workshop* Blaikie Lynch Bradley	
13.00		**LUNCH**	**LUNCH**	**LUNCH**	**LUNCH**
14.00		*Sympos. A* Denny Evans *Environ. & Analytical* Quilliam Hinton	Plenary Lecture 7 **PAUL CLEMONS**	Plenary Lecture 11 **HAWKER**	Gooch Borrmann Chen
15.00	**Registration**	More Lane Hill (S) *Cyclic* White Hajós Halton Gaw (S) Baronian Kilmartin	Plenary Lecture 8 **JOHN TALLARICO** *Sympos. B* Sherrington *Sympos. C* R Smith	*Sympos. D* Parbhu Ballantyne(S) Grigsby *Synthesis* Narasaka Edmonds Ferreira *Workshop* Wiseman J Johnston Gabbitas	Wagner **Coffee Break**
16.00		**Coffee Break**	**Coffee Break**	**Coffee Break**	Abrahamson Edgar Spencer
16.30	**WELCOME** **MIXER**	Plenary Lecture 4 **I. SHAW**	*Sympos B* Downard Peake Travas-Sejdic *Coordin* Howell (S) Ainscough Blackman *Sympos. C* Robinson Singh Van Enckevort	Plenary Lecture 12 **C. ABELL**	
17.30				**Conference Closing and Student Prizes**	
18.00	*Opening* Plenary Lecture 1 **SEEBACH**	**POSTER SESSION I** **(Mixer)**			
19.30	Free for dinner		**CONFERENCE BANQUET**		

Symposium A – Interface of Chemistry and Biology; **Symposium B** – Techniques and Technologies of Chemistry at the Interface; **Symposium C** – Interface of Chemistry with the Commercial Sector; **Symposium D** – Interface of Chemistry with Materials and Nanotechnology:

BRANCH NEWS

NZIC Chemical Education Trust 2003 Distribution

The NZIC Chemical Education Trust Trustees (Philips, Peterson and Holland) announce that about half of the applications received for Chemical Education Trust grants this year were successful. Moreover approximately half of the trust income for the 2002/3 financial year has been committed to the grants with the balance held to ensure that the fund monies keep pace with inflation, a policy they plan to continue into the future. While the grants range from $200 to $600, and are small in themselves, they can make a significant difference in an environment where school funding is limited. For this reason the Trustees encourage members and readers to make donations to the Chemical Education Trust (to the NZIC Secretariat) noting that amounts above $5 are deductible for income tax purposes under the law.

The 2003 recipients are:

North Southland College *(Jean Little)* - towards the cost of chemicals for magic show(s).

Queen Margaret College, Wellington *(Suzanne Boniface)* - towards the cost of Molymod kits.

Taihape College *(Harry Nichol)* - towards the cost of a distillation still column.

Tararua College *(Arthur Forster)* - towards the cost of Polchem CD software.

Wanganui High School *(Ian Thomas)* - towards the cost of Efofex software.

Brian Halton

CANTERBURY

The presentation for our September meeting was from the 2003 Royal Society of Chemistry Australasian Lecturer. **Geoff Jameson**, a former graduate of the University of Canterbury and now a Professor at Massey University, gave a seminar *Structural Basis of Redox Tuning and Metal Specificity of Mn and Fe Superoxide Dismutases* and explained how superoxide dismutases are important virulence factors of mammalian pathogens. He went on to present crystallographic structures of the Y147F mutant of Mn-Superoxide Dismutase from *Escherichia coli* at a resolution of 0.90 Å. This unprecedented resolution provides insight into the active site, in particular into the location of hydrogen atoms in the vicinity of the metal centre. Geoff's presentation was well received and a very lengthy questions and answers session followed.

In October **Professor David Bibby** gave his Presidential address to the NZIC Canterbury Branch. Despite being billed as *Chemistry in the 21st Century - One Person's View*, the talk was actually much more wide-ranging, covering four key issues for the 21st century: population change, energy sources, biotechnology, and climate change. Examples included:
- the dominant effect in population in this century will be a shift to an older age distribution (particularly in China), rather than huge population growth
- energy sources involve significant trade-offs between inherent energy value and storage requirements and portability, which will affect our future energy choices
- nanotechnology and the development of circuits and components at the molecular level. Dave also spoke about the changes in the NZIC in recent years, particularly the changes that must come as a result of reduced membership - from a peak of around 1500 to under 1000 in recent years. Despite these difficulties, Dave was complimentary about the meetings and enthusiasm of the Canterbury Branch. At the conclusion of this meeting we drew our second raffle for the year in support of the Chemistry Olympiad. Again the winner was a member of the chemistry department's technical staff. Congratulations to **John Davis**.

ESR News

Professor Ian Shaw, programme leader of ESR's Food Safety group, was appointed to the New Zealand Food Safety Advisory Board. The board advises Annette King (Minister for Food Safety) and the New Zealand Food Safety Authority on issues of food safety.

Dr. Paul Fitzmaurice joined the ESR Food Safety Group in Auckland as a senior scientist (toxicologist) in October. Paul has come to New Zealand from the position of head of the toxicology laboratory at the Centre for Addiction and Mental Health in Toronto, Canada. His areas of research interest include antioxidants, oxidative stress, and xenobiotic toxicology. Whilst furthering his work in these areas, Paul will also be managing the Auckland-based activities of ESR's Food group.

University of Canterbury

There have been a number of successes in the Chemistry Department recently. Apart from the mentioned awards

we have survived, so far a Contributions Margins exercise, the PBRF exercise, and the first round of restructuring.

Firstly, the department congratulates **Professor Jim Coxon** who has won the Canterbury University Research medal for 2003. Jim said, "The big honour for me was having my colleagues nominate me...that was what has delighted me the most." This is only the 6th time this medal has been presented and the second win for chemistry.

Peter Steel is the principal investigator on a recently awarded Marsden grant entitled *Molecular Cages of Controlled Size and Shape*. He also features in the latest ARC research grant round, where he is a partner investigator in a project with **Richard Keene** (Townsville) and **Jo Hupp** (Northwestern University) entitled *Intervalence Transfer in Polymetallic Assemblies*, which was awarded $A240,000 over 3 years. Well done Peter. **Andrea Cusiel** and **Sam Yu** jointly won the Fenwick prize for the best Honours or Masters student demonstrator. The Ralph Earle prize for the best second year PhD student seminar went to **Liesl Marsh.**

Science Outreach, based in the Chemistry Department, has just obtained a $11,000 grant from the Community Trust to assist with the running of physics workshops for science teachers and to contribute to travel and accommodation for teachers from the Nelson-Marlborough regions. This means that they will add two workshops next year to the one that they had already planned for late November.

Again the department's life has been enriched by a number of visitors. We have been pleased to have **Professor Edwin Constable** (University of Basel, Switzerland) for a month, as a visiting Erskine Fellow. Ed is a leader in the field of metallosupramolecular chemistry (indeed he coined the term). As well as undertaking a series of undergraduate lectures he presented two departmental seminars. The first, *From supramolecular chemistry to nanoscience* dealt with the design of photoconversion systems based upon photoactive coordination compounds. The seminar covered the methodology of supramolecular coordination chemistry and its extension to self-assembly reactions on surfaces. The second of his seminars subtitled *The Wonderful World of Self-Assembly* gave solace to a number of students by proving that academic supervisors don't always understand everything! He outlined some of the more unexpected results obtained when investigating self-assembly reactions between silver salts and bipyridyl-pyridazines and tetrazines.

We have recently welcomed **Professor Arnon Shani** (Department of Chemistry, Ben-Gurion University of the Negev, Israel) for a five-week visit. Arnon is an organic chemist with specific interests in the chemistry and entomology of pheromones, their isolation, identification, synthesis and application in pest control; slow release of pheromones; Jojoba wax chemical transformations and industrial application.

And our old friend **Dr. James Edgar Hudson** arrived on the 24th October for another stint of six months or so working with **Peter Harlan's** research group. Jim has been a long-time Adjunct Senior Fellow and we always look forward to his annual visits.

Chemistry Department staff have also been on the move. **Rod Claridge** spent some time in Germany after attending the Denver ESR Conference, which he reported as being very good, as usual. He said for him it was especially good to have to have three of his former students, **Allan McKinley**, **Charles** and **Nick Lees**, presenting work there. Also at the meeting, for the NMR stuff, was **Gillian Nichols**. **Bryce Williamson** attended the Gordon Research Conference on the Chemistry and Physics of Matrix Isolated Species (Bates College, Lewiston, Maine) in July, where he presented an oral paper on *Jahn-Teller coupling in the ground and excited states of the ferricenium radical isolated in argon*. In August he not only attended but also was on the organising committee of the 14th International Conference on Dynamical Processes in Excited States of Solids, held in Christchurch. **Leon Phillips** is back after spending three months at UC Irvine and attending Molecular Dynamics and (Gordon) Atmospheric Chemistry conferences. **John Blunt** attended both the SMASH 2003 NMR Conference in Verona, Italy, in September, and the International Symposium on Chemistry and Biology of Marine Organisms, at Kolympari, Crete, later that month.

The annual Chemistry Department Ball was held on August 30 at the Centra Hotel and was a great success.

Above: The Belles of the Canterbury Branch Ball.

MANAWATU

In September, we entertained the 2003 NZIC President, **David Bibby** (Victoria University of Wellington) with dinner at a local restaurant and then heard him deliver his Presidential Address. He challenged us with his view of the role of the chemist in the 21st century and indicated that there will be changes and new opportunities for those starting their careers now or in the near future as well as those in mid-career. The topic for the October meeting was *Soliciting a Sex Pheromone Response – Elephants and Moths Speak the Same Chemical Language*. **David Greenwood** (HortResearch, Mount Albert) asked the question, "What do Asian elephants, some moths and bark beetles share in common?" In a very interesting lecture,

he told us that it is the ability to synthesise and detect identical pheromones.

The Branch has been active in supporting students at the secondary level with prizes at local science fairs. The winners of the NZIC prizes at the EIT Hawkes Bay Science and Technology Fair were **Troy Brownlie** and **Joshua Corich** (Taradale High School) for their project, *Acid Fuels* and **Alex Gunn** (also Taradale High School) for the project *Chloride and the Estuary*. The winner of the NZIC prize at the Fonterra Manawatu Science Fair was **Lina Schroeter** (Awatapu College) for *Accumulation of Arsenic by Aquatic Plants: Implications for Human Health*. Seven Massey University students, **Scott Walker**, **Ben Mulchin**, **Jenness Guthrie**, **Mee-Kyung Ahn**, **Amy Keedwell**, **Celia Webby** and **Hasmukh Patel**, were awarded grants of $250 each to attend the NZIC conference in Nelson.

Landcare Research

Benny Theng has been selected to receive the *Marilyn and Sturgis W Bailey Distinguished Member Award* of The Clay Minerals Society (USA) for 2004. This is the highest award of the society and is presented for scientific eminence as represented primarily by publication of outstanding original research in clay science. The President of the Society said that Benny's technical contributions in clay-organic and clay-polymer interactions have made a strong impact in the professional community and were being recognized with this award. As a recipient of the Bailey Award he becomes a Distinguished Member of the Society. The award will be presented at next year's Clay Minerals Society meeting in June at Richland, Washington. Benny is presently in France for about 8 weeks to finish the editing of a handbook on clay science.

HortResearch

Simon Fielder has left HortResearch for Sydney where he will be employed by a private research and development company, Silverbrook Research Pty Ltd. Simon had worked at HortResearch since 1992, mainly on the synthesis of terpene oxidation products and deuterium labelled flavour compounds. Most recently he led a team of chemists completing the synthesis of the painted apple moth pheromones. **John Allen** has also left HortResearch for Australia, going to the mass spectrometry laboratory at the Australian National University, Canberra.

Massey University

Above: New Chemistry Professor: Roger Reeves.

Massey chemists were very pleased to hear that **Roger Reeves** has been awarded a Personal Chair. His work in electrochemistry, analytical chemistry, environmental chemistry, geochemistry and plant chemistry has earned him recognition as a world-class researcher across this whole field. His publications appear in the most prestigious and leading international journals and he has co-authored or co-edited several books and contributed to many others. Roger's many international collaborations testify to the very high esteem in which scientists around the globe hold him, and his expertise and innovative ideas are in demand the world over. Honoured for his work both in New Zealand and overseas, Roger is a leader not only in research but also he has led developments in chemistry teaching over many years, particularly in the analytical field.

Above: John Ayers awarded a NZ S&T Bronze Medal.

John Ayers has recently been awarded a New Zealand Science and Technology Bronze Medal that will be presented to him at his retirement function later this year. *Massey News* reports, "The medal, administered by the Royal Society, honours those who have made exceptional and continuing contributions to New Zealand society and culture through activities in the broad fields of science, mathematics, social science and technology. Dr. Ayers' medal recognises his significant contribution to the development of novel cellulose-based ion exchangers that have led to the incorporation of new processes in the dairy industry, and innovative quality products being produced for the export market. Dr. Ayers' success is a direct result of his experience in a number of areas, from development of new chemical syntheses for resins used for the isolation and purification of milk proteins, through patenting of the resins, to transfer of the technology to industry. The most successful outcome of his work is the use of his cellulose resins for the recovery of whey protein for use in nutritional supplements such as fortified sports drinks and foaming agents for whipped products. Dr. Ayers has developed other processes for making new protein products from milk and cheese whey and as a result has helped the University negotiate five new licence agreements with Fonterra for the production of protein products using his resins. His processes are used by the dairy industry world-wide – all generating a quarter of a million dollars in royalties for the University annually."

Former Palmerston North, chemistry academic staff member, **Ian Watson**, was farewelled recently at functions both at Albany and Palmerston North. Since 1993 Ian has been Principal of Massey University's Albany Campus, where he has led the unprecedented growth. At the Academic Board farewell, the many tributes paid included an address by **Professor Robert Anderson**, Pro-Vice-Chancellor of the College of Sciences: "Ian Watson has not only *made a genuine difference* to this University (and a very big difference at that), but also, he epitomises those fundamental human qualities of honesty, integrity, loyalty, humility and above all, service beyond self. His passion for, and dedication to, advancing the best interests of Massey University and all that it stands for during the past 33 years is remarkable". In closing, Professor Anderson said "I can think of no more appropriate – and deserved – accolade than to say *When I think of him in the years ahead I will be reminded that, as founding Principal at Albany,*

Above: Ian Watson with the citation presented to him at the Palmerston North function.

Ian was to that campus in the 90s all that Sir Geoffrey Peren was to Massey Agricultural College in the 30s, 40s and 50s" (from *Massey News*). At the following staff function, **Emeritus Professor Geoff Malcolm**, spoke about Ian's contribution to the discipline of chemistry, reminding many that Ian started life as a chemist and played an important role in the early development of Massey chemistry.

Among more routine happenings on campus, **Carol Taylor** has been awarded a Marsden grant for $585,000 for the project, *Sweet Nothings – Molecular Complexity Beyond the Genome.* Another successful Chemistry Teachers' meeting, organised by **Adrian Jull**, was held in October on the theme *Ruminations on Chemistry.* A research focus to the meeting was given by **Geoff Jameson**, with his talk, *pHlexibility, pHunctionality and hydropHobicity of bovine β-lactoglobulin* and then in the lab the teachers had a chance to try out some experiments for the classroom. A useful discussion was also held with them on NCEA and entrance to Massey University chemistry papers.

OTAGO

Dr. Markus Weitzer has joined **Associate Professor Sally Brooker's** research group as a Leopoldina Postdoctoral Fellow. He comes to us from Erlangen, Germany (ex-**Professor S. Schindler's** group) with his wife Bele and 1.5 year old twins Paul and Hanna. **Dr. Udo Beckmann** (Marsden Postdoctoral, ex-**Professor K. Wieghardt's** group) has returned to Germany and taken up a trainee patent attorney position with Kutzenberger & Wolff (Cologne) after a very successful stint in Brookers Bunch. Udo has been replaced by **Dr. Carsten Brandt** from Wurzburg, Germany (ex-**Professor M. Broring's** group). **Dr. Graham Motson** (RS Postdoctoral Fellow), ex the group of **Professors M Ward** and **J McCleverty** at Bristol University, having completed a major review *Potential applications for the use of lanthanide complexes as luminescent biolabels* with **Sally Brooker** and **Dr. Jean Fleming** (Anatomy and Structural Biology), has returned to the UK and begun a career in the Ministry of Defence. **Dr. Wolfgang Mohr** (University of Otago Postdoctoral), ex-**Professor J. Gladysz's** group in Erlangen, has taken over from Graham very effectively on our fledging lanthanides research program. After completing her first class BSc (Hons) and a period as a research assistant with us, **Tanya Ronson** has just started her PhD with **Professor Mike Ward** who is now in Sheffield, UK. **Sally Brooker** has returned from the Federation of Asian Chemical Societies conference in Hanoi, Vietnam, where she was awarded the FACS Distinguished Young Chemist Award and presented a plenary lecture. Finally, thanks to a new Marsden grant, two new group members, a PhD student and a postdoctoral fellow, are currently being sought.

