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Chemistry IN NEW ZEALAND

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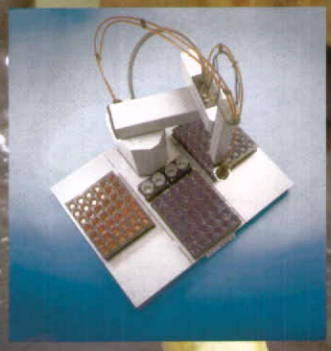

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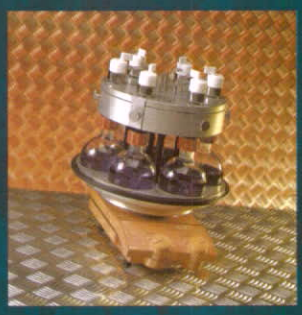

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Chemistry
IN NEW ZEALAND

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On the cover ...

Chemistry of Antarctic Lakes: Ancient and Modern **21**

NZ Science Scene

NEW TECHNOLOGY DEGREE AT MASSEY UNIVERSITY

The School of Engineering and Technology at Massey University is planning to launch a new Bachelor of Technology degree, starting in February 2005 at the Palmerston North campus. The degree will be called Bachelor of Technology (Design and Manufacture: Sports Equipment). Students who study for this degree will be educated in the fields of sports science, basic engineering, design and manufacturing, which will give them a career entry point into the ever-growing sports and adventure equipment industry. A large proportion of the four-year programme will involve 'design and make' project work leading up to a major industry-sponsored project. Maths, Physics and Technology would be good subjects for students to have, although Massey does have a bridging scheme if students fall short in these areas. If you are interested in finding out more then contact:

Joan Brookes, Institute of Technology and Engineering, Massey University, Palmerston North
J.M.Brookes@massey.ac.nz
Tel: (06) 3505115

2004 MARSDEN MEDAL RECIPIENT

Professor Peter Barrett FRSNZ, Director of Victoria University's Antarctic Research Centre, is the recipient of the 2004 Marsden Medal from the New Zealand Association of Scientists (NZAS), awarded annually to scientists who have contributed a lifetime of outstanding service to science in New Zealand. Professor Barrett has been at the forefront of Antarctic earth science for the last 40 years. As a graduate student he made a "missing link" discovery (published in *Science* in 1968) of the first tetrapod fossil to be found in Antarctica, thereby clinching the land connection between Antarctica and the other Gondwana continents.

Professor Barrett has supervised many postgraduate students, most of whom he has given the unique opportunity of working in Antarctica. Many of his students have themselves progressed to notable careers, both in New Zealand and overseas. Professor Barrett is currently a Principal Investigator in two Government-funded programmes that are linked to research in Antarctica and climate change.

The medal was presented at the Royal Society of New Zealand's 2004 Science Honours Dinner in Christchurch on 17 November.

APPOINTMENT OF PETER MORTEN AT MORST

Peter Morten, currently Chief Policy Adviser at FRST, has accepted a new role at MoRST as Principal Adviser, Investment and Performance Group, Vote RS&T Policy. The new role will take effect from 31 January 2005. Prior to joining FRST in 2000, Peter held a Senior Analyst role at the OECD in Paris, and has an academic background in Chemistry, Business Administration, Public Policy and Accountancy.

FRST MANAGEMENT APPOINTMENTS

Dr Tricia Harris has been appointed to the role of Chief Science Advisor for the Foundation of Research, Science and Technology (FRST). Tricia will start with the Foundation on Monday 15 November. The Chief Science Advisor's role is to lead FRST's Science Strategy, manage the portfolio and target outcome framework, oversee the appointment of reference groups and the assessment of the science performance of the Foundation's investments.

Dr John Smart takes up a new appointment in the Foundation as Group Manager: Investments. John and his team have responsibility for the investment processes including the preparation of RFP's and the subsequent contracting, and the monitoring and management of investments once they have been made. John is well known to the Foundation's stakeholders.

Paul Atkins has joined the Foundation as Director of International Investments. In this role he is responsible for bringing an international focus to FRST's investments, including the investment strategy and management of the new International Opportunities Fund, and for developing linkages between funding agencies that will assist to leverage New Zealand's science investment. He is also responsible for further developing the Foundation's scholarship programme and where possible enhancing it with international opportunities.

The other existing members of the Senior Management team: Nick Allison and Wayne Smith, continue in their roles of Group Manager: Policy, Planning and Evaluation and Group Manager: Corporate Services.

QUEENSLAND INVESTS IN NEW ZEALAND LIFE SCIENCE

Queensland Premier Peter Beattie has announced that his government is prepared to invest up to A$6m over the next five years in the New Zealand-based biotech venture capital fund Life Science Ventures (LSV). Last year New Zealand and Queensland signed a biotechnology collaboration agreement, and New Zealand is set to join the Australia-

New Zealand Biotechnology Alliance. The Queensland investment complements the $15m commitment by the New Zealand Government's Venture Investment Fund.

NEW ICT PROGRAMME FOR SCHOOLS

Thousands more students and teachers will get a boost to their ICT skills when they join up to an $11 million nationwide information communications technology (ICT) professional development programme.

The clusters of schools represent a range of geographical and socio-economic locations throughout the country. Each cluster will have $120,000 available each year for the duration of the three-year programme to support ICT professional development activities.

TERTIARY EDUCATION SURVEY

Students enrolled in tertiary education will be surveyed about the quality of the programmes they are studying as part of a new measure that encourages a greater focus on helping students to succeed. The introduction of the new Performance Measure completes the redesign of the way that universities, polytechnics, colleges of education, wananga and private providers are funded. Previous changes included the regulation of tuition fees, a performance-based research fund, and the introduction of new funds that providers can apply for. One indicator used in the Performance Measure will be a sector-wide survey, undertaken at qualification level in order to reflect the views of the learners themselves. It will be professionally designed with involvement from the tertiary education sector, drawing on similar models in the United Kingdom and Australia. After being trialled next year, the first formal survey will take place around July 2006, with results available around September. The Tertiary Education Commission will also collect information on course retention rates and successful course completions at each funded provider.

PROMOTING EXCELLENCE IN SCHOOLS

Education Minister Trevor Mallard has announced a new policy designed to reward schools that are successfully lifting the education standards of their students, and that are sharing their experiences with other schools. At present there are a number of initiatives in place that assist poorly performing schools, but nothing that recognises and rewards schools that work well to raise the educational standards of all their students. It's estimated that up to 270 schools will benefit over four years, with at least a 10 per cent overall increase to their existing operational funding. Schools which apply will be assessed using a value-added approach to ensure that the schools identified as high performing are increasing the performance of their students over time. Over the next six to nine months, the Ministry of Education will be working with the school sector to develop appropriate eligibility criteria and frameworks to support this initiative.

THE ROYAL SOCIETY ELECTS 12 NEW FELLOWS

The Royal Society elected 12 new Fellows at a gathering of its Academy Council in Christchurch on 17 November. There are now 322 Fellows of the Royal Society of New Zealand.

The new Fellows are: Dr Ross E. Beever, Senior Scientist, Landcare Research, Auckland. Professor Ian F. Collins, Department of Engineering Science, The University of Auckland. Professor John D. Fraser, Department of Molecular Medicine and Director of the School of Medical Sciences, The University of Auckland. Professor Boris S. Pavlov, Department of Mathematics, The University of Auckland. Professor James (Jim) Cole, Department of Geological Sciences, and Director, Natural Hazards Research Centre, University of Canterbury. Professor Peter R. Joyce, Department of Psychological Medicine, Christchurch School of Medicine and Health Sciences. Professor Leslie T. Oxley, Department of Economics, University of Canterbury. Professor Graeme C. Wake, Professor of Industrial Mathematics and Centre for Mathematics in Industry, Massey University at Albany, and Adjunct Professor of Mathematics, University of Canterbury. Professor Stephen D. Wratten, Professor of Ecology, Lincoln University. Professor C. Gerald (Gerry) Carrington, Department of Physics, University of Otago. Professor Grant R. Gillett, Professor of Medical Ethics at the Bioethics Centre and Professor of Neurosurgery at the Dunedin School of Medicine, University of Otago. Professor Helen M. Leach, Department of Anthropology, University of Otago.

2004 ROYAL SOCIETY MEDALS AND AWARDS

The Royal Society of New Zealand Academy Council has awarded the following medals and awards for 2004:

Hutton Medal (Earth Sciences): Professor Campbell Nelson FRSNZ, Department of Earth Sciences, University of Waikato, for major contributions in the fields of sedimentology and paleoclimate research.

Sir Charles Hercus Medal (Clinical Sciences and Technologies and Public Health): Professor Jim Mann FRSNZ, Department of Human Nutrition, University of Otago, for his extended series of related studies of nutrition in relation to diabetes and cardiovascular disease.

T. K. Sidey Medal: Dr Pablo Etchegoin, MacDiarmid Institute, Victoria University of Wellington, for his theoretical and experimental work in elucidating Surface Enhanced Raman Scattering and Professor Ian Hodgkinson FRSNZ, Department of Physics, University of Otago, for his work in creating a new class of highly selective optical filters sensitive to the 'handedness' of electromagnetic wave polarisation.

Cooper Medal: Dr Peter Saunders, Industrial Research Ltd, Lower Hutt,

for development of a new mathematically based method for simplifying the measurement of high temperatures using radiation thermometry.

Thomson Medal: Dr John Ayers, Institute of Fundamental Sciences, Massey University, Palmerston North, in recognition of his outstanding contribution to the application of science and technology.

Hamilton Award: Dr Thomasin Smith, Institute of Fundamental Sciences, Massey University, Palmerston North, for pioneering contributions to the mathematics of the structure and function of proteins and the geophysics of two-phase flows in fractured porous media.

Hatherton Award: Dr Paul Gardner, formerly of the Institute of Fundamental Sciences, Massey University, Palmerston North, for his contribution as lead author of the paper 'Optimal Alphabets for an RNA World' published in *Proceedings of the Royal Society London B*, **2003**, 1177-1182.

Fleming Award: Dr Steve Dawson, Department of Marine Science, and Dr Liz Slooten, Department of Zoology, University of Otago for their very significant contributions to the conservation of marine mammals in New Zealand, most notably but not exclusively the endemic Hectors and Maui dolphins.

Thomas Kirk Medal for high scholarship in contributions to scientific forestry in New Zealand. Awarded by the New Zealand Institute of Forestry to Dr Michael Wilcox.

Jubilee Medal for an outstanding contribution to primary resource science. Presented by the New Zealand Institute of Agricultural Science and the New Zealand Society for Horticultural Science to Emeritus Professor Alan Frampton.

ACADEMY COUNCIL ELECTIONS

The Academy Council of the Royal Society held its Fellows' Annual General Meeting in Christchurch recently. At the meeting Professor Marston Conder, already an Academy Councillor, was elected President Elect for two years. Professor Paul Callaghan, President of the Academy Council from 2000 until 2003 and Past President this year has completed his term on the Academy Council. Professor Joyce Waters from Massey University, Albany, and Dr Stuart Corson from Forest Research, Rotorua, have completed their 4-year terms on the Academy Council. Professor Tom Barnes from the University of Auckland, Dr Garth Carnaby, formerly of Canesis Ltd and now a Consultant, and Dr Brent Clothier from HortResearch, Palmerston North were elected on to the Academy Council for 4-year terms.

2004 SCIENCE HONOURS

A variety of awards, from the Rutherford to the Chemistry Olympiad Silver Medal, were presented at the 2004 Science Honours dinner held in Christchurch this week. The Science Honours event is organized by the Royal Society of New Zealand on behalf of the science and technology community. Next year, it will be in Wellington.