From the Viking group, **Henrik Kjaergaard** just returned from a six-week funded visit to Japan under the auspices of the Japan Society for the Promotion of Science. Most of his time was spent in **Professor Masaaki Fujii's** laboratory at Tokyo Institute of Technology working on the separation of rotational isomers with overtone spectroscopy of jet-cooled aminophenols. A hint for affordable living in Japan: near the closing time of supermarkets, approximately coinciding with the time one gets back on the train from the laboratory, all remaining sushi/sashimi usually goes half price, and so a significant amount of raw fish, squid *etc.*, was consumed during the six weeks. During the visit he gave an invited talk entitled *Atmospheric applications of vibrational local modes* at the National conference on molecular structure in Kyoto and was the invited speaker at the IR and Raman symposium in Yokohama with the talk *IR and NIR spectroscopy of atmospheric relevant molecules.* Our research assistant, **Ruth Waldrom** is leaving the Viking group in November to take up a permanent job as laboratory technician at the PPCS plant Finegand in Balclutha.

Dr. David Bibby, NZIC President, visited the local branch on October 21st and gave his presidential Address *Chemistry in the 21st Century* to a small but attentive audience. His suggestions for the future of the Institute were particularly thought-provoking and will hopefully be discussed at the conference in Nelson. Speaking of which, **Dr. Eng Wui Tan** is planning not to be hospitalised again .....

WAIKATO

Don Llewellyn entertained the Waikato Branch with a fascinating story about his involvement in making *The Bomb.* In what turned out to be one of the biggest turnouts for the Branch meetings, Don's talk gave a fascinating insight into the times and the innovation required and demanded by wartime scientists. The story of the bomb is often clouded by the USA-dominated account of events and the role of the physicists but Don pointed out that the UK and chemists also played a role and helped speed the production of the bomb. A talk appreciated by those closer to the time and the younger chemistry branch members with a sense of history. **David Bibby** gave an interesting talk outlining some of his personal thoughts on where the world in general and chemistry in particular was heading over the next few years. This stimulated a lot of discussion."

NIWA, Hamilton

Bob Wilcock attended the 7th Gordon Research Conference on Catchment Science: Interactions of

Hydrology, Biology and Geochemistry, held in Colby-Sawyer College, New Hampshire, USA. Most of the Aquatic Chemistry and Ecotoxicology group at NIWA gave presentations for the Society of Environmental Toxicology and Chemistry (SETAC) Asia/Pacific – Australian Society for Ecotoxicology (ASE) meeting, held in Christchurch in late September. **Chris Hickey** is President of SETAC Asia/Pacific and from 1 January 2004 will be President of SETAC World Council.

University of Waikato

A very successful end of teaching year barbeque was held on October 15 for chemistry staff and second and third year chemistry students to mark the conclusion of the final laboratory classes for the year. On October 17 the Chemistry Department held an evening for local School teachers on the topic of illicit drug manufacturing - the chemistry behind clandestine lab operations, and the chemicals and equipment that are in demand so need to be kept secure. About thirty teachers attended. A recent Waikato graduate, **Melanie Snow**, who is now a scientist with the "Clan Lab" Forensics group at ESR Mt Albert gave some background information on the problem in New Zealand. This was illustrated with some photographs of labs that have been busted (and you thought your lab was untidy ...), and some of the gruesome consequences when illicit chemistry goes wrong. Clearly the OSH requirements for chemistry labs are not adhered to by the drug "cooks". **Brian Nicholson** then outlined some of the chemistry involved, and the problems the University has had with theft of chemicals and equipment. Discussion amongst the teachers and Chemistry Department staff continued over pizza, washed down with a licit drug!

ChemQuest 2003, the annual quiz for sixth form students run by the Chemistry Department at Waikato was held on Wednesday 22nd October. Invitations were sent to schools in the Waikato/Bay of Plenty region to send teams of three students to the University for a fun packed night of chemical questions in the following four categories: *Periodic Puzzlers*, *Sensing the Senses*, *The Wide World of Chemistry* and *Demon Demos*. A total of 47 teams entered this year, with students coming from all around the greater Waikato region to compete for the James and Wells trophy, medals and cash prizes. After each of the four rounds of questions, it was *Teachers' Turn* with four teachers per round competing for a small prize for themselves and a textbook for their school, donated by the Chemistry Department. It was a most enjoyable night for contestants, presenters and spectators and the following prizes were awarded:

1st Prize to ***HID*** from Forest View High School (**Hayden McLennan, Isaac Merrie, Danielle Blair**).
2nd Prize to ***Suits*** from St Pauls Collegiate (**Jason Cho, Jason Wang, Caleb Rose**)
3rd Prize to ***Chemtrolls*** from St Pauls Collegiate (**Richard Curtis, Vikram Joseph, Scott Kendall**)
4th Prize to ***Clueless*** from St Pauls Collegiate (**Kirstie Allen, Dani Haultain, Preeya Reddy**)
5th Prize to ***Or something*** from Waihi College (**Melissa West, Emma Parangi, Irene van Woerden**)

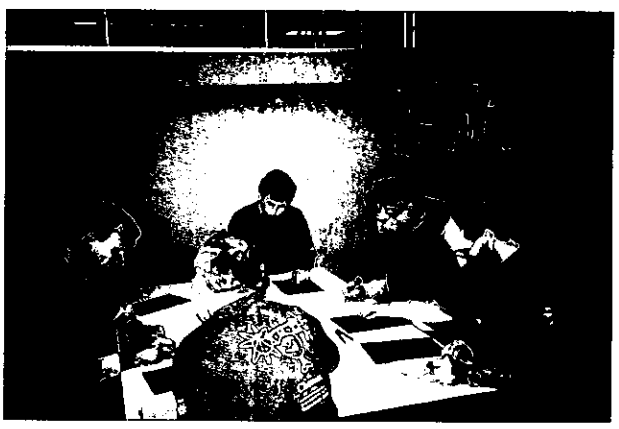
Teachers turn:
Round 1: **Lisa Janek** (Fairfield College)
Round 2: **Lisa Colin Beeston** (Otorohanga College)
Round 3: **Graham Hill** (Fairfield College)
Round 4: **Leon Ruttersmith** (Waihi College)

The quiz was presented by **Richard Coll** and **Michèle Prinsep**, with **Bill Henderson** running his *Demon Demos*. Numerous other people contributed to the success of the occasion including many of the staff and students of the Chemistry Department and School of Science and Technology, University of Waikato (organisation, marking and publicity) and Kate Wilson from James and Wells (prize presentation).

The sponsors of the quiz were as follows and their contributions are gratefully acknowledged:
- James & Wells Patent Attorneys, Hamilton
- School of Science & Technology, University of Waikato
- Department of Chemistry, University of Waikato

Wade Mace has completed his PhD, and has headed off to Ireland with his wife Louise (nee McCaffrey) who is also a Waikato graduate. Wade's place in the Lyndsay Main/Brian Nicholson manganese carbonyl group has been taken by new PhD student **Navendra Prasad**, who has come from Fiji. **Lucia Ying** has started an MPhil with **Bill Henderson, Brian Nicholson** and **Michael Mucalo** in the area of ionic liquids. **Michèle Prinsep** recently gave an oral presentation at the International Symposium on the Chemistry and Biology of Marine Organisms in Kolympari, Crete (once her luggage finally turned up!) **Bill Henderson** will be giving an invited talk at the Singapore International Chemical Conference in December on applications of ESMS in directing synthetic chemistry.

Above: HID from Forest View High School. From left: Danielle Blair, Isaac Merrie, Hayden McLennan.



Above: The ChemQuest judges.

Nuclei of Hydrogen Atoms

Water constitutes about two thirds of the human body weight, and this high water content explains why magnetic resonance imaging has become widely applicable to medicine since there are differences in water content among tissues and organs. In many diseases the pathological process results in changes of the water content, and this is reflected in the MR image.

The hydrogen nuclei of water are able to act as microscopic compass needles. When the body is exposed to a strong magnetic field, the hydrogen nuclei are directed into order or *stand at attention*. When submitted to pulses of radio waves energy is adsorbed and then, after the pulse, a resonance wave is emitted when the nuclei return to their previous state and the small differences in the oscillations of the nuclei are detected. By advanced computer processing, it is possible to build up a three-dimensional image that reflects the chemical structure of the tissue, including differences in the water content and in movements of the water molecules. This results in a very detailed image of tissues and organs in the investigated area of the body. In this manner, pathological changes can be documented.

Rapid Developments in Medicine

The medical use of magnetic resonance imaging has developed rapidly. The first MRI equipment in health was available at the beginning of the 1980s, but by last year approximately 22,000 MRI instruments were in use worldwide with more than 60 million MRI examinations performed. A great advantage of MRI is that it is harmless according to all present knowledge. In contrast to X-ray (1901 Prize in Physics) or computer tomography (1979 Prize in Physiology or Medicine) examinations MRI does not use ionizing radiation. However, patients with magnetic metal in the body or a pacemaker cannot be examined with MRI due to the strong magnetic field, and patients with claustrophobia may have difficulties undergoing MRI.

Today, MRI is used to examine almost all organs of the body. The technique is especially valuable for detailed imaging of the brain and the spinal cord. Almost all brain disorders lead to alterations in water content that is reflected in the MRI picture. A difference in water content of less than one percent is enough to detect a pathological change. In multiple sclerosis, examination with MRI is superior for diagnosis and follow-up of the disease as the symptoms are caused by local inflammation in the brain and the spinal cord. Not only can these be seen by MRI, but also the location within the nervous system where the inflammation is, how intense it is, and also how it is influenced by treatment. A further example is prolonged lower back pain, leading to great suffering for the patient and to high costs for the society. It is important to be able to differentiate between muscle pain and pain caused by pressure on a nerve or the spinal cord. MRI examinations have been able to replace previous methods that were unpleasant for the patient. With MRI, it is possible to see if a disc herniation is pressing on a nerve and to determine if an operation is necessary.

Since MRI yields detailed three-dimensional images, it is possible to get distinct information on where a lesion is localized. Such information is valuable before surgery. For instance, in certain microsurgical brain operations, the surgeon can operate with guidance from the MRI results. The images are detailed enough to allow placement of electrodes in central brain nuclei in order to treat severe pain or to treat movement disorders in Parkinson's disease.

MRI examinations are very important in diagnosis, treatment and follow-up of cancer. The images can reveal exactly the limits of a tumour, which contributes to more precise surgery and radiation therapy. Before surgery, it is important to know whether the tumour has infiltrated the surrounding tissue and MRI can achieve this more accurately than other methods. MRI has also improved the possibilities to ascertain the stage of a tumour, and this is important for the choice of treatment. For example, MRI can determine how deep in the tissue a colon cancer has infiltrated and whether regional lymph nodes have been affected.

Such examinations replace previously used invasive methods thereby reducing the suffering for many patients. Thus, MRI can replace investigation of the pancreatic and bile ducts using contrast media injection via an endoscope, which can in some cases lead to serious complications. Likewise, diagnostic arthroscopy (examination with an optic instrument inserted into the joint) can be replaced by MRI. For example, in the knee it is possible to perform detailed MRI studies of the joint cartilage and the cruciate ligaments.

The 2003 award is not without controversy as the *invention* of MRI imaging remains a subject of dispute. Dr. Raymond Damadian, a US medical doctor who did not share the prize, makes claim for the *invention*. In 1972, he filed a patent application for using NMR to scan for cancerous tissue in the human body, which was subsequently granted and his group went on to build the first MRI scanner. His dissatisfaction in not sharing the award was at the level that he took out a full-page advertisement in the Washington Post to denounce the panel for not giving him a share of the prize.

The Chemistry Prize - Channels in Cell Membranes

To maintain even pressure in a cell it is important that water can pass through the cell wall. This has been known for a long time, but the appearance and function of these pores remained as one of the classical unsolved problems of biochemistry. It was not until as recently as 1990 that Peter Agre discovered the first water channel. Like so much else in the living cell, it was all about a protein. Water molecules are not the only entities that pass into and out of the cell. For thousands of millions of cells to be able to function as something other than one large lump, coordination is required. Thus communication between the cells is necessary and is achieved by signals sent in and between cells that consist of ions or small molecules. These start cascades of chemical reactions that cause our muscles to tense, our eyes to water and, indeed, control all our bodily functions.

It was in 1998 that Roderick MacKinnon succeeded for the first time in showing what ion channels look like at atomic levels, an achievement which, together with Agre's discovery of water channels, opened up entirely new research areas in biochemistry and biology. The medical consequences of these discoveries are also important as a number of diseases can be attributed to poor functioning in the water and ion channels of the human body. With the help of fundamental knowledge of what they look like and how they work, there are now new possibilities for developing new and more effective pharmaceuticals.

Membrane channels (Figure 1) allow rapid, selective, and regulated transport of water, ions and small solutes across biological membranes. They are found in all living cells, and underlie critical cellular functions such as neuronal signaling, muscle contraction, cardiac function, water resorption in the kidney, water uptake in plant roots, and the response to osmotic stress in microorganisms.

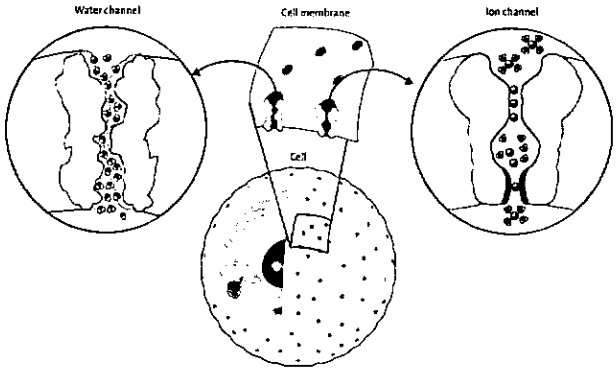


Figure 1. The dividing wall between the cell and the outside world is far from an impervious shell. Various channels, many of which are specially adapted to one specific ion or molecule and do not permit any other type to pass, perforate the cell. Here to the left we see a water channel and to the right an ion channel.

Living cells are enclosed by a lipid bilayer membrane that separates them from other cells and the extracellular medium. Cells also contain membrane-enclosed organelles such as the nucleus, mitochondria and chloroplasts. Lipid bilayer membranes are generally impermeable to water, ions, and other polar molecules; yet, in many instances, such entities need to be rapidly and selectively transported across a membrane, often in response to an extra- or intracellular signal. Membrane channel proteins mediate transport along a concentration gradient, whereas transport against a concentration gradient is mediated by membrane pumps such as the Na^+/K^+ ATPase (a protein discovered in 1957 by Jens Skou, 1997 Nobel Laureate in chemistry).

Water channels allow the cell to regulate its volume and internal osmotic pressure, and are needed when water must be retrieved from a body fluid such as occurs when urine is concentrated in the kidney. In plants, water channels are critical for water absorption in the root and for maintaining the water balance throughout the plant. Water channels are crucial for life and are found in all organisms, from bacteria to man. In contrast, ion channels make it possible for cells to generate and transmit electrical signals, and are the basic molecular building blocks in the nervous system. Ion channels can be made to open and close in response to different stimuli such as ligand binding, transmembrane voltage, temperature, mechanical stress, *i.e.* they are gated. Many ion channels are highly selective for a particular ion (Na^+, K^+, Ca^{2+}, Cl^-), and can reach very high transport rates (~10^8 ions per second). In man, ion channels are involved in a whole range of diseases in organs such as the brain, the heart, and the muscles.

Water channels

The existence of channels mediating the flow of water and small solutes through biological tissues such as the wall of the urinary bladder or even across the membrane of individual cells was postulated as early as in the mid-nineteenth century. In the late 1950s, it was found that water is rapidly transported through the red blood cell membrane via water-selective channels that exclude ions and other solutes. Studies of water transport in various organisms and tissues over the next 30 years suggested that water channels have a narrow selectivity filter that prevents proton (H_3O^+) flow while maintaining a very high permeation rate for H_2O (up to 10^9 molecules per second). However, even as late as 1987 nobody had been able to identify a water channel protein and the very concept of water-specific channels was still controversial.[1]

In the mid 1980s, Agre was studying Rh blood group antigens from the red cell membrane and in 1988, he isolated a new 28 kDa membrane protein of unknown function, CHIP28, from both red cells and renal tubules.[2] After obtaining an *N*-terminal peptide sequence and then the whole cDNA sequence of CHIP28, he realized that this might be the long-sought-after water channel.[3] Shortly thereafter, Agre proved this conclusively by demonstrating that expression of CHIP28 in *Xenopus* oocytes made the cells swell rapidly when placed in a hypo-osmotic medium (Figure 2).[4] The same phenomenon was observed when purified CHIP28 was reconstituted into liposomes.[5] In both cases, swelling was inhibited by Hg^{2+}, a treatment known to block water transport across the red cell membrane.