Rutherford Medal for an exceptional contribution to New Zealand society in the field of science and technology. Awarded by the Royal Society of New Zealand on behalf of the New Zealand Government. Awarded to Professor David Penny, Research Director of the Allan Wilson Centre for Molecular Ecology and Evolution, based at Massey University, Palmerston North.

Pickering Medal to recognise excellence and innovation in the practical applications of technology. Awarded by the Royal Society of New Zealand on behalf of the New Zealand Government. Awarded to Dr Bob Buckley, Industrial Research Limited, Lower Hutt.

R J Scott Medal to recognise excellence in engineering sciences and technologies. Awarded by the Academy of the Royal Society of New Zealand to Professor Emeritus Jos Arrillaga, University of Canterbury, Christchurch.

Marsden Medal for a lifetime of outstanding service to science. Awarded by the New Zealand Association of Scientists to Professor Peter Barrett, Antarctic Research Centre, Victoria University, Wellington.

Research Medal for outstanding research. Awarded by the New Zealand Association of Scientists to Associate Professor Richie Poulton, Dunedin School of Medicine, Dunedin.

Liley Medal to recognise research which has made an outstanding contribution to health and medical sciences. Awarded by the Health Research Council of New Zealand to Associate Professor Richie Poulton, Dunedin School of Medicine, Dunedin.

Te Tohu Pae Tawhiti Award for research in Maori education. Awarded by the New Zealand Association for Research in Education to Professor Russell Bishop, University of Waikato, Hamilton.

McKenzie Award for educational research. Awarded by the New Zealand Association for Research in Education to Professor Sue Middleton, University of Waikato, Hamilton.

Silver Olympiad Medal, awarded by the International Chemistry Olympiad to Reed Roberts, student at Scots College, Wellington.

Outstanding Physiologist, awarded by the New Zealand Society of Plant Physiologists to Dr Ralph Bungard, University of Canterbury.

Applied Biosystems Award, awarded by the New Zealand Society for Biochemistry and Molecular Biology to Associate Professor Iain Lamont, University of Otago, Dunedin.

NZMS Research Award, awarded by the New Zealand Mathematical Society to Associate Professor Eamonn O'Brien, The University of Auckland, Auckland.

Three R's Award for excellence in humane use of animals in research, teaching and testing. Awarded by the National Animal Ethics Advisory Committee to Cawthron Institute, Nelson.

Genesis Energy 'Realise the Dream' premier award, awarded by the Royal Society of New Zealand in association with Dexcel Limited to Bridget Nicolson, first year student at The University of Auckland.

NEW PROCESS TRIALLED TO SELECT RESEARCH INVESTMENT

The Foundation for Research, Science and Technology is piloting a new system for selecting the research investments that it funds. The Foundation has investments of $465 million of public money in a range of research initiatives in New Zealand. The new investment process, which is being trialled with the 'natural ecosystems' funding round, focuses on the ultimate objective of the research and is called 'Outcome Based Investments' (OBIs).

Under the new process, research providers such as Crown Research Institutes and Universities will make investment proposals to the Foundation to deliver results from research that will benefit New Zealand. With the example of possum control, an organisation may put up a proposal to reduce numbers of the pest by "x" percent by 2020 through new research-based innovation. While they will have to prove that they can achieve such an outcome, the finer points of how this will be achieved is up to the organisation. They will be required to report progress on a regular basis and careful monitoring of their project will be undertaken by the Foundation.

Under the present system, there is more emphasis on the actual process to be followed to achieve an outcome.

APPLICATIONS INVITED FOR ISAT LINKAGES FUND 2004-05

International Science & Technology (ISAT) Linkages Fund: NZ/Deutsche Forschungsgemeinschaft Programme
In September 1997, a Memorandum of Understanding was signed between the New Zealand Ministry of Research, Science and Technology and the Deutsche Forschungsgemeinschaft of Germany, to foster exchange of researchers between New Zealand and Germany. The Minister of Research, Science and Technology, through the International Science and Technology (ISAT) Linkages Fund, has allocated funding to the "NZ/DFG Programme" for 2004-05. Joint applications are invited, with New Zealand applications going to the Royal Society and German applications going to the German Research Foundation (Deutsche Forschungsgemeinschaft). Funding will be provided for joint seminars and workshops, in areas where the exchange of information promises to improve the level of co-operation between scientists of the two countries. The joint seminars and workshops can be held in either country.

The co-organisers are responsible for the scientific programme, the organisation and the financial management of the joint seminars and workshops. It is expected that costs between $20,000 and $60,000 (GST inclusive) will be sought for the proposed joint seminars and workshops. Successful applicants will be required to provide a written report on the joint seminars and workshops detailing significant immediate and expected long-term outcomes from the activity.

Applications will close with the ISAT Fund Manager, Royal Society of New Zealand at 4.00 p.m. on Monday 17 January 2005. Guidelines and Application Forms are available for downloading at http://www.rsnz.org/funding/isat

SCHOLARSHIP FOR STUDY IN SCOTLAND

Want to study for a Masters in Scotland? The British Council and the Scottish Executive are working together to offer a scholarship to a New Zealand resident for the academic year 2005/6. The scholarship is available for courses at any Scottish higher education institution and applications in science and technology and creative industries will be given priority. The deadline for applications is Friday 18 March 2005. For the application form and eligibility criteria visit http://www.scotlandscholarship.com/ or for further information, contact felicity.connell@britishcouncil.org.nz

SUPPORTING EXCELLENCE IN TERTIARY TEACHING

Speaking to the Association of University Staff conference in Wellington, Steve Maharey said a National Centre for Tertiary Excellence will be established next year to build on the work already undertaken to acknowledge and reward excellence in tertiary teaching. The government has agreed to provide up to $4 million a year for the Centre's operating costs.

The National Centre for Tertiary Teaching Excellence will promote effective teaching and learning through: describing the components of effective teaching and learning; documenting systems and practices (with examples and case studies) required for effective teaching and learning; providing a clearing house for research on teaching and learning; networking educators at local and regional levels; undertaking research into teaching and learning.

The National Centre will also explore the need for tertiary teaching qualifications and support the development and availability of quality professional development options for tertiary teachers.

UK SCIENCE COMMUNICATION BURSARIES

The Association of British Science Writers (ABSW) has student bursaries of up to £10,000 for postgraduate training in a Science Communication or Journalism course. While the study must be undertaken within the UK, the bursaries are available internationally. The bursaries are available for full-time or part-time study and will cover course fees and living costs. Anyone with an interest in science and a talent for communicating it, of any age, is eligible for the scheme funded by the Wellcome Trust. For further information see http://absw.org.uk/bursaries.htm

Schoolboy Home Laboratory Supplies In The 1940s:

A Sequel To Analysts Three - L.W. Ruddle.

Rob H. McKeown
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A failed attempt to collect oxygen released by aquatic plants in a fresh water stream, in a small glass (ink) bottle, was my introduction to science. On reporting this lack of success to our Standard 4 (year 6) teacher, his student assistant - a trainee teacher - responded *if you want oxygen why not make it in the laboratory, it's a standard preparation in secondary school chemistry classes.* With some suggestions for needed chemicals and apparatus I set out for a firm near the *Gas Company Offices* that turned out to be Steele Chemical Proprietary Ltd. of 186 Oxford Terrace, Christchurch. It had closed but a former Manager had set up in his own right as Law's Scientific and Manufacturing Co. Ltd., 124 Lichfield Street; there I was provided with potassium chlorate, manganese dioxide, test tubes, glass and rubber tubing, and rubber stoppers. At home the beehive shelf was fashioned from a circular tobacco tin and the pneumatic trough was a large (cake) baking tin. Jam jars served for gas jars and the flame source was the base of a kerosene bicycle lamp filled with methylated spirits. All was assembled and set up in the workshop attached to the garage and, after a very late night's effort, the collection of oxygen was again unsuccessful! In retrospect, it seems likely that leaks in the apparatus were probably responsible. However, interest in apparatus and chemicals, *etc.*, had been initiated. This, together with meeting Kevin Ecroyd, an older boy whose father owned a bees' wax factory that housed a simple laboratory and had purchasing access for most scientific suppliers,[1] opened doors and facilities were acquired, *e.g.* mortar and pestle, thistle funnels, evaporating dishes, beakers, *etc.* Each Saturday night he would put on an experiment, usually something he had done at secondary school. This conveyed the purpose of the experiment and the pre-planning needed for assembling the chemicals and apparatus especially.[2]

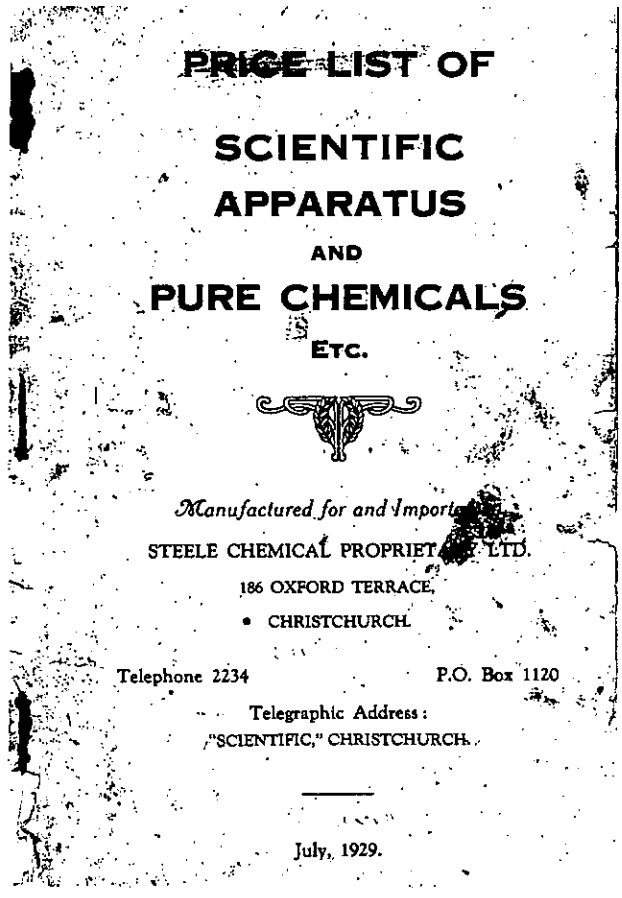
While several makeshift laboratories in undedicated locations followed for me from 1942, a more serious beginning came about when we moved to a large home at 47 Mansfield Avenue in 1944. The outbuildings, over roofed from the house, included a laundry storage or linen room *ca.* 15 ft. x 6 ft. next to the wash house, which was made available to me for a laboratory. It was lined with tongue and groove panels but these were cut away to provide shelves for chemicals. The main workbench was at the end of the room with a latch window that overlooked the garden behind it. Gas was piped in, plumbing[3] set up for water, and there was an electric light and power point. This was my *Schoolboy Home Laboratory* in which most of what follows took place from 1944 after the special apparatus sale at Law's Scientific and a visit to Wilton's, *etc.*, in 1943.

Above: The author in 1943 with avian friends photographed by a young neighbour about to go to Canada for Air Force war training. This was his first camera and I his first subject; I had to pose with all my pets.

A familiarisation with qualitative analysis, early attempts at titrimetry and Soxhlet extractions of bees' wax from filter cake, preparation of lead sulfide (for crystal sets[4]) and photographic developers (from a mixture of chemicals[5]) for printing negatives, *etc.*, and the acquisition of books (borrowed copies[6] of J. B. Cohen and F. Mollwo Perkin before my own were obtained), *etc.*, all preceded my introduction to Mr. Les Ruddle. Thereafter (1946) previously unobtainable chemicals and apparatus followed, and these allowed the experiments that are specifically referred to. Moreover, I had many unanswered questions with no one available to properly answer them until LWR.

An older boy who knew him took me to meet Mr Ruddle in 1946. I was in my second year at secondary school and went with a group all from his old school. By then I had decided that to become an Analytical Chemist would offer variety and challenge, and the consulting that would be involved appealed, and I would have my own laboratory. To be truthful, I couldn't imagine the other areas of chemistry and how one would be paid to pursue them - rather naïve admittedly but not as strange then as it might seem now.

An analytical chemist's reputation (there were few other kinds then) appeared to depend on accuracy and the ability to deal with details, and criticisms seemed to arise quickly if shortcomings were detected, or so it seemed to me. Along these lines, I was especially interested in the details for the preparation of standard volumetric solutions (everyone made their own then) for titrimetry. Choice of reference



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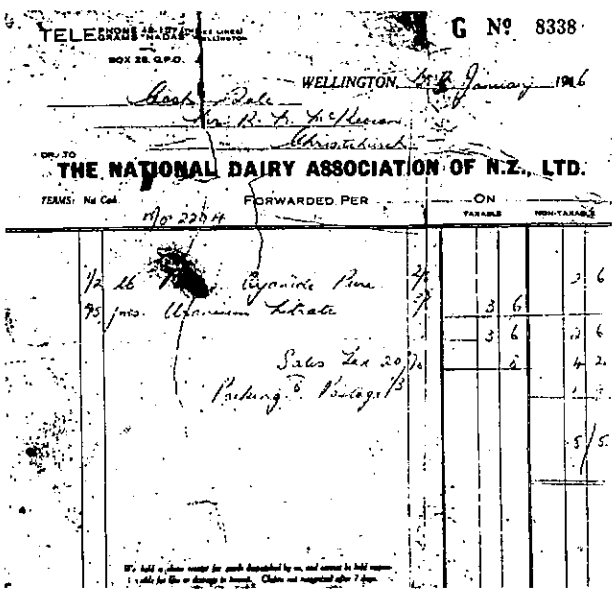
Above: 1929 Scientific Supplies Catalogue.

standards and indicators, the need for getting strengths exactly 0.1 M (Normality then), or similar (one of my misconceptions), the large volumes (outside the range of standard volumetric flasks) involved in making stock were all matters I sought information on. Les Ruddle (LWR) explained how use of factors circumvented the need for the exact normality values (always cited in the BP Assays), and that solutions were prepared during the winter months because the temperatures were closer to those specified for volumetric glassware, and that there was less variation in the laboratory thermal ambience. Sodium carbonate, after ignition, was a favoured standard substance for acidimetry. My encased balance weighed to 1 milligram, which allowed reasonably good results to be obtained for most situations; I'm not sure that anything more accurate would have been any more advantageous for the stage I was at.

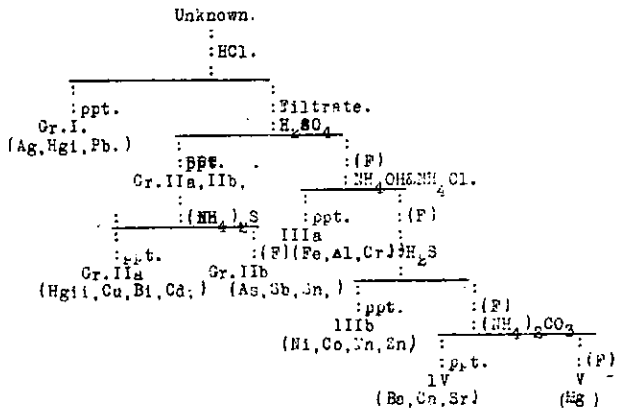
The calculations needed for the back titration[7] in Kjeldahl nitrogen determinations, were rather a mystery until a worked example was found in *Practical Organic Chemistry* (Mann and Saunders, 2nd Edn.,1946, p. 297); the determination of nitrogen in phenacetin was carried out by this method. The Kjeldahl digestion flask, distillation splash head, and dropping funnel for aqueous NaOH additions were all obtained from LWR. Furthermore, in my home lab, iodine-thiosulfate titrations with starch indicator were carried out. Procedures for use of Dean and Stark equipment in *water determinations* and *Soxhlet extractions* (with apparatus obtained from LWR) were found in *Agricultural Chemistry* (F. T. Addyman, 1904)[6] and other references, some at the public library. As an ongoing project, I used to carry out Soxhlet extractions of bees' wax with ethanol (a poor choice of solvent!), from a diatomaceous earth filter cake that came from the factory owned by my school friend 's father, Arthur Ecroyd. An accumulated mountain of this cake had been retained because it was thought it might contain significant amounts of valuable wax. I believe it was eventually sold and shipped to the UK for commercial extraction, but this could not have been economical. My estimates were that there was no more than 10% wax in it, and that was not of good appearance; its only use would have been as a boot polish mixed and coloured with other substances. In addition to the very good facilities I had for volumetric analysis - on reflection more should have been achieved than was - my laboratory was very well set up for *Systematic Qualitative Inorganic Analysis*, which I had begun before being introduced to LWR. The secret was the abundance of small beakers, funnels, evaporating dishes, stirring rods, H_2S inlet tubes, test tube holders, and racks of test tubes so that the whole *Analytical Table* could be worked through without pausing or having to tip stuff out to free-up apparatus before proceeding again; proper stands for filtrations, retort stands with rings and clamps, and Bunsen burners were on hand. Many of these facilities had been obtained from a visit to Geo. W. Wilton & Co. Ltd. (156 Willis Street, Wellington) while on a holiday trip to Auckland in 1943. Initially, typed[8] Qualitative Analysis Tables (ex-Canterbury College) were used but then Vogel's *Qualitative Chemical Analysis* (1945) became available and then his 1944 *Quantitative Inorganic Analysis*. A wash bottle was in frequent use and the H_2S generator was constructed following an article in the Chemist-Analyst journal. For organic identifications, including alkaloids, glucosides and xanthines, *etc.*, *Qualitative Chemical Analysis (Organic and Inorganic)* by F. Mollwo Perkin was used from an early stage. Its front coloured plate - spectra of metals from salts - was always a fascination. A second-hand set of *Allen's Commercial Organic Analysis* was obtained from Newbold's Bookshop in Dunedin, following a tip-off from LWR. I took out subscriptions to *The Analyst* and *Analytical Chemistry,*[9] and even the Journal of the NZIC from 1944. A copy of *BDH Spot Tests* from LWR, Winter-Blyth's two volume *Foods: Their Composition and Analysis* and *Poisons: Their Effects and Detection,* A. Bernthsen (revised by J. J. Sudborough) *Organic Chemistry*, and Bloxam's, *Chemistry, Inorganic and Organic* were obtained. This last was notable and could be recommended as the single chemistry book to have if stranded on a desert island. Julius B. Cohen's *Practical Organic Chemistry,*[10] was the source for many experiments with aniline, phthalic anhydride, phenol, benzaldehyde, resorcinol, *etc.*, especially for the preparation of synthetic dyes and colouring materials, *e.g.* fluorescein. These, as well as a number of other well known reference texts, made for quite a good beginning for a boy still at 'Secondary School'. Undoubtedly LWR had a large influence on this as I would have been unaware of much chemistry had it not been for the opportunity to visit his laboratory and observe and question. Looking back on all of this, the most surprising aspect is its short duration from meeting LWR. External school examinations from 1947 intruded on the freedoms of earlier carefree years and time given to a home laboratory was correspondingly curtailed.

As can be seen much effort went into sourcing scientific materials and this account would be incomplete without a brief mention of the suppliers. Of the firms devoted to laboratory supplies, Steele Chemical Proprietary Ltd. had gone by my time (1942), but a former Manager (Mr. George D. Law [11]) was at Law's Scientific & Manufacturing Co. Ltd. (124 Lichfield St.). Prominently displayed at the second floor entrance to Law's Scientific was a notice that they were an agent or contact for Dr. Roy Gardner, Consulting & Analytical Chemist, Dunedin (about whom we will hear more later). George Law had come from Dunedin with a background in pharmacy as had Roy Gardner at the outset of his career in Masterton. Law's supplied most of the apparatus and laboratory chemicals for the region during the difficult shortage years of WWII and it was also involved in the manufacture of *Cosmetic Products* for even wider distribution. An interesting aspect of the latter was the supply of perfumes in specific gravity bottles and *Lavender Water* in volumetric flasks; this glassware was from cheap Japanese sources and used in place of otherwise hard to obtain glass containers. Purchased chemicals were supplied in paper bags or cardboard cartons whenever feasible.

In 1943 Law's Scientific held an unusual sale - a fairly large collection of used apparatus that was displayed on a table. From this I obtained my first Soxhlet extractor and a spiral condenser of the kind for *Thorpe's Inland Revenue Alcohol Determination Apparatus*. With a *Beer Flask* and a distillation head from LWR, it was possible to determine *Alcohol* like he did except the specific gravity bottle was an ordinary one. Sadly, the sale arose from the death of Stanley J. M. Hewitt in Wellington from burns in a laboratory fire involving a solvent recovery still.[12] This was before his graduation ceremony[13] for BSc and his father (Stanley Hewitt Snr.), a prominent Christchurch pharmacist, had the home laboratory apparatus sent to Law's Scientific for disposal to remove the associated memories, especially for Mrs Hewitt.



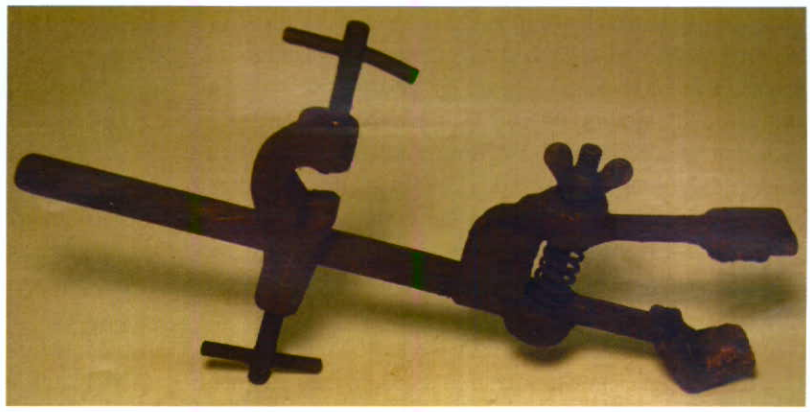
Above: Uranium nitrate and potassium cyanide by post - to *a boy in short pants*. Wouldn't Authorities have a time with that today?



Above: Cation Group Separation Table - from 1940s.