The discovery of CHIP28 (now termed aquaporin 1 or AQP1) was a decisive moment in the study of cell water channels. Aquaporin-like proteins have since been found throughout the living world and, in humans alone, there are at least 11 different aquaporin-like proteins, many of which have been linked to various diseases. Plants have an even higher number of aquaporins, with no less than 35

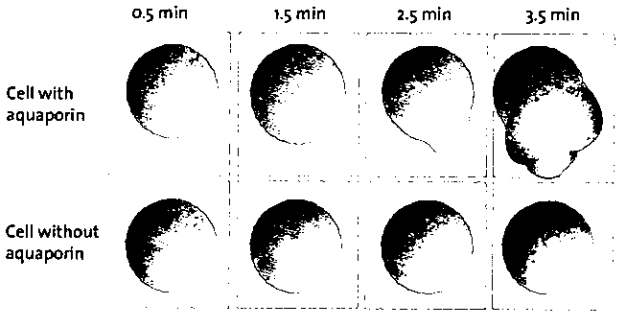


Figure 2. *Xenopus* oocytes microinjected with AQP1 mRNA swell rapidly when placed in a hypo-osmotic medium, in contrast to noninjected oocytes.

different versions found in the model plant *Arabidopsis thaliana*.[6]

The physiological importance of the aquaporins is perhaps most conspicuous in the kidney, where some 150-200 litres of water need to be resorbed from the primary urine each day. This is made possible mainly by the AQP1 and AQP2 aquaporins. AQP1 is expressed in the proximal tubules and the descending vasa recta, while AQP2 is expressed in the collecting duct. The expression of AQP2 at the plasma membrane is regulated by vasopressin, and decreased or increased AQP2 levels have been associated with nephrogenic diabetes insipidus as well as with several conditions associated with fluid retention such as congestive heart failure.[7]

In 2000 and 2001, the first high-resolution 3-D structures of AQP1 and a related glycerol-selective bacterial channel protein (GlpF) were reported.[8] Based upon these structures, detailed models have been put forward to explain the high permeation rate, the strict water selectivity, and the ability of AQP1 to prevent proton leakage. In essence, the architecture of the channel allows water molecules to pass only in single file, and positively charged residues in the channel repel H_3O^+ (Figure 3). Furthermore, the local electrostatic field generated by the protein switches polarity in the middle of the channel, forcing the passing water molecules to rotate in such a way that their dipole moments are oriented in opposite directions in the upper and the lower halves of the channel. This reorientation prevents the formation of a continuous network of hydrogen-bonded water molecules across the channel, and thus blocks the passage of protons via *proton hopping* (the Grotthuss mechanism).

In the short period of just over ten years, an almost complete atomic-level understanding of water channel function has been reached, the physiological roles of water channels in both eukaryotic and prokaryotic organisms have been elucidated, and their role in health and disease are becoming increasingly well documented. Agre's unexpected discovery of the aquaporins revolutionized the study of water transport, and laid a firm biochemical foundation for a very important area of physiology and medicine.

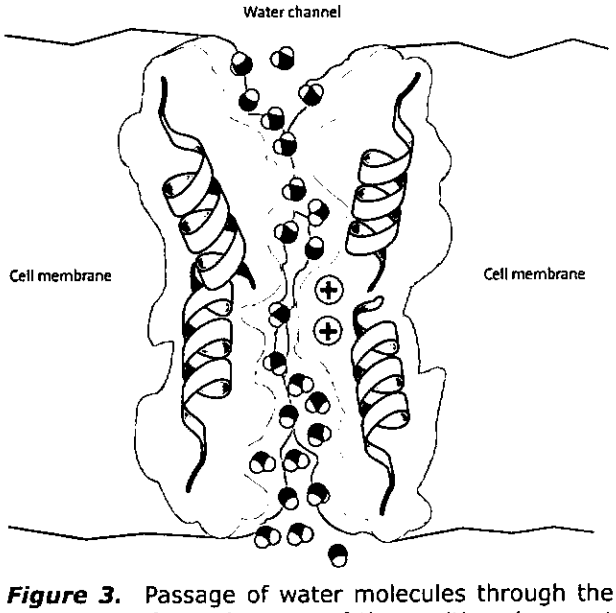


Figure 3. Passage of water molecules through the aquaporin AQP1. Because of the positive charge at the center of the channel positively charged ions such as H_3O^+ are deflected. This prevents proton leakage through the channel.

Ion channels

Based on experiments with artificially prepared colloidal membranes, Wilhelm Ostwald (1909 Nobel Prize in chemistry) suggested in 1890 that electrical currents in living tissues might be caused by ions moving across cellular membranes. Work in the early 1900s then established that membrane potentials are electrochemical in nature, and in 1925 the existence of narrow ion channels was proposed.

Work by Hodgkin and Huxley (1963 Nobel Prize in physiology or medicine) in the early 1950s on ion transport across the membrane of the squid giant axon ushered in the modern era of neurophysiology. It rapidly led to a very detailed model for the action potential in nerve cells based on the idea that separate, voltage-gated ion channels for Na^+ and K^+ (and sometimes Ca^{2+}) are present in the membrane.[9] It was also demonstrated that potassium ions move through the membrane in single file, further substantiating the idea of membrane-embedded channel structures.[10] The central concepts of rapid transport, ion selectivity, channel gating, and channel inactivation were clearly identified already at this early stage, but the underlying molecular mechanisms were totally unclear.

Biochemical work in a number of laboratories during the 1960s and 1970s on the ligand-gated acetylcholine receptor (a member of the Cys-loop ion channel family) from the electric ray *Torpedo californica* led to the first biochemical identification of an ion channel protein, and low-resolution structural studies of the acetylcholine receptor showed a large extracellular funnel leading to a narrow membrane channel.[11]

By the early 1970s, the dimensions of the *selectivity filter* in neuronal voltage-gated Na^+ and K^+ channels (members of the P-loop ion channel family) had been measured using biophysical techniques, and the notion that the gate and the selectivity filter are separate structural elements was established.[12] Very detailed studies of ion permeation were made possible by the technique of single-channel recordings introduced by Neher and Sakmann (1991 Nobel laureates in physiology or medicine), and when this technique was combined with the possibility to clone (mutagenize) and express ion channel proteins in cells such as *Xenopus* oocytes, rapid progress in mapping different functional regions of various ion channels was made.

By the mid 1990s, it was clear that the P-loop ion channels must have a narrow selectivity filter near their extracellular end and a separate gate near their intracellular end. It was proposed that selectivity was achieved by the proper placement of oxygen atoms in the selectivity filter in a way that ions of the correct radius could be preferentially desolvated when entering the narrow filter. The segment of the protein that forms the selectivity filter – the P-loop – had thus been identified. However, the detailed molecular design of the selectivity filter and the mechanisms responsible for gating were unknown, and it was clear that little further progress would be possible unless high-resolution structural data could be obtained.[13]

High-resolution 3-D structures for membrane proteins are not easy to determine, and ion channels are no exception. In particular, eukaryotic membrane proteins seem to be more difficult to handle than prokaryotic ones, and the cloning and overexpression of a bacterial K^+ channel with high homology to eukaryotic K^+ channels suggested to some workers that prokaryotic channels might finally provide the missing key to structural studies of ion channels. The breakthrough came in 1998 when Roderick MacKinnon succeeded in determining the first high-resolution structure of an ion channel, the KcsA K^+ channel from *Streptomyces lividans*.[14] The design of the selectivity filter was seen to be perfectly adapted to the job of desolvating potassium ions while keeping smaller sodium ions out (Figure 4), thus explaining the high K^+ selectivity and the high transport rate. At higher resolution, hydrated potassium ions could even be seen in *hold position* on both sides of the selectivity filter,[15] and it became clear that the selectivity filter is composed of a succession of K^+ binding sites that each almost exactly mimics the hydration shell normally present around a potassium ion.

The KcsA structure showed the channel in a closed conformation. The structure of the Ca^{2+}-activated bacterial K^+ channel MthK, again solved by MacKinnon,[16] captured the channel in an open conformation. A comparison of the KcsA and MthK structures suggested a general mechanism for channel gating, in which a conformational change in the sensor domain pulls the transmembrane helices apart near the intracellular end of the channel (Figure 4).[16]

Some K^+ channels conduct ions in only one direction, serving as *molecular diodes*. Such inward rectifying channels are blocked by Mg^{2+} and polyamines that penetrate into the channel from its cytosolic end when the membrane is depolarized. The first structure of a domain responsible for inward rectification, presented[17] by MacKinnon in 2002, shows a cytoplasmic extension to the basic pore structure lined with acidic and hydrophobic residues that lengthens the ion channel to almost 60 Å and provides internal binding sites for polyamines. The molecular basis for another important kind of channel inactivation process, *ball-and-chain inactivation*, was clarified by mutation analysis of a eukaryotic K^+ channel homologous to KcsA.[18]

As already shown by Hodgkin and Huxley, in excitable cells such as nerve, muscle, and endocrine cells, voltage-induced gating of ion channels is the central principle of activation. Very recently, MacKinnon solved the structure of the archaeal voltage-gated K^+ channel KvaP in a complex with antibody fragments directed against the voltage sensor domain.[19] Interestingly, the antibody fragments appear to have pulled the sensor domains away from the ion channel itself. The precise structure of a non-perturbed voltage gated channel is thus still unknown, but the work nevertheless provides a first insight into the structural details of the voltage-sensing mechanism. During the past few years, structural work has also begun to shed light on the molecular function of mechanosensitive and Cl^- selective ion channels. In parallel, X-ray and electron crystallography studies have led to successively better structural models of the acetylcholine receptor.

MacKinnon's structural and mechanistic work on K^+ channels has unraveled the molecular underpinnings of ion selectivity, gating, and inactivation. It has opened up entirely new possibilities for very detailed biochemical, biophysical, and theoretical studies of ion channel function. His discoveries also provide a firm basis for a molecular understanding of many neurological, muscular, and cardiac diseases opening up new possibilites for drug design.

Conclusions

The rapid progress in our understanding of membrane channel function over the past decade is in large part due

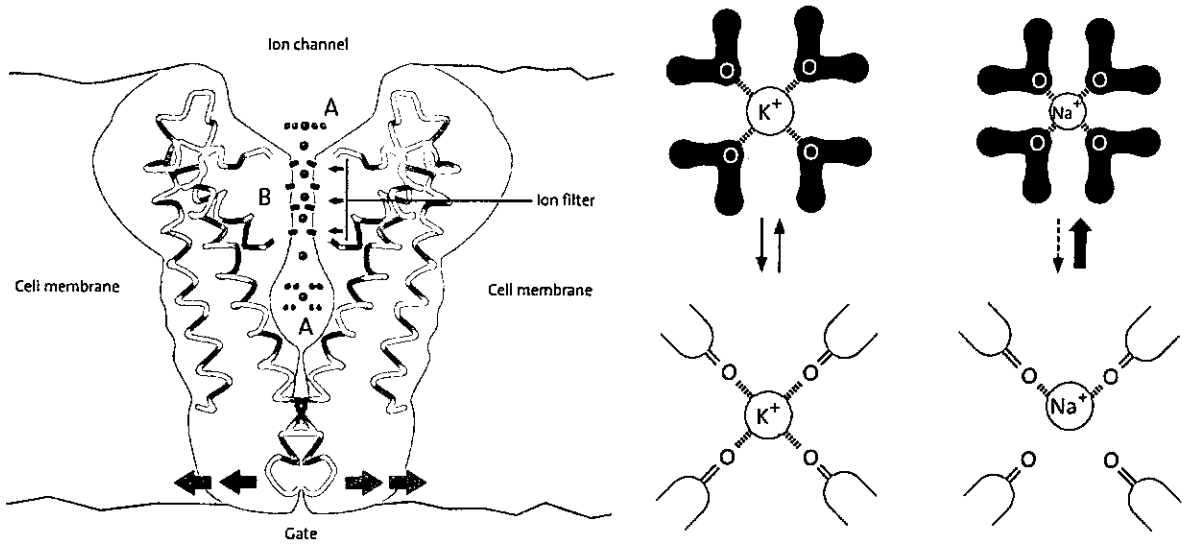


Figure. 4. (Left) The KcsA K^+ ion channel permits passage of potassium ions but not sodium ions. The oxygen atoms of the ion filter form an environment very similar to the water environment outside the filter. The cell may also control opening and closing of the channel. **OUTSIDE THE ION FILTER (A):** Outside the cell membrane the ions are bound to water molecules with certain distances to the oxygen atoms of the water. **INSIDE THE ION FILTER (B and right)** For the potassium ions the distance to the oxygen atoms in the ion filter is the same as in water. The smaller sodium ions do not fit in between the oxygen atoms in the filter and this prevents them from entering the channel.

to fundamental discoveries concerning water and ion channels. Peter Agre's discovery of the aquaporin water channels and Roderick MacKinnon's detailed structural and mechanistic studies of K^+ channels are singular achievements that have made it possible for us to see these exquisitely designed molecular machines in action at the atomic level.

Acknowledgement

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FORCED CARBONATION OF CEMENT PASTES AND MORTARS WITH SUPERCRITICAL CO_2

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Abstract

A series of Portland cement paste and mortar samples were treated with supercritical CO_2 at 60 °C and 200 bar for 24 hours. Chemical analysis by XRD and TG/DSC demonstrated that the extent of the carbonation achieved was strongly controlled by the dryness of the samples prior to treatment. Significant reaction does not occur when the internal concrete humidity exceeds 50% RH and optimum results are obtained at 25% RH or below. The carbonated material is primarily derived from calcium hydroxide and crystalline calcium silicates. Very little reaction of the hydrated calcium silicate gel making up the bulk of the cement paste occurs, limiting the potential of the method as a means of CO_2 sequestration. The carbonated mortars demonstrate significant improvements in their mechanical properties, particularly compressive strength.

Introduction

'Carbonation' is the term given to the reaction which takes place between atmospheric carbon dioxide and the components of a hardened Portland cement matrix. The principal reaction involves the dissolution of $Ca(OH)_2$, which is re-precipitated as calcium carbonate. The process can be summarised as shown in Equation 1, although the actual reaction mechanism and the ions involved may be much more complex:[1]

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2O \quad (1)$$

The hydrated calcium silicates, which form the bulk of the cement matrix, are similarly decomposed into calcium carbonate and a low-lime amorphous silica gel:

$$x CaO.SiO_2.nH_2O + CO_2 \rightarrow xCaCO_3 + SiO_2 + nH_2O \quad (2)$$

Carbonation is generally considered undesirable in concrete because it lowers the pH of the pore solution as $Ca(OH)_2$ is consumed. This eliminates the passivating alkaline environment that ordinarily protects carbon steel reinforcement from corrosion. However, carbonation is not detrimental *per se*. Indeed, since the pore network provides the sites for the precipitation of these secondary minerals, carbonation can bring about a refinement of the pore structure, with commensurate improvements in strength, durability, and dimensional stability. Due to this

potential, attention has been paid to methods for increasing the level of carbonation in cementitious materials. This has primarily been motivated by the need to reduce the leachability of encapsulated wastes, but the potential environmental benefits of using this technique to re-sequester the CO_2 emissions from cement kilns etc. have also been noted.[2,3]

The difficulty with achieving large-scale carbonation is that the reaction is controlled by the diffusion of the carbon dioxide into the pore network in response to a concentration gradient. For it to be sustained, CO_2 has to continually migrate through regions of the concrete that have already been carbonated. Eventually the pores become blocked, not only by precipitation of calcium carbonate but also by the accumulation of water from the reaction. Attempts to accelerate carbonation with high concentrations of CO_2 have generally stumbled at this point, creating specimens with an exterior rind of completely carbonated material, protecting a largely unaltered interior. Recently, a number of investigators have claimed that the improved mass transport properties of CO_2 in the supercritical state enable substantial carbonation to be achieved. The effect of supercritical CO_2 ($scCO_2$) on cements was first studied in a limited manner in the oil industry, where down-well temperatures and pressures are such that this phase occurs naturally in the headspace above reservoirs.[4] Since that time, the treatment of cement with $scCO_2$ has been patented in the USA and publications have begun to appear documenting the improved materials performance possible by using this technique for the manufacture of fibre-cement composite products.[5-8] There is, however, comparatively little data quantifying the benefit of treating conventional Portland cement mortars, the degree of carbonation achievable or the optimum conditions under which to perform the reaction. The study described was a preliminary investigation of the feasibility of supercritical carbonation, both as a method of beneficiating cement products and as a means of CO_2 sequestration.