As a supply house, Wilton's (Geo. W. Wilton was a pharmacist who had entered the scientific supplies business) in Wellington has been mentioned. In addition to the purchases discussed earlier, my visit there in 1943 also resulted in supplies of potassium metal (under kerosene), red phosphorus, and ether. These were packed in the same small suitcase[14] with the wooden burette stand, burettes, retort stand clamp, Liebig condenser, *etc.*, all of which returned the 150 miles by sea with us in the cabin on the overnight ferry to Christchurch! Additionally, when WWII finished with a great flash in Japan in 1945, news broke of a bomb that involved uranium. On reading of this I thought *I should have some of that* and placed an order for 75 grams of uranium nitrate with the National Dairy Assn. of NZ Ltd. (P. O. Box 28, Wellington). It arrived by post and was an interesting substance. It emits yellow flashes when the jar is shaken, and was used to entertain friends. The jar would be passed from chair to chair around the lounge, at night with the lights out, for all to have a shake - girls seemed most apprehensive of it as if *another good shake and we all might go West!*" Contrary to conjured imaginations the yellow flashes arise from triboluminescence (uranium nitrate is the best known example) and have little to do with radioactivity, except to provide an ionizing atmosphere perhaps. I still have the jar if anyone has the urge for a shake! The invoice for this purchase, it has more recently been realized, included additionally ½ lb. of potassium cyanide, which arrived in the same parcel *by post to the same boy in short pants!*

In Christchurch supplies could also be obtained from H. F. Stevens Ltd. and Kempthorne Prosser & Co. Ltd., 136 High Street, both principally suppliers of pharmaceuticals but also other in-demand chemicals, *e.g.* conc. sulfuric, hydrochloric, and nitric acids could be obtained in bulk or down to 1 lb. packs. Potassium chlorate, most often used for making explosives, could be purchased in 1 lb quantities; the hardest part was finding the money to pay for it. An *Account* had to be held with the supply house, which my friend's father had, and we just made it a cash sale. In addition, conc. ammonia (0.880) could be obtained from these companies and also from the Gas Works (if you took your own bottle), which similarly could supply benzene, toluene, naphthalene, *etc.* I was able to purchase, from a pharmacy (admittedly after some questioning) two sticks of yellow phosphorus (stored under water to stop it igniting) in 1945 or 1946; the jar was carried home on a bicycle! All of the above *treasures* were conveyed

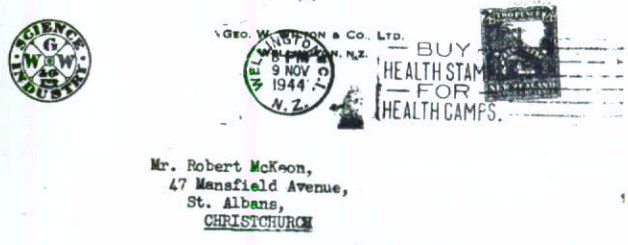


Left: Author's modified Bunsen burner with Rose attachment - used from 1944 and ***Above right:*** Clamp from 1943.

similarly, or by tram or trolley bus (if bicycle transport wasn't available) usually wrapped in paper or even stored in a school bag. As will be realized times have changed, but in those days if a source could be found there was no great difficulty in obtaining chemicals, although instructions and warnings were usual. Sadly all of these company names have become casualties of takeovers, amalgamations, closures, *etc.*, in recent years and are now memories, although their advertisements may be found in back issues of this *Chemistry in New Zealand.*

In those days, pharmacies around Christchurch were also a source of chemicals. Thus salicin (glucoside), caffeine, theobromine (xanthines/-purines), quinine, strychnine, brucine, atropine (alkaloids), and many other drug substances became available in sufficient quantities to allow identification tests to be conducted on a white tile or in micro test tubes. Cinchona bark (a source of quinine) and Coccus Cacti (dried insect bodies - a source of carmine colouring), indigo, *etc.*, were also purchased from pharmacies in the area. I also obtained some of the former as well as a small amount of barbitone from LWR and

Above: The author's apparatus for (left) Kjeldahl nitrogen determination and (right) Soxhlet extraction with sampling stopcock and filter cake (foreground) *ca.* 1946 (from L.W. Ruddle).



Above: Left: Geo. Wilton & Co. Ltd., 156 Willis Street, Wellington (*ca.* Feb. 1993); the company name is still visible. Right: Response to schoolboy enquiries for supplies.

other chemicals that he supplied have been listed already.[15] It needs to be realized that the amounts were small and drug abuse was foreign - it never entered anyone's head to contemplate anything like that in those days. There was far more concern about distilling methylated spirits to remove the colouring and other additives in efforts to obtain high concentrations of ethanol for genuinely scientific purposes. Such activities were suspected to be illegal, but I never knew of any schoolboy with a home lab to get in trouble over this; nearly all were at an age where even alcoholic beverages inspired little interest! Watson Victor Ltd. had premises in Christchurch also and they supplied microscopes and accessories, and physical apparatus (lenses and electrical equipment), *etc.* From them I obtained a selection of milliammeters (with shunts to allow range changes) with huge 6-8 inches diameter dials from an old X-ray machine.

References and Notes

1. Arthur Ecroyd's factory processed bees' wax into foundation for hives, and white wax for cosmetics, *etc.* The author had several holiday and after school jobs there. AE had been an Officer in WWI and his advice to son Kevin and I on safe handling of explosives at every stage was so sound it couldn't be advanced even today. An abiding admiration for his sound advice on this and so many other issues endures. The availability of safe fuse was a major contribution to *gunpowder without tears*, as was grinding all components separately - with clean ups between - mixing powders by shaking in a paper bag or the use of a wooden stick (or other non abrasive object), use of blotting paper wads to wrap the fuse and allow it to be screwed very firmly into place to avoid ejection (like a rocket) without the container exploding, *etc.* A 25 ft length of Blue Jacket Blasting Fuse could be purchased from the Farmers Trading Co., for 1s-9d, and we would bicycle home with the coil hanging over the handlebar, like a cowboy with a lasso hanging on the saddle!

2. A simple example from my home lab was to demonstrate that air comprised 21% oxygen. A glass tube was wetted, iron filings sprinkled into it and, after placing in a beaker of water, the top was sealed. The iron filings adhering to the tube wall rusted consuming oxygen, and the water level gradually rose until 1/5th of the original void was occupied. The displacement measured with a ruler gave a result as near perfect as could be wished for. The secret was to seal the tube without affecting the water level. This was achieved with an inserted cork through which a needle was passed to allow air entry, and then sealed with bee's wax once the levels had equalised. Some year's later (*ca.* 1947) I was asked to provide a class demonstration experiment, for oxygen in air, and I repeated the above. When all was completed the chemistry teacher was called to see if it met his needs and I was asked to be on hand to explain if necessary. His reaction was disbelief; it was so simple and the result was *too good to be true and had to have been faked*! I stood my ground refuting any such suggestion and offered to repeat it again with every step witnessed.

3. The plumbing for my home lab that became available has an interesting twist that only became known many years later. Pipes lying in a horse paddock on the adjoining McDougall Estate (*Fitzroy)* were thought suitable and enquired after from Mr. Blakeway (chief gardener and *Manager of all things practical*). He declared *they weren't his to dispose of but he would see what he could do.* He duly advised me *to go to 51 Browns Road, Merivale, at 4 pm on Thursday* and explain my interest. He was not forthcoming about who I would meet except to say *they would be there and to be punctual.* I set out across the paddock, through the orchard, and entered the back garden. I was admitted through the back door into a living room with a large farm-table, with a scrubbed top, at which sat an older white haired man writing notes in a pad. He advised *that he had a use for the pipes but if he hadn't what would I do with them?* I told him, and many questions followed about laboratory chemists and shop chemists (pharmacists). I responded to all his questions, offering opinions, *etc.* Then, when he was about to announce his decision, a diminutive well-dressed lady swept around from an adjoining kitchen/room and proclaimed *let him have the pipes Hugh, it's great to be young and have ambition.* Later I learnt that he was Sir Hugh Acland, a prominent surgeon with a distinguished military career who also advised Ngaio Marsh about poisons to give authenticity in her detective novels. Many thanks to Lady Acland for a shove at the right moment!

4. A furnace, not unlike an interplanetary rocket in appearance, heated from the bottom with a fierce gas flame was used for PbS preparation. The crucible was large, triangular, and ceramic. An excess of sulfur was heated with lead and the resulting PbS was separated from this. The crucible had been obtained from a favourite uncle (see ref. 7) where it would have been used in the foundry for melting precious metals such as gold, into ingots. A *Crystal Set* operated without an external power source and I remember a boy, in disbelief, calling to inspect this device that had allowed my brother to hear radio news during a power cut in Christchurch!

5. Jack F. Fuller, the husband of an auntie, was a very accomplished photographer, and the source of formulae of components for developers (Metol was the most difficult to obtain), which were recorded on printing paper acknowledging the Armed Service Establishments of origin (HMS Hermes with RAF copyright).

6. Borrowed from my classmate (Ray) whose father, Mr. La Roche, BAgrSc., had kept some of his student reference books. I obtained my own copies later from Newbold's.

7. Distillation of ammonia into boric acid solution allows direct titration of the base thereby circumventing the need for a back-titration (Bradstreet, R. B., *The Kjeldahl Method for Organic Nitrogen*, Academic Press: New York, 1965, pp.150-152). However, I didn't know this at the time and the (M&S) reference was brought to my attention by Mr. John H. Borland (a long-term relief teacher on loan from the Chemistry Department of Canterbury College for our teacher, Lt. Col. J. F. Moffat, BA, MSc, Dip. Ed., Hon. FNZIC, away as *aid-de-camp* to the Governor General of New Zealand in 1946). John Borland is probably best known as a former New Zealand High Jump Champion who could clear the bar at more than his own height – which sounds a surprising feat.

8. Mrs. Veda Fuller, an auntie, typed the tables from a copy borrowed by an older boy from a university chemistry student. Copies are still available but it was quite a feat of typing compared to normal office work; there were no

copying machines then!

9. After my father died in 1947, a favourite Uncle (Archie W. Fraser, owner of a *Brass, Bronze and Aluminium Foundry*) on learning of these subscriptions paid them until I started work and was able to manage myself.

10. Mann and Saunders *Practical Organic Chemistry* was available and used for many experiments, *e.g.* diazonium coupling, preparation of ethylene, *etc.* However, it did not have the diversity that made Cohen so fascinating and captivating as natural products (for which synthetic routes had been established) and other similarly intriguing content was omitted. The first edition of Vogel's *Practical Organic Chemistry* was not published until 1948 and, although obtained at the time, it was not used until the more ordered demands of university study.

11. George D. Law was auditor for the NZIC Canterbury Branch in its early years.

12. *J.N.Z.I.C.*, **1944**, *8*(1), 4.

13. *The New Zealand University Calendar*, 1947, p. 279 (Graduates 1944) and p. 248.

14. Mr. George Wilton, an older, courteous, and genial man, dealt with my scientific order. Helpfully and wisely, he offered to take care of the suitcase for collection on the way back from Auckland, which followed. In addition, he had very recently employed a lady from Europe with knowledge of the preparation of litmus paper and they planned to manufacture test papers upstairs. He regretted that she was not there that day to show me around.

15. See *Chem. in NZ.*, **2004**, *68*(3), 22-30.

Bio-Strategy Secures Key Distributorship

Bio-Strategy Distribution has been appointed distributor of **Pall Laboratory Products** in New Zealand, effective 1 January, 2005.

Pall New Zealand specialises in filtration separation solutions, and is the local arm of US-based Pall Corporation. Globally the corporation has annual sales exceeding $US1.77 billion and invests approximately 10 percent each year into R&D.

Bio-Strategy Managing Director Earl Stevens says this deal is another key opportunity for the company to assist in developing the New Zealand biotech industry.

"It is exciting to watch the growing breadth and depth of agencies we represent. Pall is held in extremely high esteem and is at home amongst our portfolio of specialist biotech industry goods and consumables suppliers. Pall prizes innovation and the highest quality standards and is therefore consistent with our mission of developing New Zealand's biotech industry capability."

This deal follows hard on the heels of September's announcement that Bio-Strategy had been appointed a distributor for Merck.

"While still a relatively new distribution company, there is considerable industry experience guiding it, which has provided the credibility necessary to attract quality agencies seeking a new distribution partner.

"Our strength comes from linking our biotech and international business experience and expertise with an understanding of what our customers are seeking from laboratory products, consumables and apparatus. With our in-depth knowledge of the industry, we can add value to customers' purchase decisions."

Pall New Zealand Limited Managing Director Les Brown says the decision to realign their distribution with Bio-Strategy was based on the company's marketing focus and demonstrated customer service ability.

"I was impressed with Bio-Strategy's operation, and could see advantages for Pall to tap into Bio-Strategy's marketing capability and added-value approach. We believe our customers will receive the best service on offer, and appreciate the advantages that Bio-Strategy Distribution brings."

Pall's business is organized around two broad markets: Life Sciences and Industrial. The Company provides leading-edge products to meet the demanding needs of customers in biotechnology, pharmaceutical, transfusion medicine, semiconductor, water purification, aerospace and broad industrial markets.