Method

Three series of samples were produced. The first series consisted of a set of 25 mm diameter neat paste cylinders, mixed at a water to cement (w/c) ratio of 0.5 using Golden Bay Type GP cement with a theoretical Bogue composition of 63% C_3S, 19% C_2S, 6% C_3A and 7% C_4AF. After 7 days wet curing the specimens were conditioned to one of several 'degrees of dryness' relative to the loss of all evaporable water. These were obtained by sealing the samples into containers whose internal humidity was controlled by saturated salt solutions (Table 1). Following conditioning, the samples were carbonated for 24 hours in a 10-litre stainless steel reaction vessel using water-saturated $scCO_2$ maintained at 200 bar and 60 °C. The treated specimens were subsequently dried, ground and analysed for the extent of their carbonation, primarily using X-ray diffraction (XRD), thermogravimetry (TG), and differential scanning calorimetry (DSC) techniques.

Two subsequent sets of mortar (paste plus aggregate) samples were produced at w/c ratios of 0.6 and 0.45, primarily for mechanical strength testing. These w/c ratios signify a cement matrix with a very open pore structure

Table 1. Conditioning regimes for cement paste samples.

RH (%)	Controlling Salt	Drying (%)
–	(Oven dried)	100
23	$KC_2H_3O_2$	72
52	$MgNO_3$	47
75	NaCl	22
95	K_2SO_4	6

and a matrix for which percolation theory suggests the pore structure is becoming discontinuous, *i.e.* of relatively 'low' and 'high' durability, respectively. Following curing, the samples were conditioned to 30% and 80% degrees of dryness. The cement paste test results indicated optimum carbonation required aggressive drying, but this was considered likely to be an onerous requirement for an industrial process. Accordingly, 30% drying was included as a more feasible alternative. This equates with drying to equilibrium with an environment at 23 °C and 65% RH; 80% drying of the larger mortar samples required an oven.

Results

Cement Pastes

X-ray diffraction patterns of the cement pastes are shown in Figure 1. The uncarbonated control sample is at the top of the figure with the $scCO_2$-treated samples below, in order of the degree of drying imposed during the pre-treatment conditioning phase. The control is dominated by peaks for portlandite [$Ca(OH)_2$] at 34.1° and 18.1° 2θ. This is expected because it forms the main crystalline phase in freshly hydrated Portland cement, occupying approximately 25% of the paste by volume. The bulk of a Portland cement matrix (50–75%) is composed of gel-like calcium silicate hydrates (CSH), which is essentially non-crystalline, *i.e.* X-ray amorphous. Some unhydrated cement is present in the control, emphasised by the peaks for belite (dicalcium silicate) at 32.2° and 32.7° 2θ. Alite (tricalcium silicate) may also be present because the major peaks of the two phases are closely coincident, but the slower hydration of belite makes it the more likely candidate. There is also evidence for some calcite in the uncarbonated paste sample with a major peak at 29.4° 2θ. This is attributable to the fact that the Portland cement clinker is interground with 5% limestone filler during the manufacture of Golden Bay GP cement.

The general trend apparent from the $scCO_2$-treated samples is that the amount of carbonation strongly depends upon the extent to which the sample was dried during the conditioning step. Carbonation depletes both the portlandite and unhydrated dicalcium silicate phases and calcite is the predominant $CaCO_3$ polymorph produced by the reaction. It is not possible to determine from the XRD patterns whether the CSH gel is also carbonated. While the oven-dried paste resulted in the greatest formation of calcite during the $scCO_2$ treatment, maximum carbonation appears to occur in the specimen conditioned to a 72% degree of dryness. This sample has lesser quantities of

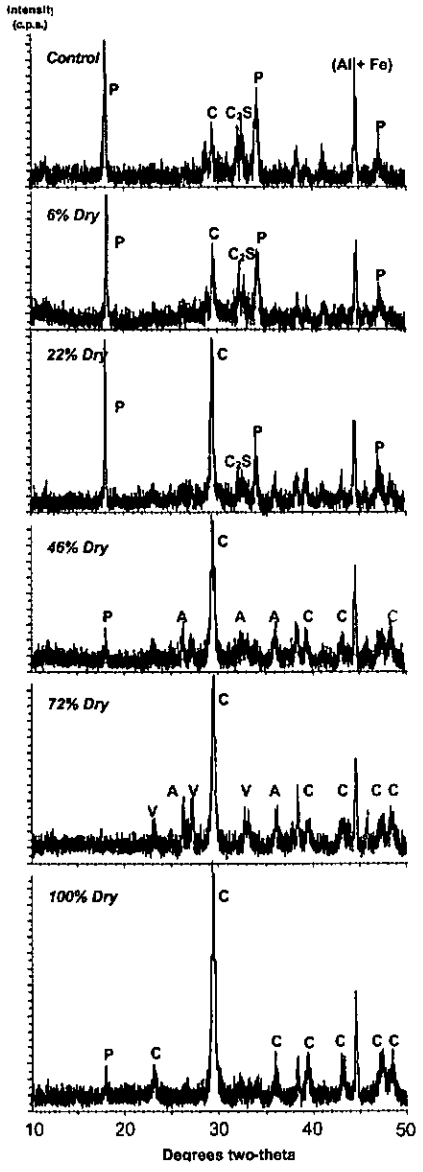

Figure 1. X-ray diffraction patterns of cement paste specimens (P = portlandite; C_2S = dicalcium silicate; C = calcite; A = aragonite; V = vaterite; Al+Fe = internal standard reflections).

calcite but significant supplementary amounts of the aragonite and vaterite polymorphs. The 72% sample also shows a minimum for portlandite content, whereas the oven dried sample retains a small peak at 18.1° 2θ. It is possible this peak may be wholly or partly attributable to gibbsite [$Al(OH)_3$], which would reasonably be expected if the tricalcium aluminate minerals in the cement were carbonating as it has a major peak at the same location. Arguing against this is absence of other gibbsite peaks in the XRD pattern. The 100% dry sample is notable for the absence of calcium carbonate phases other than calcite, likely to be a desirable feature for the dimensional stability of the carbonated material.

Figure 2 shows thermogravimetry results obtained for the carbonated cement pastes. The endotherm at ca. 450–460 °C in the DSC trace relates to the dehydroxylation of $Ca(OH)_2$.[9] In confirmation of the XRD results, the degree to which calcium hydroxide is depleted depends on the degree of drying imparted to the samples prior to treatment. The combined TG/DSC information indicates that portlandite is effectively eliminated from samples which have received > 50% drying. The endotherm at 700–800 °C indicates the decarbonisation of calcium carbonate and grows as the $Ca(OH)_2$ is depleted.[9] Quantitative analysis of the TG results, shown in Table 2, confirms that drying to 72% yields the optimal conditions for maximum formation of $CaCO_3$. Quantification of the CO_2 evolved is complicated because of the broad overlapping region to the left of the peak that relates to the loss of chemically combined water in the CSH gel. This feature becomes more pronounced in the drier samples and the endotherm at 100–200 °C resulting from dehydration of physically adsorbed water becomes less distinct, suggesting that the gel is changing, *i.e.* being decalcified, by the $scCO_2$ carbonation. However, mass balance calculations indicate that there is relatively little $CaCO_3$ formation in the carbonated samples which cannot be accounted for by their depleted $Ca(OH)_2$ content compared with the control paste. In the most favourable case, the 72% dry sample, only about 25% of the total calcium carbonate appears to have been formed through carbonation of the CSH gel.

Using the commonly accepted stoichiometry for cement hydration, a fully hydrated Golden Bay GP cement would comprise 54% w/w CSH gel of the approximate composition $3CaO.2SiO_2.3H_2O$, and 28% $Ca(OH)_2$.[10] Assuming both of these cement components reacted completely with CO_2, and ignoring any reaction of the minor aluminate phases, an upper bound on the calcium carbonate content of the carbonated cement pastes is 66% $CaCO_3$. Thus the supercritical treatment process is, at best, only about 40% effective in sequestering carbon dioxide.

Mortar Specimens

The mortar samples were cast primarily to determine what, if any, improvement in their mechanical properties was obtained on carbonation. Figure 3 illustrates the compressive strength developed by carbonated and uncarbonated mortars, manufactured at 0.45 and 0.6 w/c ratios and conditioned to either a 30% or 80% degree of drying. All of the carbonated samples showed a statistically significant improvement in compressive strength when compared with their corresponding controls. Consistent with the cement paste results the greatest benefit was experienced by the strongly dried samples, which demonstrated strengths of 2.5–3.0 times their respective controls. Some of this increase is exaggerated because the early age drying has clearly compromised the cement hydration achieved in the control samples, as evidenced by comparing the strengths achieved under the two different drying regimes. However, there is no doubt that ultimate strengths in excess of 75 or 100 MPa are a testament to the cementing ability of the precipitated calcium carbonate.

Tensile strengths also benefit by carbonation, although the improvement is less dramatic with an increase of 60–65%, as shown in Figure 4. As would be expected from the greater strength, the stiffness of the treated samples also increases, with the modulus of elasticity measured in direct tension rising from 22 to 27 GPa for the 0.45 w/c mortars. Because of the strength of the samples it was not possible to evaluate their ductility from the post-peak behaviour of the stress-strain curve measured in compression. However, the explosive nature of the failures experienced suggests that the carbonated mortars are considerably more brittle than their untreated counterparts.

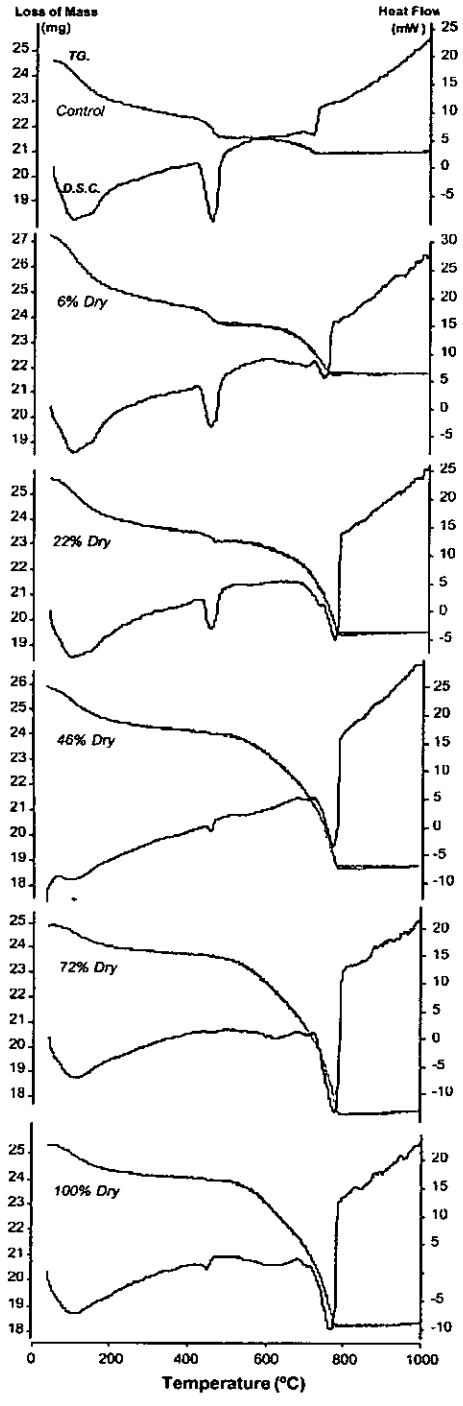

Figure 2. Thermogravimetry and Differential Scanning Calorimetry results for the carbonated cement pastes.

Table 2. Quantitative analysis of TG traces for the cement pastes. 'Excess' $CaCO_3$ represents the carbonate not accountable for by depletion in $Ca(OH)_2$, *i.e.* is suggestive of the carbonation of CSH).

Sample % w/w	$Ca(OH)_2$ % w/w	$CaCO_3$ % w/w	'Excess' $CaCO_3$ % w/w
Control	12.8	2.3	–
6% Dry	9.2	6.6	0
22% Dry	5.7	13.5	2
47% Dry	1.8	20.1	3
72% Dry	2.0	27.0	10
Oven Dry	1.8	23.1	6

Examination of the highly carbonated mortars using a scanning electron microscope revealed significant modification of the pore structure of the mortars. The image shown in Figure 5 is typical, consisting of a rather featureless mass of lime-depleted calcium silicate hydrate, which occasionally resolves into large calcite crystals with a characteristic scalahedron (*sharks tooth*) habit where space has been available to grow undisturbed. By contrast, the uncarbonated mortars show a mixed mineral assemblage characteristic of hydrated cement. These minerals include long needle-like crystals of ettringite (calcium aluminosulfate), hexagonal plates of $Ca(OH)_2$, and interlocking tendrils of CSH (Figure 6).

Thin section petrography confirmed that the entire volume of 50 mm mortar cubes was carbonated during the $scCO_2$ treatment when preconditioned to 80% dryness. Though the carbonation was widespread in extent, it had not developed the characteristic fretted texture associated with the most intensive reaction, suggesting some proportion of the cement paste remains uncarbonated.[11] This was supported by calculations from the TG/DSC results which indicated that, at best, only 50–55% of the available calcium was converted to $CaCO_3$, and again $Ca(OH)_2$ was preferentially carbonated

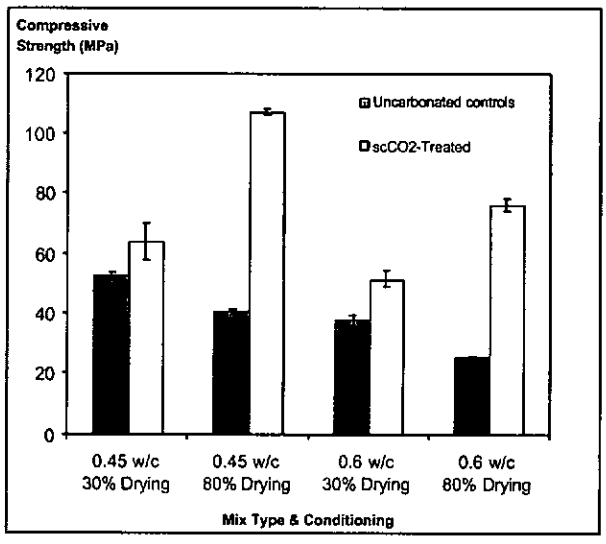

Figure 3. Compressive strength of mortar samples before and after carbonation with $scCO_2$. The error bars represent a one standard deviation confidence limit.

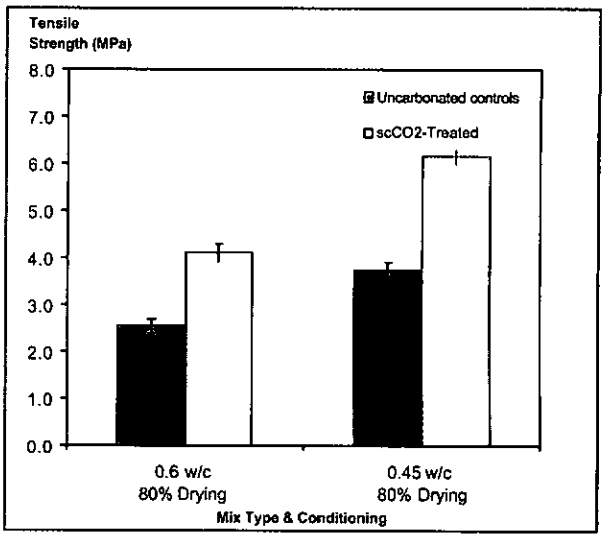

Figure 4. Tensile strength of mortar samples before and after carbonation with $scCO_2$.

to CSH. The 30% dry samples showed limited carbonation that occurred as a distinct front, demonstrating that diffusion of CO_2 is still a limiting factor where the cement matrix pores are water filled, even with the better mass transport properties offered by the supercritical state.

Conclusions

The carbonation of Portland cement pastes and mortars can be greatly accelerated by the use of carbon dioxide in the state of a supercritical fluid. The extent of the reaction, as measured by depletion of calcium hydroxide and unhydrated calcium silicates, depends strongly on the moisture content of the sample prior to exposure to $scCO_2$. Under optimum conditions, a 50 mm mortar cube can be completely carbonated in less than 24 hours. Drying to remove 70–80% of the evaporable water in the samples appears to offer the best result, but the issue is complex and also appears to influence the polymorphic form in which the resulting calcium carbonate is precipitated. Despite being in the supercritical state, the CO_2 is not able to diffuse rapidly through water-saturated pores of less thoroughly dried samples and the economics of using this process on an industrial scale will be affected negatively by the consequent need for severe drying.

The carbonation process significantly improves the mechanical properties of the treated samples with large increases in their compressive and tensile strengths, due to carbonate precipitation infilling capillary pores and the margins of aggregates. The carbonate is primarily calcite, the thermodynamically stable form under ambient conditions, but some vaterite and aragonite are also present which may give rise to dimensional instability if these phases revert. Mass balance calculations show that the majority of the calcium carbonate arises from the reaction of calcium hydroxide or unhydrated calcium silicates and that much of the calcium silicate hydrate remains relatively unaltered in the carbonated matrix. This is supported by the carbonation textures observed in thin sections. Because of this, treatment with $scCO_2$ is only partially successful as a means of re-sequestering the CO_2 released during the production of cement, limiting its viability, especially considering that the generation of a supercritical fluid is itself an energy intensive process that requires costly equipment.

While $scCO_2$ treatment offers an interesting means of changing the properties of a cement matrix, it would seem to confer too little benefit for routine use in the manufacture of cement-based products. It may find niche applications where the properties of the carbonated matrix offer particular advantages. Some examples include improved compatibility with low-cost E-glass for glass fibre reinforced cement composites because of the reduced pH of the cement matrix and facilitating the use of non-hydraulic calcium-rich wastes such as basic steel slag as a cementing material.

Acknowledgements

This work was funded by the Foundation for Research, Science and Technology under the contract BRAX0203 'Better Built Environments'. The assistance of Industrial Research Limited, SpectraChem Analytical and Don St John is gratefully acknowledged.

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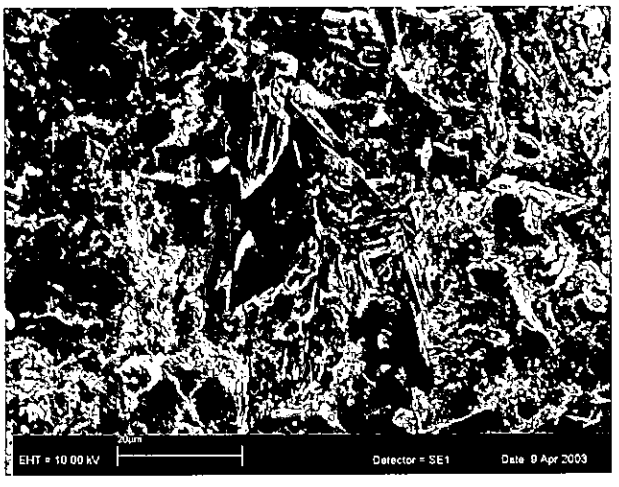

Figure 5. Scanning electron microscope image of calcite crystals (centre of picture) infilling a void in the matrix of a carbonated mortar (0.6 w/c–80% dry).

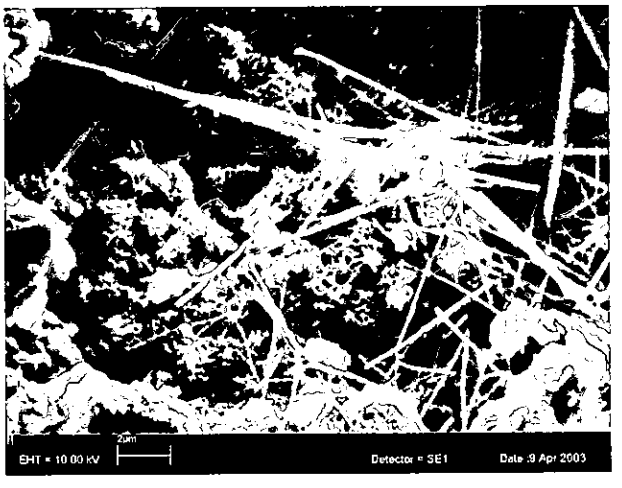

Figure 6. Close-up of the uncarbonated cement mortar showing CSH ground-mass (fine tendrils), ettringite (long needles), and calcium hydroxide (hexagonal plates on the left and bottom right of the image).

Patent Proze

By John Landells and Helen Palmer

TRADITIONAL KNOWLEDGE

Traditional knowledge is commonly understood to be valuable knowledge held by indigenous peoples. Traditional knowledge relating to natural medicines and healing methods is potentially a valuable source of information for the pharmaceutical and biotechnology industries. However, there are growing concerns amongst indigenous populations worldwide about the exploitation of traditional knowledge.

The San people, one of South Africa's oldest groups, have recently signed an agreement with the Council for Scientific and Industrial Research (CSIR) of South Africa to recognise and reward them for their traditional knowledge of plants and herbs.

A plant called 'Hoodia' had been used by the San people for thousands of years to suppress thirst and hunger during long hunting trips. The previously unknown hunger suppressing compound was isolated from the plant and patented by scientists in the parastatal CSIR. The compound was eventually licensed to Pfizer for commercialisation as a hunger suppressing drug for combating clinical obesity.

The potential profits for this drug are huge. The San people could now potentially receive up to about $2 million in milestone payments and about $14 million annually in royalties during the lifetime of the patent.

For the San people, who have resided in the region for over 40,000 years, the financial rewards come at an opportune time. Poverty and unemployment is rife and their language is almost extinct.

Indigenous groups throughout the world may find that their traditional knowledge has potential for sourcing income to improve quality of life or preserve their cultural heritage.

This example demonstrates the type of collaboration and equitable profit-sharing that is possible for indigenous groups holding valuable traditional knowledge but not possessing the technological capabilities to determine any active agents responsible for the known desirable properties. The agreement with the San did not develop out of any legal requirement. The political climate in South Africa, supported by strong human rights legislation, compelled the CSIR to agree to the equitable profit-sharing arrangement.

Intellectual property law, particularly patents, is not well-suited for protecting traditional knowledge. The collective nature of traditional knowledge, where the knowledge is known by a large number of people for perhaps thousands of years, means that the requisite novelty test for patents would not be met because the knowledge has been publicly disclosed and used. It is also not possible to assert patent rights over naturally occurring resources possessing desirable properties. You may recall in an earlier issue of *Patent Proze* (see *Chemistry in New Zealand*, **65**, 3), which concerned the patenting of natural products and life forms, that new substances as they exist in nature are not patentable. For the San people of South Africa the knowledge that a hunger suppressing compound existed in the Hoodia plant would not be enough to gain patent protection over the unknown active agent.

In a patent portfolio, it is often a patent covering the compound(s) *per se* that provides the strongest patent protection. Consequently, it is the isolation and characterisation of new compounds that provides the potential for effective patent protection. However, isolating active agents or new compounds is typically outside the resources of most indigenous groups.

The collective nature of traditional knowledge does not fit with the private rights associated with intellectual property ownership. Traditional knowledge of indigenous peoples is a collective right not necessarily seen as an ownership right. In addition, the limited term of protection afforded by patents is typically inappropriate to provide protection over traditional knowledge.

Patents are also territorial in nature. For example, if the South African government was to allow protection of traditional knowledge, the protection could only be enforced in the South African jurisdiction. A locally operating New Zealand company would be relatively free to use and exploit the traditional knowledge outside of South Africa.

John Landells

Helen Palmer and John Landells of Baldwin Shelston Waters specialise in chemistry and biotechnology patents. Helen joined BSW in 2000. She has a PhD in chemistry from The University of Auckland and postdoctoral research experience. John joined BSW in 2003. He has a PhD in chemistry from the University of Otago and is in the final stages of completing an LLB at Victoria University of Wellington.

Helen Palmer

In many cases, indigenous peoples want to indefinitely protect their knowledge and practices to prevent commercial behaviour that is culturally offensive. A local example is seen with the recent popularity of the moko – facial and body tattooing, which is culturally offensive to Maori people if used out of context.

Internationally, there are moves in place to attempt to protect traditional knowledge. How this will eventually be achieved is unknown.

The link between the protection of traditional knowledge and the protection of indigenous peoples is very close. Developments are underway to protect indigenous peoples' knowledge. An example from the Commission on Human Rights is the Draft Declaration on the Rights of Indigenous Peoples (see <http://www.usask.ca/nativelaw/ddir.html>). The likely resolution to the exploitation of traditional knowledge will be to implement an international treaty to ensure consistency of protection across the globe.

In the event that future protection of traditional knowledge is put in place, scientists may need to obtain consent before undertaking research into elements of traditional knowledge. Such consent may need to be obtained from a controlling body representing the rights of indigenous peoples. Licensing fees or other types of remuneration may also be required.

No doubt the moves to protect traditional knowledge will attempt to strike a careful balance between the protection of indigenous peoples and society's rights to benefit generally from further developments of such knowledge.

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

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Email: communicatorsworkshop@rsnz.org
http://rsnz.org/news/communicators/

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http://www.conference.canterbury.nz/wildlife2003

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http://www.deepsea.govt.nz/legal/pre-conference.asp

10-12 December 2003
Communicators' Training Workshop
Science House, Thorndon, Wellington
Contact: Matt Novack, Phone: (04) 470 5770
Communicators' Workshop, Royal Society of New Zealand, P O Box 598, Wellington
Email: communicatorsworkshop@rsnz.org
http://rsnz.org/news/communicators/

25-29 January 2004
17th IEEE International Conference On MEMS 2004 Maastricht, The Netherlands
Email: info@mems2004.org
http://www.mems2004.org

26-30 January 2004
(ANZIAM) Mathematics-In-Industry Study Group
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Professor Graeme Wake
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http://iims.massey.ac.nz/research/cmi

1-5 February 2004
Science And Technology Studies Network Conference On The Theme Technologies, Publics And Power
Akaroa, Canterbury, New Zealand
http://www.stsnetwork.canterbury.ac.nz

8-12 February
27th International Symposium On Microscale Separation And Analysis
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Email: hpce2004@congress-innsbruck.at
http://www.hpce2004.at

10-12 February 2004
Communicators' Training Workshop
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Contact: Matt Novack, Phone: (04) 470 5770
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http://rsnz.org/news/communicators/

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Email: sally.boult@stonebow.otago.ac.nz

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Email: m.zampaglione@oie.int
http://animal-welfare.oie.int

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Royal Society Council Meeting
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http://www.pittcon.org

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19-23 April 2004
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http://207.195.94.13/isoecol/

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http://www.asms.org/confASMS.php

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Email: norm.mcfarlane@ec.gc.ca
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http://www.forestresearch.co.nz/iufro2004

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In conjunction with the New Zealand Society for Biochemistry and Molecular Biology
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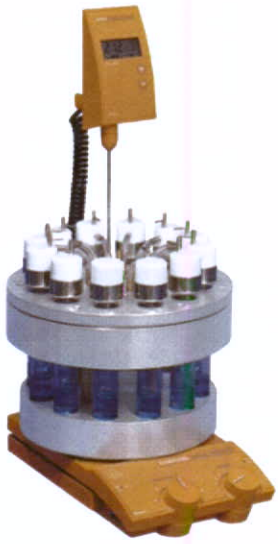

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- Quick and easy access to synthesis tubes
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Advantages of liquid phase system

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Advantages of multiple evaporator

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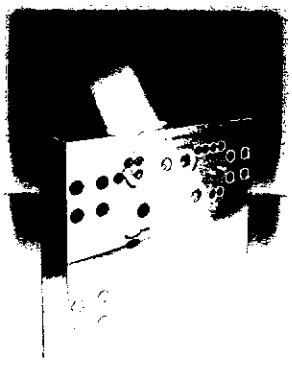
SHIMADZU UNIBLOC TOP LOADING BALANCES WEIGH IN AS MARKET LEADERS



Internationally Shimadzu is an undisputed leader in the market for electronic balances. Established in 1875, the company introduced it's torsion balance and top loading balance products into the market in 1918. These were followed by analytical balances in 1925.

In New Zealand, Atrax Group markets the Shimadzu range of electronic balances. This export-award winning company is the country's leading supplier of weighing solutions and systems. Tony Jarman, National Service Manager for Atrax says that Atrax and Shimadzu have formed a powerful partnership based on technology, experience and Shimadzu's 85-year history developing and manufacturing weighing instruments.

"Atrax Group has a strong reputation for supplying off-the-shelf products or engineering custom solutions to meet the specific demands of their customers. Just as Shimadzu is a world-leading brand, Atrax is the market leader in New Zealand," he says. Atrax takes responsibility for Shimadzu at a time when UniBloc technology is beginning to dominate the market for high performance scientific scales. The UniBloc mechanism, pioneered by Shimadzu in 1989 brings superior all round performance to the balance market. It is rapidly replacing the traditional core assembly of the electro-magnetic balances found in most laboratories and offers significant advantages to the operator such as unrivalled quick response, excellent stability and durability, making it able to support any imaginable weighing application or situation. Display stability can be digitally, adjusted to suit the environmental conditions such as vibration and airflow. A draftshield is also available for some models.

" Liquids, pharmaceuticals, animals, whether in the laboratory or in the field, Shimadzu can do the job," and "the slightest change in ambient temperature can affect results", says Jarman. "The new UW range features automatic internal calibration to compensate for temperature changes during the day and can be programmed to perform this task at set times via the built-in clock which enables the operator to work without interruptions, and not be concerned about these temperature induced inaccuracies".

Other unique features include the Windows Direct function enabling the user to easily link the scales by cable to a PC for direct recording of results. A built-in clock provides calibration reporting that meets GLP/GMP/ISO9000

requirements, unit conversion such as ounces, pounds, carats, specific gravity and percentage, can be measured and a piece counting function is also included as standard.

The analog display mode offers three alternatives. The full range, which is measured by a bar graph clearly indicates the total weight (including the tare) as a proportion of the balance capacity. The fill-in, which selects a target weight and tolerance and clearly displays when these are reached, and check weighing that enables the user to see if the item being weighed is within, over, or under the desired weight range.

A key feature of the Shimadzu UniBloc range is that it offers a very wide selection of balances. "What we have here is a range that comes in ten different variants within the two product types, or a selection of twenty units. This 'something for everyone' approach is essential in the demanding environment of scientific laboratory measurement," says Tony Jarman. The range is competitively priced with pricing varying from $1800 to $2200.

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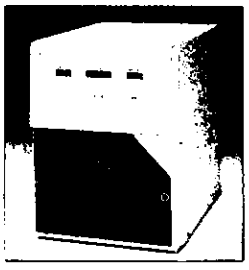
EVAPORATIVE LIGHT SCATTERING DETECTOR FOR HPLC



Shimadzu has completed its family of HPLC detectors with the introduction of the ELSD-LT, a detector ideally suited for applications in food and beverage, drug discovery, natural products development, and combinatorial chemistry.

The ELSD-LT is a universal detector that identifies analytes even if they do not contain a chromophore or an electroactive group. It is not a spectroscopic detector instead it removes the mobile phase through evaporation and makes a light scattering measurement of the dried analyte particles.

The ELSD-LT provides excellent performance during gradients (unlike RI detectors) for optimized separations and reduced run times. A unique cell design reduces band broadening to a level similar to UV-visible detectors while its single mode, low-temperature operation (user defined from ambient to 80 °C) enables you to see all analytes, even semi-volatile compounds down to the high pictogram level.

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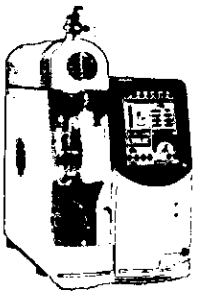
ECLIPSE PURGE-AND-TRAP SAMPLE CONCENTRATORS

Used for sample introduction of volatile organics to GC and GCMS systems. The new generation Eclipse Purge-and-Trap Sample Concentrators by OI Analytical, provide multiple innovative features for unprecedented ease of use, improved productivity, and instrument reliability.



The new pH Express option completely automates sample pH measurement, ending costly, labour-intensive manual measurement and reporting.

The Foam Buster, Foam Sensor, and foam filter provide three levels of defence for the ultimate protection against foaming samples, trap contamination, and instrument downtime. The SOS option prevents sparge tube overfilling, further guarding against potential maintenance problems or expensive downtime. Electronic pressure monitoring provides automated leak checks, alarm functions, and a digital pressure display. Built on proven technology, the Eclipse's new features combine with standard OI Analytical patented advantages - Cyclone Water Management, rapid direct trap heating, and Infra-Sparge Sample Heater.

With its intuitive Windows CE user interface, the Eclipse is exceptionally easy to use. The large, full-colour integrated touch screen LCD provides real-time instrument status at a glance. Program, edit, or view methods and sequences from the touch screen, eliminating external keypads or controllers. Access instrument logs and system diagnostics with one-touch icons to simplify and automate equipment use and maintenance.

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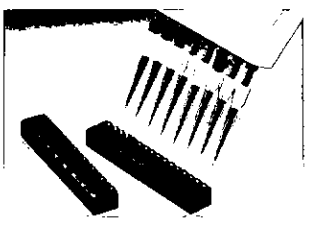
RAPID THROUGHPUT OF UV SPECTRO MICRO SAMPLES



Now you can analyze 16 samples at a time, with as little as 50 µL of sample. Plus, you can continue to use your multi-channel pipette.

The Micro Multi-Cell holder is available as a standard model or with constant temperature control for use with the Shimadzu UV-1601, UV-1700 and BioSpec-1601 spectrophotometers.