Pall filtration and separation equipment is used to develop and manufacture goods across a vast range of industries such as food and beverage, medical, fuels and chemicals, graphic arts, microelectronics, hydraulics and dairy.

A transition period from 1 December will ensure Bio-Strategy a smooth path into the distribution role so Pall customers are not disadvantaged during the hand over from the previous distributor.

THE 2004 NOBEL PRIZES - CHEMISTRY AND PHYSIOLOGY OR MEDICINE

Synopsis

Above: 2004 Nobel Laureates Axel and Buck.

The Nobel Prize in Physiology or Medicine for 2004 has been awarded jointly to **Richard Axel** (Howard Hughes Medical Institute, Columbia University, NY) and **Linda B. Buck** (Basic Sciences Division, Fred Hutchinson Cancer Research Center, Seattle) for their discoveries of *odorant receptors and the organization of the olfactory system* in publications that date from 1991. The Chemistry Prize, announced on October 6, is for the discovery of *ubiquitin-mediated protein degradation* by Aaron Ciechanover and Avram Hershko (Technion – Israel Institute of Technology, Haifa), and Irwin Rose (University of California, Irvine, USA).

The Physiology or Medicine Prize - The Olfactory System

When something tastes really good it is primarily activation of the olfactory system, which helps us detect the qualities we regard as positive. A good wine or a sun ripe wild strawberry activates a whole array of odorant receptors, helping us to perceive the different odorant molecules. A unique odour can trigger distinct memories from our childhood or from emotional moments – positive or negative – later in life. Since their 1991 joint paper, Axel and Buck have worked independently, but in several elegant, often parallel, studies clarified the olfactory system, from the molecular level to the organization of the cells. It has been one of the least well understood and puzzling of the senses with the basic principles for recognizing and remembering some 10,000 different odours not known.

Axel and Buck discovered a large family of *ca.* 1,000 different genes (*ca.* 3% of our genes) that give rise to an equivalent number of olfactory receptor types located on the olfactory receptor cells, which occupy a small area in the upper part of the nasal epithelium and detect the inhaled odorant molecules. Whereas fish have a relatively small number of odorant receptors, *ca.* 100, mice – the species Axel and Buck studied – have about 1000. Humans have a somewhat smaller number than mice as some of the genes were lost during evolution but the area of the olfactory epithelium in dogs is some forty times larger than in humans! Independently, they showed that every single olfactory receptor cell expresses one and only one of the odorant receptor genes. Thus, there are as many types of olfactory receptor cells as there are odorant receptors. It was possible to show, by registering the electrical signals coming from single olfactory receptor cells, that each cell does not react only to one odorous substance, but to several related molecules – albeit with varying intensity.

Buck's research group examined the sensitivity of individual olfactory receptor cells to specific odorants. They were able to empty the contents of each cell and show exactly which odorant receptor gene was expressed in that cell. In this way, they could correlate the response to a specific odorant with the particular type of receptor carried by that cell. Most odours are composed of multiple odorant molecules, and each odorant molecule activates several odorant receptors. This leads to a combinatorial code forming an *odorant pattern* – somewhat like the colours in a mosaic – that is the basis for our ability to recognize and form memories of approximately 10,000 different odours.

The finding that each olfactory receptor cell only expresses one single odorant receptor gene was unexpected. Axel and Buck continued by determining the organization of

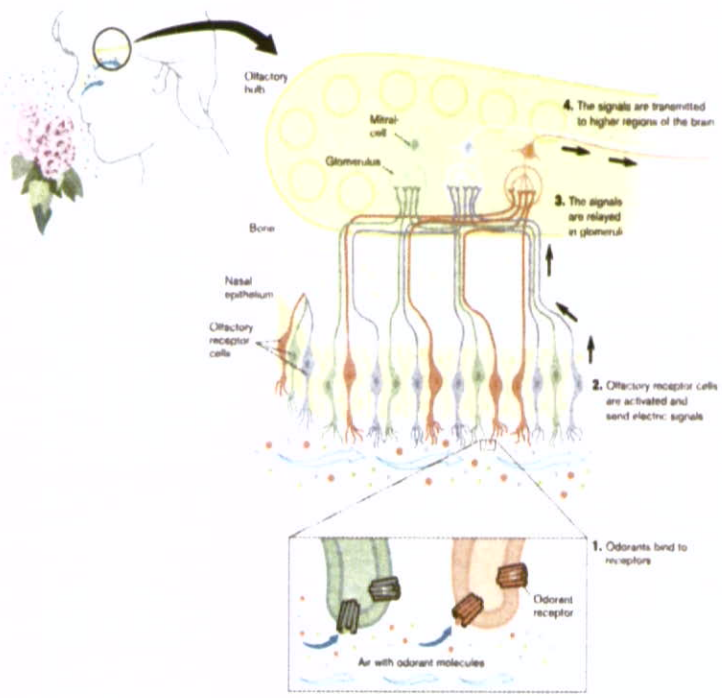


Figure 1: Odorant receptors and the organisation of the olfactory system.

the first relay station in the brain. The olfactory receptor cell sends its nerve processes to the olfactory bulb, where there are some 2,000 well-defined micro regions, *glomeruli*, about twice as many as the types of olfactory receptor cells. They then independently showed that receptor cells carrying the same type of receptor converge their processes into the same glomerulus, with Axel's group demonstrating the role of the receptor in this process in mice. The convergence of information from cells with the same receptor into the same glomerulus demonstrated that glomeruli also exhibit remarkable specificity (Fig. 1).

In the glomeruli we find not only the nerve processes from the olfactory receptor cells but also their contacts with the next level of nerve cells, the mitral cells. Each mitral cell is activated only by one glomerulus thereby maintaining the specificity in information flow. The mitral cells transmit the information to several parts of the brain via long nerve processes. Buck showed that these nerve signals reach defined micro regions in the brain cortex where information from several types of odorant receptors is combined into a pattern characteristic for each odour for interpretation, and leads to the conscious experience of a recognizable odour.

The principles discovered appear to apply to other sensory systems also as Axel and Buck independently discovered pheromones to be detected by two other families of GPCR, localized to a different part of the nasal epithelium. Taste buds of the tongue have yet another family of GPCR that associate with the sense of taste.

The Chemistry Prize - Ubiquitin-Mediated Protein Degradation

Left to Right: Chemistry Nobel Laureates Aaron Ciechanover, Avram Hershko, and Irwin Rose.

The Nobel Prize in Chemistry for 2004 is awarded for fundamental discoveries concerning the way cells regulate the breakdown of intracellular proteins with extreme specificity as to target, time and space. Aaron Ciechanover, Avram Hershko and Irwin Rose together discovered ubiquitin-mediated proteolysis, a process where an enzyme system tags unwanted proteins with many molecules of the 76-amino acid residue protein *ubiquitin*. The tagged proteins are then transported to the proteasome, a large multi-subunit protease complex, where they are degraded. Numerous

Figure 2. Ubiquitin - the polypeptide that represents the *kiss of death*.

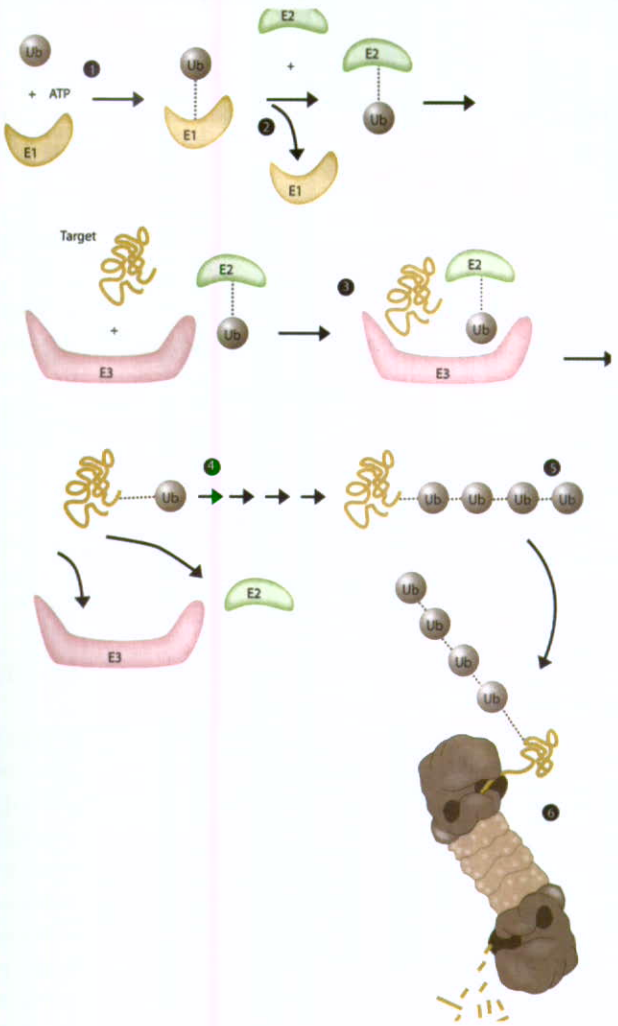


Figure 3. Ubiquitin-mediated protein degradation.

1. The E1 enzyme activates the ubiquitin molecule with energy in the form of ATP.
2. The ubiquitin molecule is transferred to a different enzyme, E2.
3. The E3 enzyme recognises the protein target that is to be destroyed and the E2-ubiquitin complex binds so near to the protein target that the actual ubiquitin label is t ransferred from E2 to the target.
4. The E3 enzyme now releases the ubiquitin-labelled protein.
5. Step 4 is repeated until the protein has a short chain of ubiquitin molecules attached to itself.
6. This ubiquitin chain is recognised in the opening of the proteasome; the ubiquitin label disconnected, and the protein admitted and chopped into small pieces.

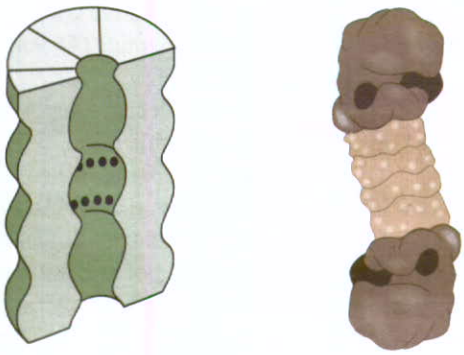


Figure 4. The proteasome: the black spots indicate active, protein-degrading surfaces.

cellular processes regulated by ubiquitin-mediated proteolysis include the cell cycle, DNA repair and transcription, protein quality control, and the immune response. Defects in this proteolysis have a causal role in many human diseases, including a variety of cancers.

While much attention has been paid to the ways a cell controls the synthesis of a certain protein (at least five Nobel Prizes in this area), the reverse, the degradation of proteins, was considered less important. A number of simple protein-degrading enzymes, *e.g.* trypsin, have been recognised and, likewise, a type of cell organelle, the lysosome, had long been studied. While these do not require energy in order to function, experiments in the 1950s showed that the breakdown of the cell's own proteins does require energy. It is this paradox that underlies this year's Chemistry Prize, namely that the breakdown of proteins within the cell requires energy while other protein degradation takes place without added energy.

A first step towards explaining this energy-dependent protein degradation was taken by Goldberg *et al.* in 1977 who produced a cell-free extract from immature red blood cells (reticulocytes) that catalyse the breakdown of abnormal proteins in an ATP-dependent manner. Using such an extract Ciechanover, Hershko and Rose, in a series of epoch-making biochemical studies shortly thereafter, succeeded in showing that protein degradation in cells takes place in a series of step-wise reactions whereby the proteins to be destroyed are labelled with a specific polypeptide - a 76-amino-acid one, isolated from calf sweetbread, and later found in numerous different tissues and organisms (but not in bacteria). It was named *ubiquitin* (Latin *ubique* - everywhere) (Fig. 2). Cells can break down unwanted proteins with high specificity, but the process requires energy. Unlike reversible protein modifications such as phosphorylation, regulation through *polyubiquitination* is often irreversible since the target protein is destroyed. Many of the studies were performed during sabbatical leaves that Hershko and Ciechanover spent with Rose at the Fox Chase Cancer Center (Philadelphia, USA).