The quartz, 8- and 16 micro-multicells allow full operation in the wavelength range of 190 to 1100 nm. They are available in two volume types for both the 8 and 16 series of multi-cell, a 50 µL type and a 100 µL type. The cell intervals of the 8 Series Micro Multi-Cell support commercial 8 x 12 microplates and 8-channel micro-pipettes making sample transfer straight forward.

Ideal for DNA Kinetics Programs:
e.g. 50 mg/mL Calf Thymus DNA in TE buffer, pH 7.4, 260 nm, 25 °C, 60 mins.

Other applications:
e.g. Xanthine Oxidase, pH 7.5, 290 nm, 25 °C, approx. 5 mins.

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BIO-RAD OFFERS FREE, DOWNLOADABLE CHEMISTRY DRAWING, PUBLISHING, AND SPECTROSCOPY APPLICATIONS FOR ACADEMIA

Bio-Rad Laboratories, Inc. announced recently the release of the KnowItAll Informatics System, Academic Edition, a free, downloadable, fully-functional software package for chemical structure drawing, publishing, and spectroscopic analyses. The KnowItAll Academic Edition, available at <http://academic.knowitall.com>, enables users to draw structures in 2-D and 3-D, perform IR and Raman functional group analysis, process IR, NMR, and Raman spectra, access the renowned Sadtler spectroscopy handbooks, and generate high-quality laboratory reports. This software is offered exclusively to the academic community as a part of Bio-Rad's continued commitment to promote learning and research initiatives in academia, providing the latest and most advanced software technology and databases for inquiry-based learning in organic and analytical chemistry. "Increasingly, universities are incorporating software programs and databases within their chemistry departments and curricula", said Gregory M. Banik, PhD., General Manager. "As a former lecturer at Northwestern University, I know how valuable Bio-Rad's products will be in an educational setting, and as a former student, I knew and trusted the Sadtler and Bio-Rad names. Our education initiative allows us to extend and deepen the many excellent relationships that we currently enjoy with professors and publishers throughout the world," continued Dr. Banik. "Also, since KnowItAll was named best spectroscopy software in *Scientific Computing & Instrumentation* magazine's 2001, 2002, and 2003 Reader's Choice Awards, professors can be assured that the KnowItAll Academic Edition offers them the very best."

The software and database tools in the KnowItAll Academic Edition can be used by students, teachers, and researchers at any level. They work particularly well in the organic chemistry curriculum to teach students fundamentals of structure and bonding and spectroscopy as well as in the analytical chemistry curriculum to teach advanced spectroscopy and spectrometry techniques. In particular, Bio-Rad's software tools for IR and Raman functional group analysis allow students to approach these sometimes hard-to-grasp concepts in a way that is both visual and interactive, thus making the learning experience understandable and memorable. The KnowItAll Academic Edition includes free on-line training movies to teach professors and students how to use and get the most out of the software. The following applications and features are included in the KnowItAll Academic Edition:

DrawIt™ for chemical structure drawing.
• Draw 2-D and 3-D structures
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ReportIt™ to generate high-quality lab reports.
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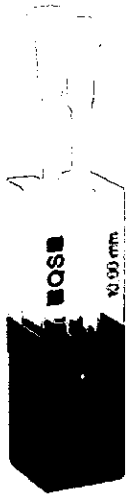
MICROCELLS FOR MICROSAMPLES AT MICRO COST



You have microsamples but don't want to buy expensive accessories to analyse them? The Hellma microcell is a cost effective alternative for most narrow bandwidth spectrophotometers. The microcell with a 10 mm light path, and an aperture size of 0.8 mm, has a volume of 5 µL requiring a sample as small as 10 µL to fill it (a 5 mm path is also available with smaller volume requirements, only 5 µL). The cell has two specially designed ports to accommodate filling the cell, recovery of the sample and flushing the cell easily by pipette. Made from black quartz a mask is not required. A variety of standard cells and flow cells are available from Hellma for low volume samples.

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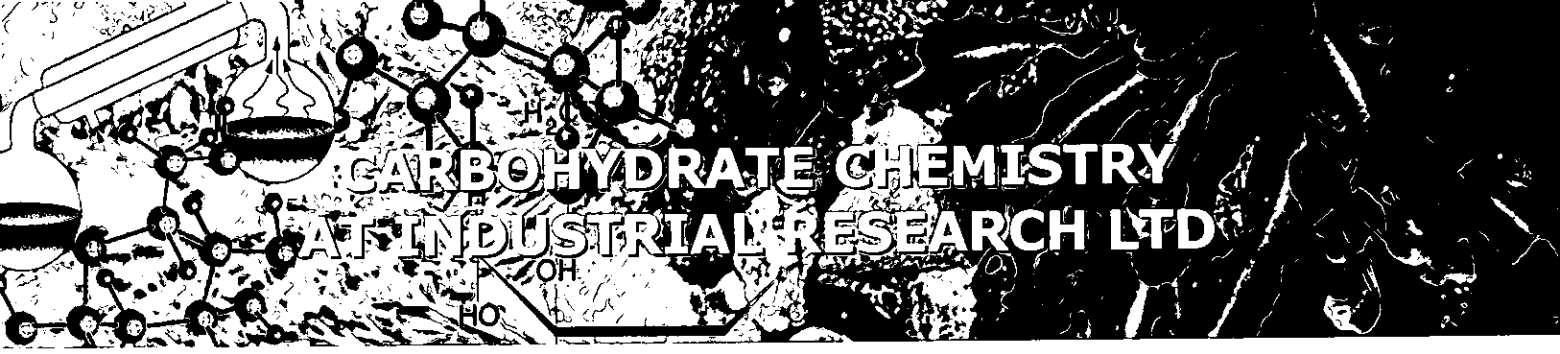
NEW PRODUCTS



Richard H. Furneaux
Industrial Research Limited, P O Box 31-310, Lower Hutt

The Carbohydrate Chemistry Team was established in 1985, in response to the discovery of a new class of carbohydrate-derived herbicide. In a four-year collaboration with ICI Agrochemicals, the Team synthesized over 350 analogues with herbicidal activity and submitted two patent applications in over 20 countries. These early experiences were a sound basis for developing a strong research team focused on carbohydrate chemistry in pursuit of pharmaceutical and dietary supplement products. The Team now specialises in the synthesis of biologically active carbohydrate-derived molecules, custom design and contract synthesis of organic molecules, and in the structural analysis of industrially useful polysaccharides. The three projects that follow below illustrate the range of research currently being undertaken within the Team, which receives financial support from New Zealand Government agencies, including the Foundation for Research, Science and Technology and the Marsden Fund, and from a variety of national and international commercial partners. The Team also operates a significant fee-for-service business. As a result, the Team now comprises 27 scientists (in world-class facilities) with a respected international profile.

The great challenge is to deliver economic benefit to New Zealand. Industrial Research has identified that a key component for success is investment in the commercialisation of the Company's technology-based product concepts. Industrial Research Ltd has now invested $7 million on a current good manufacturing practice (cGMP)-compliant chemical synthesis plant (GlycoSyn) for producing drug candidates for phase I and II human clinical trials. This is just a start, but it is a major step to facilitate a drug discovery industry in New Zealand. Industrial Research looks forward with considerable excitement to the tasks ahead.

TRANSITION STATE INHIBITORS: A BASIS FOR RATIONAL DRUG DESIGN

Gary B. Evans
Industrial Research Limited, P O Box 31-310, Lower Hutt

The recent article by Rewcastle and Denny in *Chemistry in New Zealand*[1] contained a number of sobering facts regarding drug discovery, especially as they relate to New Zealand. Despite considerable investment by various New Zealand Governments, institutions and businesses over the past 100 years, only one compound discovered or invented in this country, the anticancer drug amsacrine, has become a commercial drug. It was developed at the Auckland Cancer Society Research Centre.[1] Furthermore, until the development of Relenza® by Biota/GSK for use against influenza, amsacrine is the only drug to have been developed in the whole of Australasia. Discovery and development of pharmaceuticals are extremely expensive, high risk operations which pose the question: how, if at all, can New Zealand compete or collaborate with the massive multi-national companies in the provision of clinically useful drugs?

A vital component of drug discovery is the choice of strategy to be employed. Are natural products to be exploited, or are candidate compounds to be synthesised? If the latter, on what basis are they to be produced – rational or random? Industrial Research's rational methodology for the identification of lead compounds begins with the identification of enzymes that are key catalysts within biochemical processes that are involved in the development of disease, with literature precedents indicating that their specific inhibition may be clinically useful. Coupled to the identification of appropriate enzymes are the requirements to discover the details of the mechanisms of the reactions they catalyse and hence to design compounds likely to act as specific inhibitors.

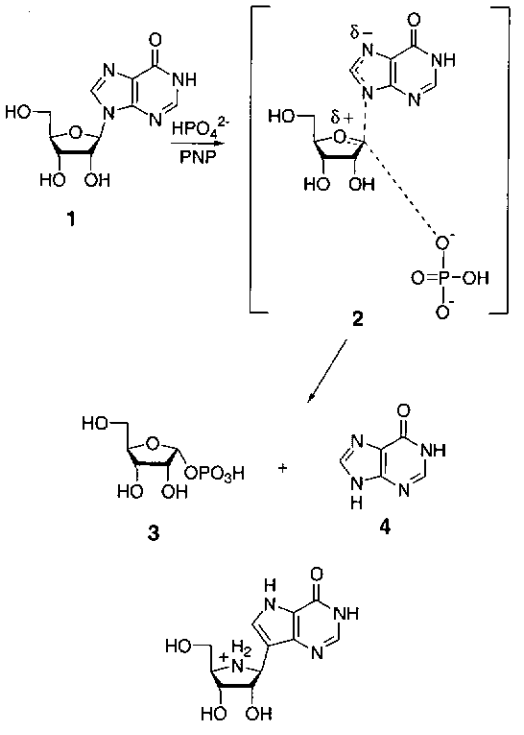
Relenza® is a product of rational design of this kind. The influenza viral enzyme neuraminidase was targeted, its "active site" was mapped in atomic detail by use of X-ray crystallography, and the drug was designed to fit into the site and act as an inhibitor. However, the design was based, not on the natural substrate in its ground state, but on the substrate in the shape it adopts in the transition state of the reaction. This represents a modern extension of the *lock and key* analogy for enzyme action proposed over 100 years ago by Emil Fischer.[2,3]

A more sophisticated method for the design of enzyme inhibitors is based on the experimental determination of the detailed structures, importantly including the charge distributions, of the substrates in the transition states. These may be determined by measuring the effects on reaction rates of replacing specific atoms in the substrates with isotopes.[4] Stable, synthetic analogues of the substrates' transition states can act as enzyme inhibitors with binding affinities many orders of magnitude higher than those for ground state analogues.

The research in which IRL chemists have been involved concerns the generation of transition state inhibitors of the enzyme purine nucleoside phophorylase (PNP) which catalyses the reversible reaction whereby, for example, inosine (**1**) and the closely related guanosine and their 2-deoxy homologues, are phosphorylised to afford ribose 1-phosphate (**3**) or 2-deoxyribose 1-phosphate and either hypoxanthine (**4**) or guanine (Scheme 1). This enzyme is crucial for the operation of the immune system's T-cells and hence is paramount for the maintenance of health. In many autoimmune diseases, such as psoriasis, inflammatory bowel disease and rheumatoid arthritis, T-cells react against the body's own cells of the skin, gut or joints. There are also a series of cancers such as T-cell leukemia and T-cell lymphoma in which the T-cells divide without control and PNP is involved.

At IRL, in a synthetic effort led by Dr. Peter Tyler in collaboration with Professor Vern Schramm, Head of the Department of Biochemistry at the Albert Einstein College of Medicine, New York, several transition state inhibitors of PNP have been synthesized, and the work has reached a most interesting state of development. Professor Schramm, using transition state theory and kinetic isotope-directed design, proposed that the substitution process catalysed by PNP is basically S_N1 in character and has a transition state approximately that depicted by **2.** It was proposed, therefore, that positive charge builds up on the sugar's anomeric centre and ring oxygen atom prior to the attack of the phosphate ion. He then predicted that compound **5**, which was called immucillin-H, would be a PNP inhibitor. In this blueprint inosine (**1**) is taken to be the natural enzyme substrate, and an *N*-containing sugar analogue, which on protonation has an ammonium ion centre to mimic the electron deficient ring oxygen atom in **2** replaces ribose. Furthermore, a chemically stable C-C bond rather than a C-N bond joins the rings.[4]

Scheme 1



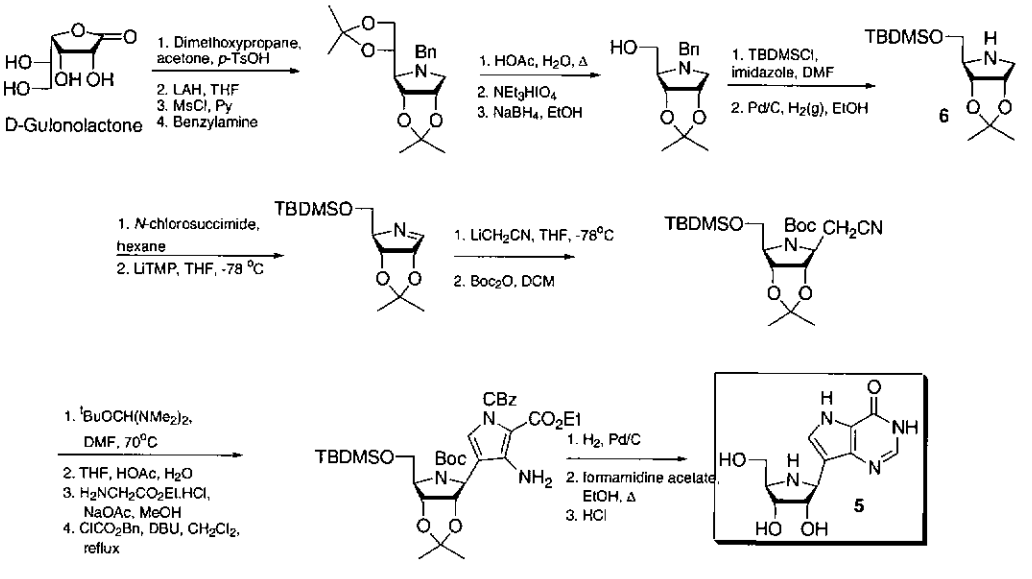
Protonated immucillin-H, **5**

The first synthesis of immucillin-H (**5**) involved 20 steps in linear sequence (Scheme 2) and took roughly three months to develop.

In vitro testing of immucillin-H, in accord with the rationale behind its development, showed that it inhibited both bovine and human PNP and exhibited the characteristics of a "slow-onset tight-binding inhibitor" of the enzyme. Slow onset inhibitors bind as reversible competitive ligands, which cause conformational change to the enzyme that leads to tighter binding. In the case of immucillin-H it is bound to PNP approximately one million times tighter than is the natural substrate inosine, and the size and molecular electrostatic potential properties of the inhibitor are similar to those of inosine in the transition state.

When it had been established that immucillin-H had extremely interesting inhibitory properties, larger quantities were needed for *in vivo* screening and toxicology studies, and a modified, convergent synthesis was developed (Scheme 3). Means of making the key iminoribitol derivative **6** (Scheme 2) in large quantities in the IRL multi-kilogram facility were required, and this can now be done without chromatographic purification in any of the nine synthetic steps that proceed with an overall yield of 45%. The procedure can be completed in approximately four weeks.