In 1977 Avram Hershko began to examine the reticulocyte extract described above. It contained large quantities of haemoglobin that upset the experiments. In attempts to remove the haemoglobin chromatographically Ciechanover and Hershko discovered the extract could be divided into two fractions, each inactive on its own, *but upon recombination* ATP-dependent protein degradation restarted. In 1978 they reported the active component of one fraction to be a heat-stable polypeptide (M_r 9000 only) they termed APF-1 (active principle in fraction 1); this later proved to be ubiquitin. The decisive breakthrough was reported in two 1980 joint publications. The first showed that APF-1 was bound *covalently* to various proteins in the extract while the second demonstrated that many APF-1 molecules could be bound to the same target protein - *polyubiquitination*. Such polyubiquitination of substrate proteins is now known to be the triggering signal that leads to degradation in the proteasome. It is this reaction that constitutes the actual labelling, the *kiss of death* if you prefer.

At a stroke, these entirely unanticipated discoveries changed the conditions for future work as it became possible to concentrate on identifying the enzyme system that binds ubiquitin to its target proteins. Since ubiquitin occurs so generally in various tissues and organisms, it was quickly realised that ubiquitin-mediated protein degradation must be of general significance for the cell. Additionally, the researchers guessed that the energy requirement, in the form of ATP, enabled the cell to control the specificity of the process. With the field so opened, Ciechanover, Hershko, Rose and their students developed (1981-1983) *the multistep ubiquitin-tagging hypothesis* based on three newly-discovered enzyme activities they termed E1, E2 and E3 (Fig. 3). We now know that a typical mammalian cell contains one or a few different E1 enzymes, some tens of E2 enzymes, and several hundred different E3 enzymes. It is the specificity of the E3 enzyme that determines which proteins in the cell are to be marked for destruction in the proteasomes.

In order to study the physiological function of ubiquitin-mediated protein degradation, Hershko and his co-workers developed an immunochemical method and, by using antibodies to ubiquitin, ubiquitin-protein-conjugate could be isolated from cells where the cell proteins had been pulse-labelled with a radioactive amino acid not present in ubiquitin. This showed that cells really break down faulty proteins using the ubiquitin system and that up to 30% of the newly synthesised proteins in a cell are broken down via the proteasomes since they do not pass the cell's rigorous quality control!

A human cell contains about 30,000 proteasomes - the cell's waste disposers. They are barrel-formed structures that can break down practically all proteins to 7-9-amino-acid-containing peptides. The active surface of the proteasome is within the barrel where it is shielded from the rest of the cell. The only way in to the active surface is via the *lock*, which recognises polyubiquitinated proteins. Once admitted, denaturing with ATP energy occurs, the ubiquitin label is removed, and transfer to the barrel for disassembly follows; the peptides formed are released from the other end of the proteasome. Thus the proteasome itself cannot choose proteins; it is chiefly the E3 enzyme that does this by ubiquitin-labelling the right protein for breakdown (Fig. 4).

More recent research

While the biochemical mechanisms underlying ubiquitin-labelled protein degradation were laid bare around 1983 its physiological significance was not fully understood. Its importance in destroying defective intracellular proteins was recognised but, to proceed, a mutated cell was needed in the ubiquitin system. By studying in detail how the mutated cell differs from a normal cell under various growth conditions, it was hoped to gain a better idea of what reactions in the cell depend on the ubiquitin system. A mutated mouse cell had been isolated in 1980 by a research group in Tokyo. Their mouse-cell mutant contained a protein that, because of the mutation, was sensitive to temperature; the protein functioned as it should at lower temperatures, but not at higher. Cells cultured at the higher temperature stopped growing and showed defective DNA

synthesis as well as other erroneous functions. Researchers in Boston quickly showed that this heat-sensitive protein in the mutant mouse cell was the ubiquitin-activating enzyme E1. Ubiquitin *activation* has to be necessary for the cell to function and reproduce itself at all. Controlled protein breakdown was not only important for degrading incorrect proteins in the cell but it probably also took part in control of the cell cycle, DNA replication, and chromosome structure. Since the late 1980s a number of physiologically important substrates for ubiquitin-mediated protein breakdown have been identified. New cell functions controlled by ubiquitin-mediated protein degradation are being discovered all the time and include its involvement in the prevention of self-pollination in plants, DNA repair, cancer and programmed cell death, and cystic fibrosis.

This article was compiled by Brian Halton (Editor) from material freely available on the Nobel Foundation web site, see: <www.nobel.se>.

Obituary: Sir Donald Rees Llewellyn (1919-2004)

The death of Sir Donald Llewellyn on 4 August 2004, aged 84, brings to a close a life devoted to chemistry, education, public service and sport. Not everyone can claim that they made several vital contributions to the development of the atomic bomb, made advances in isotope chemistry, established a new university 'from the ground up', and played a major role in founding New Zealand's foremost agricultural event.

Donald Rees Llewellyn was born on 20 November 1919 in the small Gloucestershire town of Dursley, best known as the home of Listers, manufacturers of diesel engines. He was the second son of Reginald George Llewellyn, a diesel mechanic with Listers, and Mabel Gertrude Llewellyn. Educated at Dursley Grammar School, where he excelled at tennis and football, he went on to Birmingham University with the intention of becoming a school teacher (the easiest way to get financial assistance), but quickly decided that chemistry was more to his liking.

Birmingham University 1938-41

Before he had finished his BSc Don Llewellyn was appointed Personal Assistant to Professor Sir Norman Haworth, Head of the Chemistry Department at Birmingham University. Haworth had been given charge of a section of the *Tubes Alloy* project, a project divided amongst several Universities and Government Departments. Its object was to work out the chemistry and physics of an atomic bomb. The Birmingham team's first task was to devise a large scale method for the extraction of uranium from its ore. Llewellyn developed an electrolysis method based on that used for producing aluminium.

For the process to be feasible it was first necessary to reduce the uranium from its 6-valent state to the 4-valent state. The only published method was based upon the reduction of uranyl salts by formaldehyde, formic acid, or methyl alcohol in the presence of bright sunlight (not plentiful in Birmingham). He found that the reducing agent sodium hydrogen sulfite was available commercially as *Hydrous* and with this he produced a number of uranium(IV) salts. These were subjected to electrolysis in an experimental cell made up in a biscuit tin using a carbon pot from a Leclanché cell and a molybdenum rod as cathode. Using a wide variety of electrolytes (NaCl, $CaCl_2$, $BaCl_2$, *etc.*) he produced uranium metal. This procedure was forwarded to ICI for working into a commercial process.

Clarendon Laboratory, Oxford University, 1941

Over at the Clarendon Laboratory at Oxford another group, mainly of expatriate German physicists, was working on the problem of separating the uranium isotopes ^{235}U and ^{238}U. The most promising method was to pass the only known gaseous compound of uranium, UF_6, gas through a porous membrane. However, this volatile material (of unknown physical properties) was proving very difficult to handle, so the physicists asked for the help of a chemist - Llewellyn was sent over.

His job was to purify the only available samples of UF_6, develop techniques for handling the material in vacuum, and measure its physical properties, which needed to be known for the design of the proposed membranes. Meanwhile the highly corrosive UF_6 destroyed the experimental membranes before any useful information about required pore size, *etc.*, could be obtained. Llewellyn experimented with a mixture of CCl_4 and I_2 that had a mass difference comparable to that between the isotopes. His work allowed for membranes resistant to corrosion to be designed, and a pilot plant was set up at Rhyd-y-Mwyn in Wales. As each component was tested it was subsequently

transferred to Oak Ridge in the US. While none of this could be published at the time, Llewellyn was awarded an Oxford D.Phil. for his work.

Cavendish Laboratory, Cambridge University, 1944-46

After the War Llewellyn turned his attention to the fractional distillation of water and other compounds to produce ^{18}O, ^{15}N, and ^{13}C in quantities sufficient for use in isotope tracer studies, and in the studies of chemical reactions. He developed new techniques for packing his distillation columns, one of which was 15 metres in height and stretched up through three floors of the building. Working in a series with small columns, 20 mL of 12% $H_2{}^{18}O$ could be produced. Apart from the use of ^{18}O in his own laboratory, Llewellyn was able to supply other UK and US laboratories as well as Austria and New Zealand. Llewellyn's work on stable isotopes has been published in some 30 co-authored papers.

Above: Sir Don Llewellyn.

Academic Career

From Cambridge Don Llewellyn went on to a lectureship at University College of North Wales (Bangor) and then to an ICI Research Fellowship and lectureship at University College (London). He was awarded a DSc degree by Birmingham University in 1957, and the same year was appointed Professor of Chemistry and Director of Laboratories at Auckland University; during 1962-64 he was Deputy Vice-Chancellor and Chairman of the Building Committee.

He faced his greatest challenge in 1964 when he was appointed as foundation Vice-Chancellor of the new University of Waikato, the first University established in New Zealand *from the ground up* since Victoria College in 1898. Llewellyn was determined that the new institution would have close associations with the people and institutions of the region, and for 20 years he laboured to make this vision a reality. He developed strong ties with the local/regional Maori and was held in special esteem by them that included an honorary chiefdom. The University stands today, with its 14,000 students, strong research record, and innovative teaching programmes, as a tribute to his success.

New Zealand Institute of Chemistry

Don Llewellyn had the unique distinction of being President of the Institute on two different occasions, in 1968 and in 1989. As with everything he touched the Institute was a passion of his. His support for both Branch and National activities was unquenchable. He opined that to be a member of the Institute should be seen as a necessary item on a chemist's CV. In his second term of office he created the professional secretariat in Wellington.

Other Interests

He was not in Hamilton long before his broad range of interests became evident. In 1967 he chaired the first public meeting of the New Zealand National Fieldays Society of which he had played an important role in establishing. He was President of the Society twice and served on its Board of Management for the rest of his life. He is hailed as *Father of the Fieldays*.

As might be expected, Don Llewellyn's special knowledge and abilities were in demand for memberships of a wide range of committees and organisations. He was a member of the Councils of the Pottery and Ceramics Research Association, the Fertiliser Manufacturers Association, and of the Meat Industries Research Association. He was a member of the Atomic Energy Committee, Chairman of the Education Committee of the National Development Conference and many others.

Don Llewellyn found time for sport and played tennis, squash, badminton and cricket. He was a Chief Judge for the New Zealand Equestrian Federation spending many Sundays judging show jumping events. He was patron for the New Zealand Riding for the Disabled Society and a Life Member of the Cambridge Pony Club, although he was never known to attempt to ride a horse! For 12 years he was a driver for Meals on Wheels.

Honours

Don Llewellyn was a Fellow and Life Member of the RSC, and an Hon. Fellow of this Institute. He was awarded the 1977 Jubilee Medal, Freeman of the City of Hamilton - 1985, Honorary Doctor of Waikato University - 1985, listed on a riverside plaque as one of ten Business Pioneers of Hamilton, the 1990 Medal, Paul Harris Rotary Fellow - 1993, and the Thomson Medal of the New Zealand Royal Society for outstanding contributions in the field of organisation, administration or application of science in 1994. He was created a Companion of the British Empire in 1992, and Knighted in 1999.

Nath Pritchard, (Past-President NZIC)
John McCraw, Professor Emeritus of Earth Sciences

NZIC NEWS

At the October Council Meeting, it was decided to retain the present name of the Institute but to give greater emphasis to the changing nature of our discipline by having a by-line that will go on all note paper, *etc*. A competition will be held to find this by-line with the details placed on the NZIC web page (www.nzic.org.nz) and sent out to Branches soon.

2004 NZIC Prizes

Council is please to announce and offer its congratulations to the recipients of the 2004 prizes. The 2004 Nufarm Prize for Industrial and Applied Chemistry is jointly awarded to **Dr. Richard Furneaux** and **Dr. Gary Evans** of Industrial Research Limited. The 2004 HortResearch Prize for Chemistry is awarded to **Professor David Officer** of Massey University, and the 2004 NZIC Chemical Education Award is made to **Dr. Suzanne Boniface** of St. Margaret's School, Wellington.

New Fellows

Congratulations go to the following members who were elected to Fellowship at the 28 October 2004 Council meeting: **Drs. A. Blackman, S. Boniface, S. Brooker, R. Coll, B. R. Dent, R. H. Furneaux, K. Gordon, L. Hanton, D. Harding, P. T. Northcote, Professor D. L. Officer, Drs. N. Perry, and S. Yorke.**

CET Trust Distribution

The 2004 distribution from the Chemical Education Trust has seen the award of 7 grants encompassing more than half the trust income for the year to:

Ellesmere College, Leeston (**Lindsay Cook**); Sacred Heart Girls College, Hamilton, (**Isla Taufalele**); Solway College, Masterton, (**Lynley Rawston**); Palmerston North Girls' College, (**Raewyn Claridge**); Nelson College, (**David Fairley**); St John's College, Hamilton, (**Steve Wood**); Christchurch Girls' High School, (**Kathryn Coakley**). All the grants made were for laboratory equipment of one sort or another.

BRANCH NEWS

AUCKLAND

NZIC President **Andrew Brodie** visited Auckland in October, and in addition to his two Presidential talks (*Towards new metal-rich molecular scaffolds* and *Chemistry at the crossroads - does the NZIC have a future?*) he presented the 2003 NZIC Chemical Education prize to **Dr. Sheila Woodgate.**

Above: Dr. Woodgate receiving the Chemical Education prize from NZIC President Professor Andrew Brodie.

The University of Auckland chemistry student **Shane Lal** received the *Food for Life Award* announced at the recent New Zealand Food Awards. The criterion for this prestigious award was *for an appetising food product demonstrating relevance and efficacy in meeting a recognised consumer health need and showing leadership and benefits of the product in its class*. Shane's research resulted in a product *Vital low cholesterol milk* available in all good supermarkets and dairies! This was Shane's MSc project supervised by **Professor Charmian O'Connor**.

December marks the end of an era in the chemistry section of the Auckland Cancer Society Research Centre (ACSRC) at The University of Auckland, with the ending of a 25-year collaboration with drug company Pfizer and their

predecessor, the Parke-Davis Division of the Warner-Lambert Company. Pfizer announced in May that they were cancelling their $US40 million research contract with the ACSRC in protest at cost-cutting by the Government drug-funding agency Pharmac, and that cancellation finally takes effect on 31 December. It was only last December that Pfizer renewed their contract with the Cancer Centre for a further 10 years, so the sudden cancellation came as a big shock to all concerned. Sixteen chemists working with **Bill Denny** in the Cancer Centre and a further two people working with **Ted Baker** at the University's School of Biological Sciences, are directly affected by the contract cancellation. It is sad that such a long-standing and productive collaboration has been terminated because of a dispute that has nothing to do with the excellent standard of research that has been performed by the chemists in the ACSRC.

Finally, **Peter Schwerdtfeger** has agreed to chair the Auckland NZIC Conference for 2006. We thank Peter for agreeing to take on this role. Peter is now at the Albany campus of Massey University, but his earlier time at the University of Auckland means that he is ideally suited to lead a Conference organizing committee that involves members from both Universities.

MANAWATU

The September meeting of the Branch was held at UCOL's training restaurant, *Ambitions*. After a very pleasant meal the President **Andrew Brodie**, led a very lively discussion on the future of the NZIC and presented the 2003 SGS Prize (plaque and a cheque for $1000) to **Geoff Jameson**, (Massey University).

Above: NZIC President Andrew Brodie presenting the SGS Prize to Geoff Jameson.

Landcare

Benny Theng gave an invited keynote lecture *The use of clays and modified clays for pollution control and environmental protection* to the 110 attendees at the 2004 International Symposium on Mineral-Organic-Microorganism Interactions held at Huazhong Agricultural University (Wuhan, China). Benny was the only delegate from New Zealand.

Massey University

Paul Buckley, a staff member at Massey University since 1968, is to retire at the end of the year. Paul has made a major contribution to the development of chemistry at Massey and will be missed by staff and students alike; he will be a hard act to follow. In 2005 **Trevor Kitson** will take over from **Andrew Brodie**, as subject leader in chemistry. In this role he will have the overall responsibility for the chemistry academic programme.

Carol Taylor has travelled to the US twice in recent months. She attended and addressed the Gordon Research Conference on Natural Products Chemistry in Tilton (NH) in July and then visited to Lakehead University and the University of Waterloo (Ontario, Canada). More recently, Carol spoke at the 60th birthday - 40 years in chemistry - cellebrations for **Amos B. Smith**, in Philadelphia. Carol also visited Bucknell University (central Pennsylvania) where she was a summer student back in 1988. There have been a number of comings and goings in the Taylor group recently. **Julie Locke** returned to a postdoctoral position with **Professor Stephen Pyne** at the University of Wollongong, Australia while **David Lun** (MSc: **Tony Burrell** and **David Officer**) joined the group in September. David is working as a research assistant, developing efficient synthetic routes to potential flavour compounds, in collaboration with Fonterra. **Karl Shaffer** and **Chris Thompson** will join the group for the summer.

Carrol Walkley (Palmerston North Boys High) has been awarded a NZSM&T Teacher Fellowship from the Royal Society for 2005 to work with **Mark Waterland** and **Richard Haverkamp** on a *Chemical Lithography - Nanoscale Patterning using Atomic Force Microscopy*. Carrol will also spend time with MacDiarmid Institute researchers at the University of Canterbury. **Ibrahim El Sherbiny** has arrived to work with **David Harding** for one year of his Mansoura University (Egypt) PhD programme.

Massey chemists **David Harding** (*From mucus to unique giant polymers*) and **Emily Parker** (*Unravelling enzyme mechanisms: Unexpected dis-similarities in closely related enzymes*) continued Massey success in gaining MURF Postdoctoral Fellowships.

New Zealand Pharmaceuticals

NZP has launched a bold research and development project to develop capability in chemical synthesis, using knowledge acquired over many years by a world-leading research team at Industrial Research Limited (IRL). Research and development agency Technology New Zealand will contribute $NZ1.5 million while economic development agency, New Zealand Trade and Enterprise, is committing nearly $NZ500,000 to helping NZP build business and marketing capability in what will become a new and vibrant niche carbohydrates sector.

Dr. Selwyn Yorke (NZP Market Development Manager) says the company's ongoing and successful relationship with IRL is the incentive behind the big investment. **Dr. Furneaux**, and the IRL team are world leaders in the niche

area of glycotherapeutics, discovering new drug treatments from carbohydrate materials.

WAIKATO

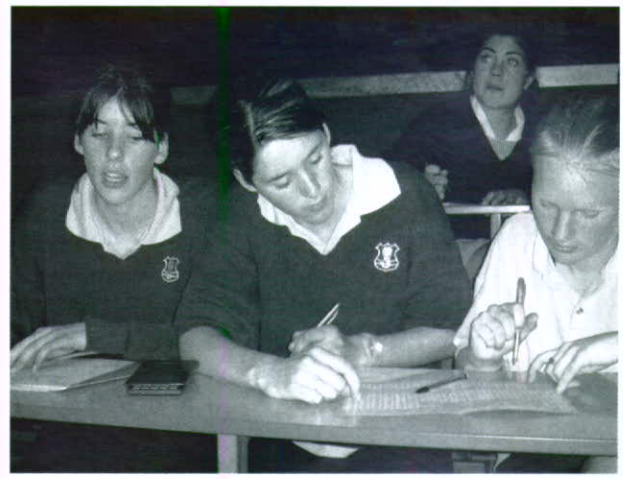
The September meeting involved a trip to Mt Maunganui to hear about OPPORTUNITY 101. This is a class that is not taught at university but, according to Ballance-Agri Nutrients projects manager **Dr. Terry Smith**, it should be. Terry completed a PhD in chemistry at the University of Waikato and then went to Australia where he worked for Carlton United Brewery – his idea of a perfect job for a chemist at that time! He was eventually tempted back to New Zealand and spent 5 years as a chemical entrepreneur helping people solve a wide range of problems and developing a large network of contacts. In his words self-employed and self-unemployed.

Terry's talk was on identifying a gap in the market and filling it no matter how simple it seemed. As chemists we all have the ability to do this. Some of the projects Terry has managed seemed so simple and the chemistry behind them so basic. Examples included making geysers erupt, formulating cleaning products, and making brine on a large scale. The talk ended with an enlightening trip into what Ballance actually does and some of the chemistry behind it. Ballance is a farmers' co-operative to produce fertiliser. It produces superphosphate from phosphate rock supplies around the world, including the Sahara desert. Terry's most recent project has been a scale up production for a pelletised bacterial mix for treating grass grub-type problems; he has scaled production from a 35 kg batch to over 200 tonnes in a season and has had lots of fun doing it.

According to Terry, there are millions of projects out there just waiting for the average chemist to take on and solve. You don't need to be a rocket scientist, just utilise a basic knowledge of chemical processes, have a wide network of contacts in many differing areas, keep your eyes open, and be prepared to have a beer with the 'operators' who are the best sources of ideas and knowledge about what is actually going on. Terry's enthusiasm for chemistry, and entertaining communication style made this an excellent evening, and the refreshments provided were greatly appreciated also.

University of Waikato

ChemQuest 2004, the annual quiz for 6th form students was presented by **Richard Coll** and **Michèle Prinsep**, with Bill Henderson running his *Demon Demos* on October 20. A total of thirty seven 3-member teams from 15 schools entered for the fun packed night of chemical questions in the categories: *Periodic Puzzlers*, *Sensing the Senses, The Wide World of Chemistry,and Demon Demos.* Competition was for the James and Wells trophy, medals, and cash prizes. Upon completion 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 with prizes awarded to *Pyrodikus* (Waikato Diocesan School for Girls (**Lisa Empson, Katie Lin, Vanessa Williams** -1st place) and *Jelly* (Tauranga Boys' College) (**Jonathan Hubert, Darren Lowes, Luke Park** - 2nd place). For the teachers: Round 1: **Duncan Smith** (St Pauls Collegiate); Round 2: **Jason McGrath** (St Pauls Collegiate); Round 3: **Leon Ruttersmith** (Waihi College); Round 4: **Anderley Middleton** (Katikati College).



Above: At Waikato's ChemQuest 2004.

Numerous people contributed to the success of the occasionand should be thanked including many of the staff and students of the Chemistry Department and School of Science and Engineering, University of Waikato for organisation, marking and publicity. Matt O'Neill and Jeremy Sim from the Auckland office of James and Wells (Patent Attorneys) came from Auckland to join us for the evening. They had a great time trying out the quiz themselves and presented the prizes to the winners. Quote from Matt *I haven't seen anyone get so excited about chemistry for a long time!*

Richard Coll has recently been awarded a Fulbright Travel Award to travel to the USA to attend the National Association for Research in Science Teaching conference in Dallas and to undertake some collaborative research with Phil Gardner from Michigan State University. Richard is also an invited speaker to the USA-based Cooperative Education and Internships Association's annual conference in Los Angeles where he will present an overview of the recently published International handbook for Cooperative Education, which he co-edited with **Chris Eames** from Waikato. Richard has also been nominated for the best emerging researcher at the NARST conference.