Scheme 2



In June 2000 immucillin-H was licensed to Biocryst Pharmaceuticals Inc. (Georgia, USA) as a PNP inhibitor, and this company has taken the compound (as "BCX-1777") through to the clinic, initially for the treatment of T-cell cancers.[5] To date, two patients with T-cell acute lymphoblastic leukemia and two with T-prolymphocytic leukemia have been treated and, most encouragingly, dramatic T-cell depletion resulted in 3 of the 4 patients. Subsequent clinical trials have been extended to the Phase I treatment of refractory hematolgic malignancies, refractory cutaneous T-cell lymphoma, and to refractory T-cell and non T-cell malignancies in twelve cancer centres throughout the USA. Such is the current interest in immucillin-H and PNP inhibition that a crystal structure of the enzyme-inhibitor complex appeared on the cover of *Biochemistry* in 2002 (Figure 1).[6]

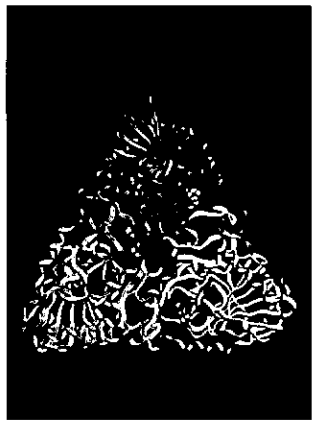
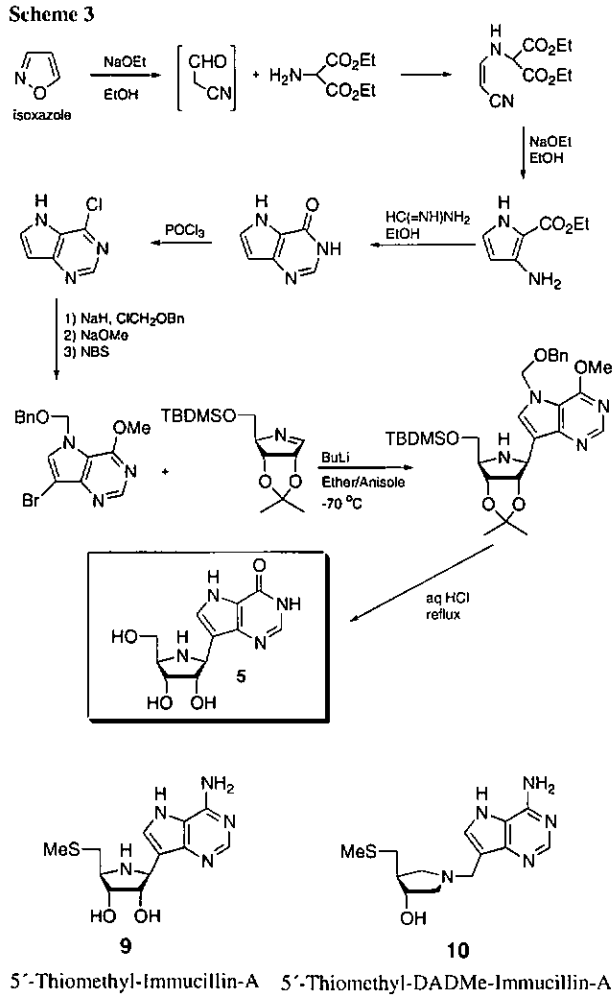


Figure 1. A crystal structure of the PNP-Immucillin-H complex on the cover of *Biochemistry*. Reprinted with permission from *Biochemistry* October 1, **2002**, *41*, cover. Copyright 2002 American Chemical Society.

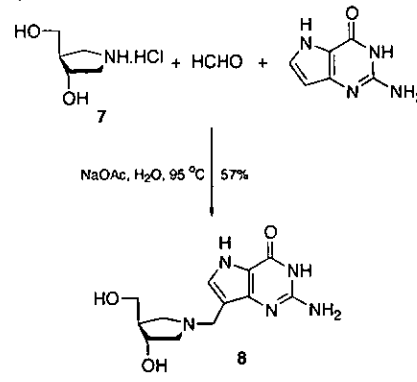
Scheme 3



5′-Thiomethyl-Immucillin-A 5′-Thiomethyl-DADMe-Immucillin-A

Recent research within the synthesis group at IRL has resulted in the design and production of a series of a second-generation PNP inhibitors one of which has eight times the bioactivity of immucillin-H.[7,8] This compound, **8**, was synthesised by use of the Mannich reaction between the hydrochloride salt of the modified sugar analogue **7**, formaldehyde, and deazaguanine in water (Scheme 4).[9,10]

Scheme 4



The same strategy for the design of other inhibitors belonging to the immucillin set has resulted in the preparation of 5′-thiomethyl-immucillin-A (**9**) which is aimed at the inhibition of specific enzymic polyamine biosynthesis and is a further potential cancer chemotherapeutic target.[11] It is the most potent inhibitor of the target enzyme reported at the time of its testing ($K_i^* =$ 90 pM), and the related compound, 5′-thiomethyl-DADMe-immucillin A (**10**), binds to this enzyme even more tightly.

In summary, the strategy described above for drug discovery has proved to be powerful and will continue to identify compounds aimed, as specific enzyme inhibitors, at specific disease conditions. It is planned that antimalarials and new generation antibiotics are amongst the types of products that will be sought and tested in the foreseeable future.

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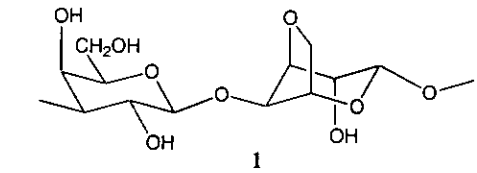
SEAWEED POLYSACCHARIDE RESEARCH

Ruth Falshaw
Industrial Research Limited, P O Box 31-310, Lower Hutt

Water-soluble polysaccharides are widely used in a range of industries such as food, pharmaceutical, cosmetic, paper and textile manufacture, and biotechnology applications such as wound dressings and bacteriological media. Because of their unique properties they can be used as thickening, emulsifying, stabilising, or gelling agents, and some compounds are biologically active against bacteria, fungi and/or viruses. A number of water-soluble polysaccharides come from marine sources such as seaweeds and cannot be made artificially, because of their size and complexity. Industrial Research is involved in research on water-soluble polysaccharides from seaweeds with the objective of developing industrial applications for these materials in New Zealand.

Terrestrial plants use the water-insoluble polysaccharide cellulose for structural rigidity. Some seaweed species contain small amounts of cellulose, but in its place, most species biosynthesise large amounts of water-soluble polysaccharides. These provide not only structural strength but also the flexibility needed for resilience to wave action and abrasion by sand and rocks. The types of water-soluble polysaccharides produced vary with the type of seaweed. ***Agars*** and ***carrageenans*** are water-soluble polysaccharides produced by certain red seaweed species, while ***alginates*** and ***fucans*** are produced by some brown seaweed species. Agars have a (1→3)-β-D-galactopyranosyl-(1→4)-3,6-anhydro-α-L-galactopyranosyl (**1**) repeating unit that can be substituted with methyl ether, pyruvate acetal, and sometimes sulfate ester groups. Some carrageenans have a backbone of (1→3)-β-D-galactopyranosyl (1→4)-3,6-anhydro-α-D-galactopyranosyl (**2**) repeating units and others one of (1→3)-β-D-galactopyranosyl-(1→4)-α-D-galactopyranosyl (**3**) repeating units (Chart 1). Most carrageenans are sulfated, with the number and position of the sulfate groups determining the type and properties of the carrageenan. Carrageenans may also be substituted with methyl ether or pyruvate acetal groups. Alginates are composed of blocks of (1→4)-β-D-mannopyranosyl uronic acid (**4**) and (1→4)-α-L-gulopyranosyl uronic acid (**5**) units, while fucans have predominantly a (1→3)-α-L-fucopyranosyl backbone (**6**) with some sulfate groups at O-4 and single fucopyranosyl branches at O-2 and O-4 (Chart 1).

Chart 1



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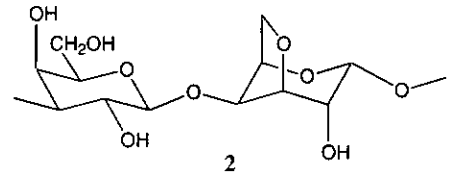

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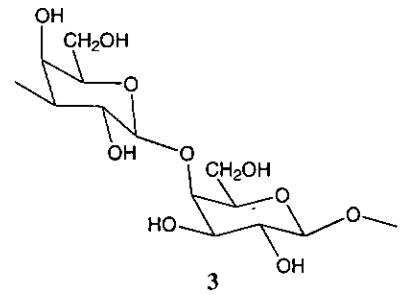

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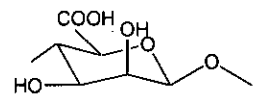

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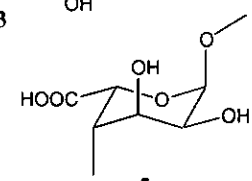

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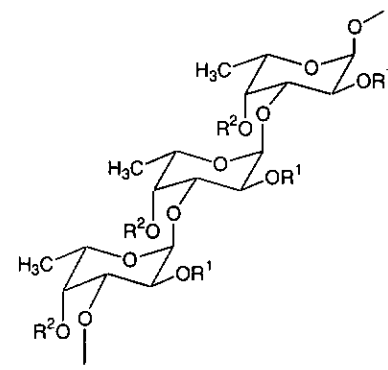
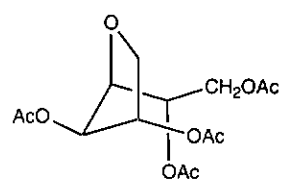


6, R^1 = H or fucopyranosyl;
R^2 = H, fucopyranosyl or SO_3^-



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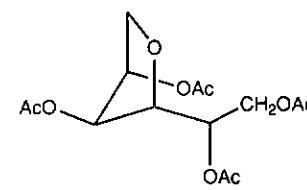

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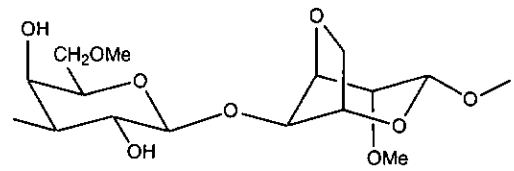

9

Historical Perspective

"Agar", "carrageenan", "alginate" and "fucan" are terms applied to whole families of water-soluble seaweed polysaccharides that can have a range of different properties. Over 800 species of seaweed growing around New Zealand's extensive coastline have been described and named, and many of these are unique to this country. Prior to 1939, the major commercial use of New Zealand red seaweed was for the production of carrageenan (from various *Gigartina* species) for "seameal custard". Production of agar started in New Zealand during the Second World War, when the supply of Japanese agar

ceased, and it is still being manufactured today. The agar is obtained from the endemic red seaweeds, *Pterocladia lucida* and *Pterocladiella capillacea* and is used primarily for microbiological applications. Because of this historical use, a permit is not required to harvest red seaweed commercially if it is beach-cast but large-scale beach-cast harvesting has been constrained by several factors. These include the unpredictable availability of beach-cast seaweeds, the practical difficulty of collecting large quantities of material (often dispersed over large areas) and the variability in condition of beach-cast seaweeds. Higher quality agar is produced from live seaweed so this is a preferable source of raw material. However, since 1971 a permit has been required to take attached red seaweed and since 1988, there has been a moratorium on the issue of new permits due to environmental concerns so raw material supply from attached red seaweed is severely restricted. Although the Ministry of Fisheries is currently considering the inclusion of certain types of seaweed into the quota management system, aquaculture is the only practical method of developing new red seaweed resources in New Zealand at the present time.

The other major seaweed polysaccharide currently used globally on a large-scale is alginate, obtained from certain brown algae, and the alginate contents of various New Zealand brown algae are comparable with, or better than, those from similar species overseas. In New Zealand, some commercial harvesting of *Durvillaea* species occurred in the early 1970s, but did not continue. A permit is currently required to take either attached or beach-cast brown seaweed, but, as there is a moratorium on the issue of new permits for collecting attached brown seaweed, no new supply of brown seaweeds is available.

Recently, IRL has been involved in a major review of the history, current status and future of marine macroalgal research in New Zealand.[1] The development of a new New Zealand-based industry based on high-value products from seaweeds is the key aim of current work by scientists at Industrial Research. Polysaccharides are being extracted from various species of seaweed and assessed for a range of useful functional properties. With this knowledge, it is hoped that the most commercially desirable species can be identified and grown economically. An understanding of the growth of seaweeds and the biosynthesis of their polysaccharides is expected to lead to improvements in the yields and functional properties of products.

Current research is focused on four main areas:

- *The development of new analytical methods.*
- *Polysaccharide structure determination.*
- *Applications* - novel properties, *e.g.* gelling, biological activity, and commercial uses, *e.g.* food, pet food, dietary supplements.
- *Raw material resources* - the production of material in optimum quantities and of highest quality.

Considerable effort has been directed towards the examination of novel structures of hydrocolloids from the many seaweed species found in New Zealand. As a result, scientists at Industrial Research have developed a number of new analytical techniques for the determination of polysaccharide structures that are now being adopted around the world. The *reductive hydrolysis* method combines acid hydrolysis of a polysaccharide with reduction using a relatively acid-stable reductant, *N*-methyl morpholine borane, followed by acetylation to produce alditol acetate derivatives. *In situ* reduction prevents degradation of acid-labile 3,6-anhydrogalactosyl units (which comprise up to 50% of some red seaweed hydrocolloids) and allows the type and quantity of these units to be determined directly.[2] 3,6-anhydro-α-L-galactitol peracetate (**7**) (produced by reductive hydrolysis of agar) and 3,6-anhydro-α-D-galactitol peracetate (**8**) (produced by reductive hydrolysis of certain carrageenans) are enantiomeric and cannot be differentiated by gas chromatography. However, the configuration of 3,6-anhydrogalactopyranosyl units can be determined using the related technique of "reductive partial-hydrolysis".[3] When combined with chemical permethylation of the polysaccharide, valuable information on the structure of the adjacent, non-reducing galactopyranosyl unit can also be obtained. For example, all the 3,6-anhydrogalactopyranosyl units in the complex polysaccharide from the New Zealand red seaweed, *Pachymenia lusoria* were found to be in the L-configuration and were linked to D-galactopyranosyl units with three different sulfate ester substitution patterns.[4] These techniques have also been applied to polysaccharide analysis of seaweed without prior extraction of the hydrocolloid.[5] Very small samples are required and consequently different parts of a seaweed frond can be analysed separately. The development of methods for the incorporation of ^{13}C into the agar of growing seaweed and its subsequent detection by gas chromatography/ mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR) spectroscopy have underpinned research into agar biosynthesis. State-of-the-art NMR spectroscopic techniques have been used to obtain the first one-dimensional ^{13}C-NMR spectrum of ι-carrageenan[6] and the first two-dimensional ^{13}C-NMR spectrum of any carrageenan.[7]

Unusual polysaccharide structures may have unusual properties, and as a result, commercial potential. Over the last twenty years, scientists at IRL, and its predecessor DSIR Chemistry Division, have studied more than 70 species of New Zealand red seaweed, and a number of new polysaccharides have been discovered. For example, the New Zealand red seaweed *Curdiea coriacea* contains agar with a high level of natural methyl-ether substitution, with a structure of alternating (1→3)-6-*O*-methyl-β-D-galactopyranosyl (**9**) and (1→4)-3,6-anhydro-2-*O*-methyl-α-L-galactopyranosyl units. Gels with an unusually high melting temperature of around 115 °C can be prepared from agar with this substitution pattern. This compares with a melting temperature of about 90 °C from unmethylated agar.[8,9] An agar gel that does not melt in boiling water can be sterilised without melting and, consequently, may have a number of potential applications. Unfortunately, *Curdiea coriacea* grows in deep water in only a few places in northern New Zealand so this discovery cannot be exploited unless the seaweed can be farmed. A separate study revealed an unusual, highly pyruvylated agar from the New Zealand red seaweed, *Gelidium allanii*.[10] The presence of

a pyruvate group confers a charge on the agar that alters its properties and application as an electrophoresis medium. *Gelidium allanii* also grows only in a few places in northern New Zealand so this discovery cannot be exploited unless the seaweed can be farmed.

Carrageenans from South America and Asia are widely used as stabilisers in dairy foods (Figure 1). The carrageenans from the New Zealand red seaweed *Gigartina atropurpurea* have been compared with commercially produced carrageenans from similar South American species for commercial potential as stabilisers in chocolate milk. The results were favourable but again sufficient raw material supply is a problem.[11] On the other hand, the agar extracted from the red seaweed *Gracilaria chilensis* collected from the New Zealand coasts, gels only weakly and is commercially useless. However, as a result of biosynthesis studies on the agar from this species conducted at IRL, a suitable gelling product can be obtained simply by depriving the seaweed of light before extracting the agar.[12] Commercially useful products, such as gelled meat products for humans and their pets, are currently under development.

Figure 1. Some dairy products containing carrageenans.

In collaboration with Marinova Pty Ltd of Tasmania, a new focus for IRL is the investigation of the relationships between hydrocolloid structure and biological activity for a complex sulfated galactofucan from the Asian brown seaweed, *Undaria pinnatifida.* Since its initial introduction and recognition in Wellington Harbour in 1987, it has spread to a number of other places in New Zealand, particularly ports. It combines a very high reproductive output with a tolerance of a wide range of growing conditions, enabling it to function as a very successful 'weed' species. It has also appeared in Tasmania, South America, and parts of Europe. While *U. pinnatifida* cannot be harvested in New Zealand at present, over 200 tonnes of this species were collected in Tasmania in 2002 and processed into a powdered extract that is currently being marketed as an anti-viral supplement.

As discussed earlier, a key issue in the development of commercial products from seaweed is raw material supply. If supplies of wild seaweed are not sufficient, or if the quality of wild material is too variable for sustainable harvest, and especially given the current moratorium on commercial collection of many seaweeds from the wild, the obvious option is marine farming (aquaculture). Over the years studies both here and overseas have shown that it is possible to grow a number of different seaweed species successfully. Seaweeds are currently farmed on a very large scale in Southeast Asia, where there is generally good light, warm seawater and cheap labour. In the cooler climate of New Zealand, the economics of production have yet to be established.

The discovery of new, high-value products in New Zealand would provide an incentive for the investment necessary to establish significant industries. Favourable results from the assessment of *Gigartina atropurpurea* carrageenans in both hot- and cold-processed chocolate milk products have provided the impetus to undertake small-scale aquaculture trials of this species in the Marlborough Sounds. These have shown that transplanted wild plants grow very well during spring with three "harvests" per year possible by pruning the plants. This indicates the aquaculture potential of this species for carrageenan production.[13] Such work on temperate species is in its infancy and current research is focusing on the production and culture of spores as a seed stock in collaboration with scientists at the NIWA.

In summary, there remain many species of seaweed in New Zealand that have yet to be examined for their polysaccharide content, composition and commercial potential. A key challenge for researchers is also to develop means to produce sufficient quantities of useful algae for industrial applications.

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PROCESS DEVELOPMENT AND REACTION DESIGN

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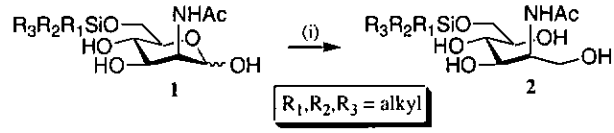
The projects that the Carbohydrate Chemistry Team work on differ in the scale, stage of development, and the sophistication of the chemistry involved. Whilst reaction volumes of around a litre are not unusual to bench chemists, some of the work at IRL for multistep syntheses requires the safe use of kilogram quantities of starting materials in multilitre volumes. Before reactions are scaled-up the inherent properties of the reaction systems need to be understood to both minimise hazards and optimise the way in which the reactions are performed. Scale-up of organic chemistry is often viewed as the exercise of finding a larger flask (or bucket) in which to do reactions. This is often followed by criticism of the chemist for *obviously not following the recipe* as the yield was not maintained on going from the milligram to the kilogram scale, the inherent assumption being that reactions are scale-independent. The job of process development is to determine what factors control the reaction outcomes on scale-up, and to specify reproducible, robust, and safe conditions for conducting reactions.

For understanding the effects of scale on reaction rates, conversion, yields and selectivity, it is important to have a good knowledge of the physicochemical processes involved, as well as the relevant reaction mechanisms.[1] A simple illustration of the point involves consideration of an exothermic reaction and the ratio of surface area to volume of the reactor vessels used as the scale increases. As an exothermic reaction takes place, the heat released is either transferred through the walls of the vessel or remains within the reaction volume resulting in a rise in the temperature or both. Consideration of the geometry of the reactor used to contain the reaction shows that the volume is proportional to the vessel diameter cubed, whilst the surface area available for heat transfer is proportional to the diameter squared. Thus, as the volume of a reaction and the size of the reactor are raised, the ability to maintain constant temperature decreases because of the decrease in surface area to volume ratio. With the loss of temperature control, side reactions can increase relative to the desired main reaction and this leads to a loss in the selectivity and yield of the required product. In the worst cases, scale-up of an exothermic reaction can lead to catastrophic exothermic 'run-away', with disastrous consequences to the workers and to the equipment. An important part of our process development work is therefore to analyse and predict the behaviour of reactions and equipment in order to avoid this sort of outcome.

To help identify and quantify reaction process hazards, IRL purchased a HEL Simular Reaction Calorimeter[2] which is similar to the Mettler-Toledo RC1. This consists of an insulated, jacketed reactor and heater/cooler unit with a number of instrumentation lines attached to a supervising interface unit and computer. In essence, this is an automated lab-scale reactor with instrumentation that allows extensive monitoring of the reactor and surroundings. Computerised methods are used for additions of liquids and gases and for temperature control of the vessel by direct electrical heating or by pumping coolant around the jacket. The pressure within the reactor can also be computer controlled. Aside from the computer's supervisory control function, the interface unit scans through the temperature and pressure probes to enable experimental data acquisition from which underlying thermal behaviour can be analysed.

An example of the calorimeter's use in process scale-up involves the reduction of the 2-acetamido-2-deoxy-mannose-based substrate **1** to the corresponding mannitol analogue **2** with sodium borohydride in methanol (Scheme 1). The experimental small-scale method used 4.5 equivalents of sodium borohydride as a slurry/solution in methanol, most of the reagent being consumed in a background solvolysis reaction that liberates hydrogen and heat, and it is this reaction that constrains the scale-up, rather than the reduction of the sugar itself.

Scheme 1



(i) $NaBH_4$, MeOH, 0 °C to RT

The solvolysis reaction was examined in the calorimeter using a similar addition regime of sodium borohydride to methanol to that used in the sugar reduction. The temperature of the reactor and the change in the jacket feed temperature required to bring the reactor under control were used as the primary data for analysis of the thermal behaviour, and the enthalpy release was then calculated (Figure 1).

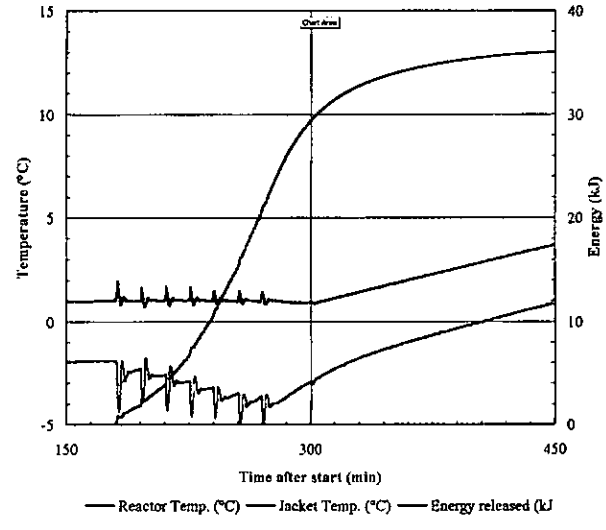


Figure 1. Calorimetry profile for the reaction of sodium borohydride with methanol. Energy release is essentially complete by 450 min.

Both before and after the reaction, the calorimeter's jacket response was determined to a known heating load supplied by an internal calibration heater. The gradual addition of the borohydride to the reaction was performed using seven aliquots between *ca.* 180 and 270 min after the start of data logging, each producing an immediate exotherm as the solid mixed, dissolved, and reacted in the methanol. The control by the calorimeter software rapidly cooled the jacket in response to each of these additions to bring the reactor temperature back to the initial temperature of 1 °C. Following the last addition, a 30 min hold period was used before the reactor temperature was raised to 'room temperature' over the next 16 h. The energy release shows that the reaction was essentially over by *ca.* 450 min, only part-way through this slow heat-up, with most of the energy release occurring during the borohydride addition and 30 min hold periods (Figure 1).

A number of calculations can be made from the calorimetric data and conclusions drawn about the reaction. Thus:

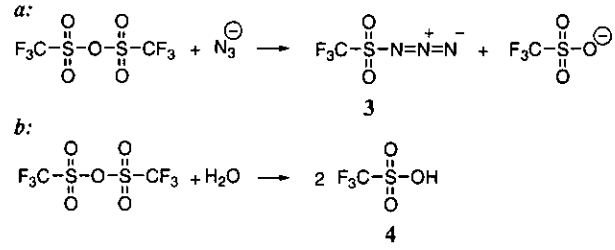
- Most of the energy is released over the addition and holding period (*ca.* 30 kJ observed released over 120 min), rather than during the warm-up period. Over these first two periods the isothermal cooling requirement for the 100 mL reaction volume is on average 42 W L^{-1}.
- In the event of cooling failure, for a reaction volume of 100 mL of methanol (r 0.87 g mL^{-1}, c_p 2.55 J g^{-1}) the total observed reaction energy (36.7 kJ) would result in a nominal adiabatic temperature rise of +165 K, *i.e.* the heat release is sufficient to raise the temperature to the solvent boiling point (65 °C), and to boil off around 20% of the solvent if the process was conducted in an open system. On the large scale, foam generation and boil-out of the reactor contents from the vessel would turn this into a dangerous situation.
- The warm up period can be safely shortened, as the solvolysis is essentially complete within 2 h of the final addition of $NaBH_4$.

This example of the use of reaction calorimetry illustrates a number of points to do with scale. The first relates to process validation. In order to run the experiment in the calorimeter under automated conditions, a plan of the experiment first had to be devised with set timings for the additions and specific reactor temperature conditions. This set plan helps to assure reproducibility of reaction conditions. Secondly, the data gained from this experiment can be used to determine the intrinsic safety of the reaction independent of the reactor and scale. With this set of experimental conditions the reaction is sufficiently exothermic to cause the solvent to boil. The reaction is fortunately sufficiently rapid to allow control of the heat release by stopping the addition of the solids in the event of a cooling failure. Thirdly, the suitability of a reactor vessel for large-scale runs can be assessed using the specific cooling requirement already determined. For example, the viability of conducting the borohydride reduction in 100 L of methanol in a 250 L reactor vessel can be examined using the same addition timing investigated in the calorimeter. The maximum cooling capacity, Q, would be obtained from the equation $Q = U A \Delta T$. The reactor heat transfer coefficient, U, can be estimated to be 100 W m^{-2} K^{-1}, the contact area for this vessel, A, is 0.9 m^2, and the temperature difference, ΔT, calculated for a reaction at 1 °C using coolant at –20 °C. The IRL reactor system can supply 1.9 kW of cooling at 1 °C. The figure for the cooling required, obtained from the calorimeter data, was 42 W L^{-1}, so that at the 100 L scale the heat load is 4.2 kW - the reactor can only supply under half of the cooling required by this system! If the process were attempted without modification, *the reaction could not be kept at constant temperature* during the borohydride addition period.

Faced with this analysis, it is up to the process chemist to determine whether strict temperature control is vital, in which case another vessel is required, or whether the process requires modification by lowering the addition rate or diluting the reaction.

The chemical and physical properties of the reagents and substrates also need to be considered in process development. An example of this requirement can be taken from the use of triflic azide to convert primary amines to azides,[3] a reaction that has been used on large scale by the Carbohydrate Chemistry Team at IRL. For example, a solution of triflic azide (**3**) is made by adding triflic anhydride to a cooled two-phase mixture of organic solvent and an excess of a concentrated aqueous solution of sodium azide (Scheme 2a).[4]

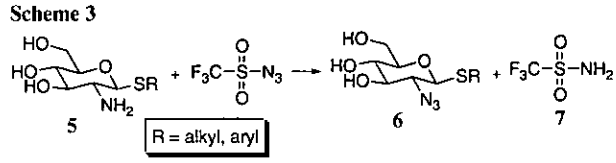
Scheme 2



3 **4**

Free triflic acid (**4**) is also formed in significant quantities during this process due to the triflic anhydride hydrolysing in contact with the aqueous medium (Scheme 2b). The exact conditions used for the preparation of azide **3** were optimised by the use of ^{19}F NMR to monitor trial reactions. After removal of the aqueous layer and of any residual triflic acid by washing, the triflic azide solution was added to the aminosugar **5** to give the desired azidosugar **6** and triflamide **7** as the main by-product (Scheme 3).

Scheme 3



5 **6** **7**

Calorimetry showed that the reaction between triflic anhydride and aqueous sodium azide was extremely facile, provided that adequate stirring was available to give thorough dispersion of the two-phase system (Figure 2). The triflic anhydride was added to the reactor at a constant rate between 125 and 185 min, and resulted in an immediate and proportionate exotherm. At the end of the addition at 185 min, the observed exotherm almost immediately stopped, with no further release of energy evident, implying

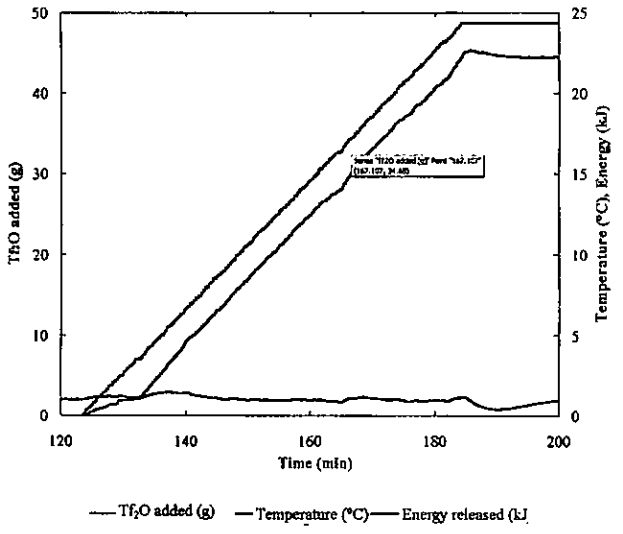


Figure 2. Calorimetry profile for the addition of triflic anhydride to aqueous sodium azide. Energy release parallels triflic anhydride addition, indicating very rapid reaction.

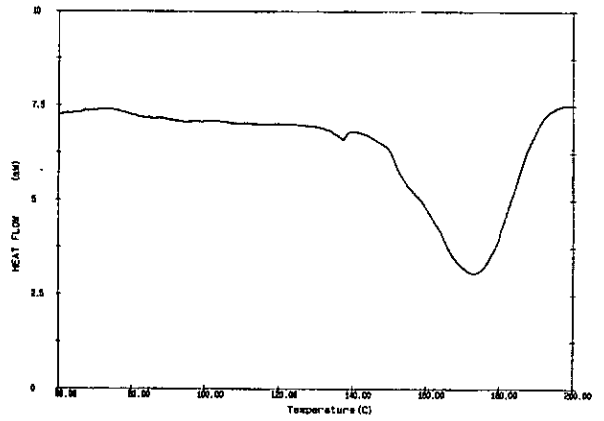


Figure 3. DSC of triflic azide (**3**) solution in dichloromethane, showing decomposition onset at 140 °C

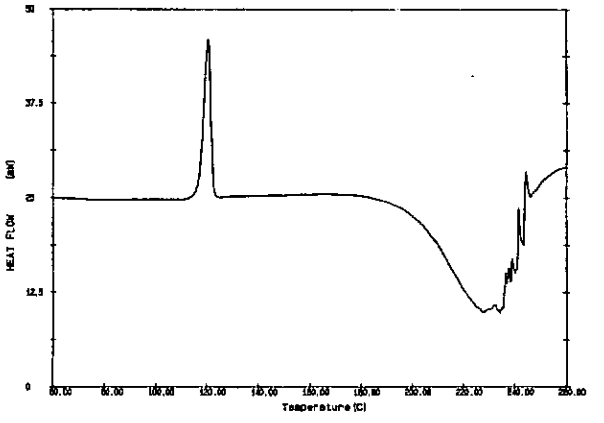


Figure 4. DSC of glucosyl azide (**6**) showing a melt transition at 117 °C and decomposition onset at 190 °C.

that the residual anhydride concentration in the reaction was very low. The adiabatic temperature rise was calculated to be only 20 °C, which was acceptable for the reaction run under these conditions, even in the unlikely event of complete coolant failure.

The preparation and concentration of solutions of organoazides has been implicated as the cause of a number of incidents reported in the literature.[5,6] The work-up of the transfer azidation reaction illustrated in Scheme 3 required concentration of the final solution by rotary vacuum evaporation; so differential scanning calorimetry (DSC) of the triflic azide reagent solution and reaction product **6** were therefore performed to determine their thermal behaviour. Because the original solvent used for this reaction was dichloromethane, the DSC for the triflic azide reagent solution (Figure 3) was run using a high-pressure capsule. The decomposition reaction starts to become evident at approximately 140 °C, giving a wide safety margin for operation with this reagent at sub-ambient temperatures. The DSC for the pure 2-azidoglucosyl product **6** shows similar high temperature stability (Figure 4), with a sharp endothermic melt occurring around 120 °C before the onset of decomposition at temperatures above 190 °C. DSC was also used to examine the intermediate solutions and evaporated product residue for thermal instability and showed these to be safe using the given processing conditions.

For this example the material properties were evaluated by DSC and the reaction exotherm was observed by reaction calorimetry leading to a complete picture of the thermochemistry. The data were then used in preparing reaction protocols and a scale-up hazard assessment prior to successfully and safely performing large-scale synthesis.

In summary, the above examples illustrate the art of process development and the place of calorimetry in assisting IRL launch into larger scale synthetic work.

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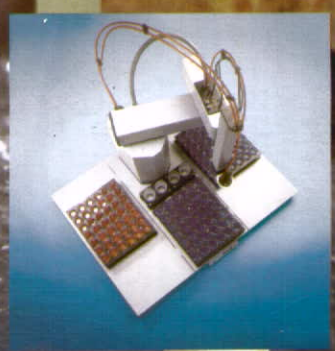

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