NIWA

Trevor Mathieson has received a Resumption of Fellowship Award from the Alexander von Humboldt Foundation (Germany) that will support a three-month stay (from October) with an analytical biochemistry group at the University of Munich. He will perform research for NIWA's marine and freshwater natural products programmes. **Michael Ahrens** was awarded $4000 from ISAT for a 3-week research sojourn in October at Novozymes (Copenhagen, Denmark) for exploratory research on producing digestive biosurfactants by recombinant technology . This work is complementing current Marsden-funded work into the chemical structure of biosurfactants.

WELLINGTON

The September meeting involved Branch Chairman **Ken MacKenzie** (Chemical and Physical Sciences, VUW, and IRL) with *Steps towards a clean green society: the future role for ecologically-sensitive materials science.* Ken started from the recognition that *Technology* is frequently blamed for the increasing degradation of our planet's ecosystems due to an excessive appetite for energy-intensive manufacturing processes, the generation of ever-increasing amounts of hazardous industrial and nuclear waste, and a reluctance to recover and recycle spent materials and products. Materials scientists have becoming increasingly aware of the urgency needed to address these issues and are developing new manufacturing processes and materials that conserve energy and reduce greenhouse gas emissions, immobilise and dispose of hazardous wastes and recover valuable commodities from used products previously dumped. The fascinating discourse briefly covered some of the latest research on these issue in which the speaker is involved.

The sixth annual NZIC (Wellington) Chemistry Quiz was held in early September at Victoria University for the benefit of year 12 and year 13 students from the Wellington region. Students and teachers from eleven schools descended on VUW, the teachers were whisked away for a session with **Professor John Spencer** and **Dr.Kate McGrath**, and the 34 teams (about 136 keen 16 and 17-year olds) led to the Student Union Hall to do battle for first place in the quiz.

Great fun was had by all involved, both students and organizers, although the age gap between the two groups was shown during a *Name that chemist* round – favourite characters from The Muppets, such as Bunsen Honeydew and assistant Beaker are no longer easily recognized by college students! The quiz masters, PhD students **Kirsten Edgar** and **Rhys Batchelor** read out a few of the more amusing alternatives, but were also pleased to note that a few of the teams recognized Alfred Nobel.

The competitors made a superb effort, and by the end of the evening three teams showed clear leads. Scots College repeated their endeavours of the previous several years and *D. R. Reed and the Others* took out first place, winning both a prize for themselves and a textbook for their school. Second place getters were *Brain Cells Will Come Later* (Newlands College), and third went to *The Amino Babies* (Wellington East Girls' College). Several spot prizes were awarded that included best team name - *Avagadro Guaca-mole-y* (Wellington East Girls' College), best table art (*Kit-Kations*, Samuel Marsden Collegiate) and best-dressed team (*Dunky and the Hydroxides* - Hutt International Boys' College).

The evening, organized by **Kirsten Edgar**, **John Ryan** (*in absentia*) and **Rhys Batchelor**, had much appreciated help from Lynne Gallie of the VUW Events Coordination team. As always though, the evening would not have been as much fun without the infamous ***Happy Helpers*** – **Wendy Popplewell**, **Thomas Borrmann**, **Andy McFarlane**, **Joanna Wojnar**, **Ray McLauchlan**, **Teck Hok Lim**, **Melissa Marshall**, **Matthew Cairns**, **Aaron Small**, **Pascale Savigny**, **Jonathan Singh** and **Kaspar Hansen**.

Above: Best named team - *Avagadro Guaca-mole-y* (Wellington East Girls' College).

Above: Quiz winners D. R. Reed and the Others (Scots College).

October saw recently arrived **Dr. Joanne Harvey** of VUW chemistry discuss *Adventures abroad with the allyl cation* to what proved to be a large audience for this more academically oriented meeting. Joanne completed a VUW BSc(Hons) in 1995, worked for a year at Massey University, ESR and IRL), then studied for PhD at ANU (**Martin Banwell**). From there she moved to York (UK) for postdoctoral research with Richard. She held an Anglo-Australian Fellowship followed by a Ramsay Memorial Fellowship during her three years of post-doctoral work.

Victoria University

Dr. Peter Northcote joined **John Ryan** at the 11th International Symposium on Marine Natural Products ***XI MaNaPro*** in Sorrento (Italy) in early September and **Dr. Brendan Burkett** arrived in mid-November to take up his lectureship in organic chemistry. November 1 saw **Prof.essor John Spencer** take over the reigns of the School from **Jim Johnston**.

Chemistry of Antarctic Lakes: Ancient and Modern

Sarah Milicich[a] and Chris Hendy[b]

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Introduction

Taylor Valley, Antarctica, is part of an extensive ice-free area in the Transantarctic Mountains that fringe the west coast of McMurdo Sound (Fig. 1). The valley trends east west at S 77°30′-77°45′ latitude and E 162°-E164° longitude with the head of the valley located near the Taylor Dome on the Antarctic Ice Sheet; it extends approximately 125 km to New Harbour in McMurdo Sound. The valley is flanked to the north by the Asgard Range and to the south by the Kukri Hills, which consist of granites to the west, intruded by numerous dykes, and Precambrian metasediments to the east. Chemical, isotopic, and mineralogical analysis of lake (lacustrine) minerals in Taylor Valley (that comprise calcite, aragonite, gypsum, and halite) indicate precipitation from three different water bodies, one of which derived its water from the Ross Sea Ice Sheet and the others from Taylor Glacier. Three ancient lakes show evidence of evaporitic precipitation while modern lakes have algal precipitation of carbonates in addition.

Currently, the Taylor Valley drains from the ice sheet in East Antarctica to fill upper Taylor Valley between Taylor Dome, at 2400 m elevation, and the terminus at the margin of the western lobe of Lake Bonney, at 57 m elevation. The eastern half of the valley is currently free of ice except for small alpine glaciers on the valley walls. Lakes, the largest of which are Bonney, Hoare, and Fryxell, occupy parts of the floor of the valley.

The Dry Valleys make up the most extreme deserts in the world, with the annual mean temperatures ranging from –17 to –20 °C.[1] Precipitation levels are low, with the mean annual precipitation of 100 mm being received as snow.[2] This is much lower than the ablation rates, that have been measured at 150 to 500 mm/year.[1] The combination of low precipitation and dry katabatic winds, *i.e.* winds caused by air that cools over the ice surface becoming heavier than surrounding air, and then draining down-valley, results in extremely arid conditions. During non-winter months this climate is controlled by variation in the solar flux and slightly more moderate winds.

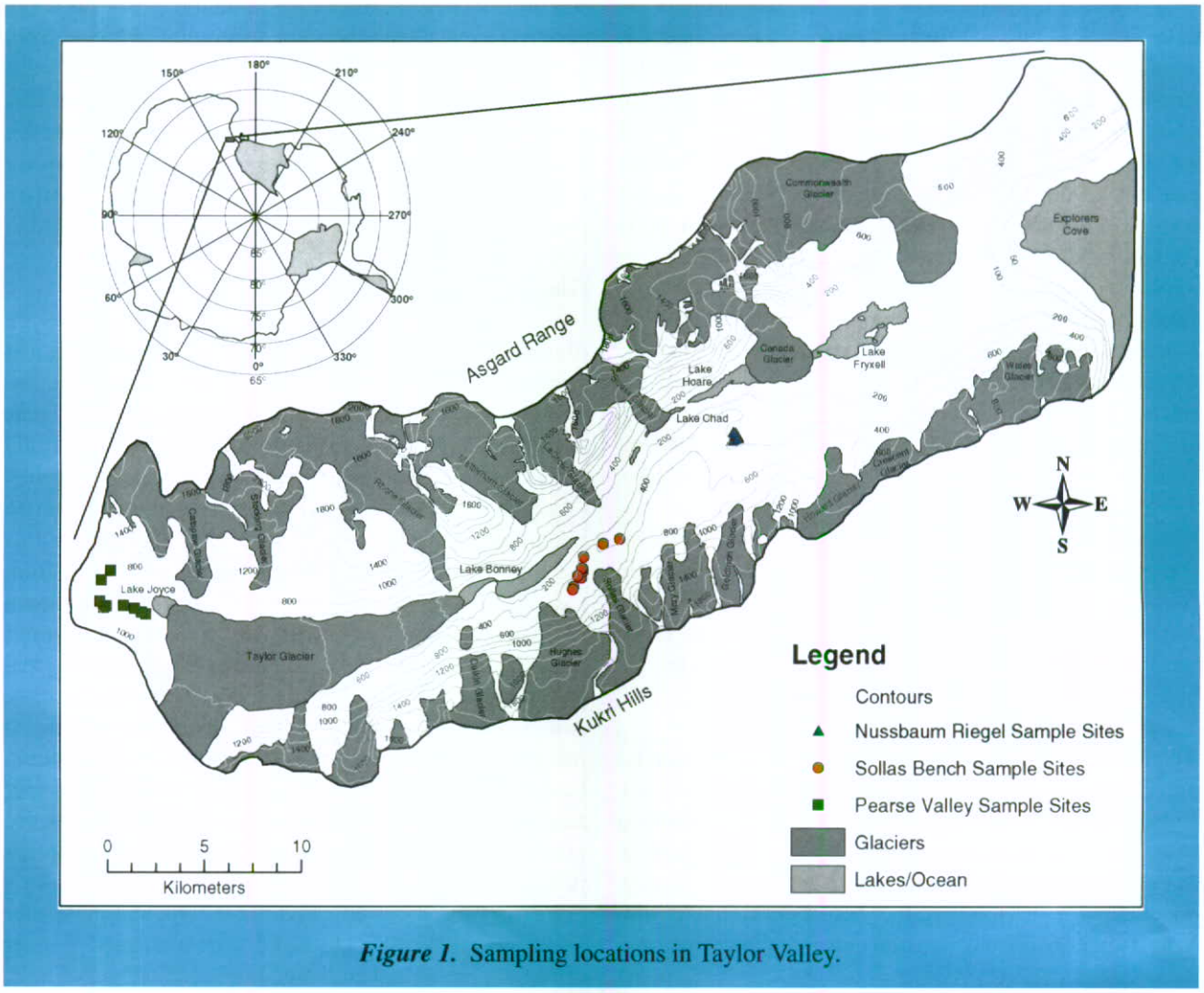

Figure 1. Sampling locations in Taylor Valley.

Lakes in enclosed drainage basins accumulate dissolved salts. A layer of brine at the bottom of the basin results from previous evaporation of the lake to low volume. Subsequent influx of fresh water creates a less dense cover of water over the brine and diffusive mixing between the two water masses causes a density gradient that prevents convection (Fig. 2). Incident solar radiation is transmitted down through the ice crystals and is absorbed within the lake, thus raising the temperature of its waters. This absorbed heat, in conjunction with strong density gradients that prevent convection, can raise the temperature of bottom waters to as much as 25 °C. Slumping of water-saturated sediments creates a *step-and-tread* shoreline, and meltwater streams deposit deltas within the moat zone.[3]

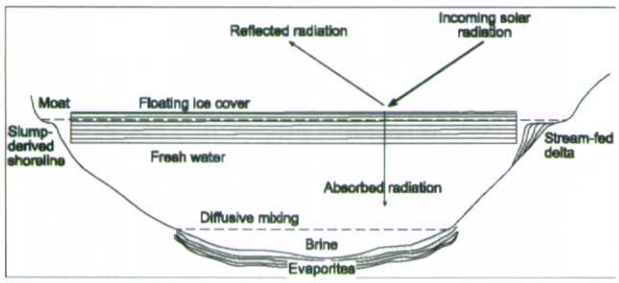

Figure 2. Schematic model of a polar lake in an enclosed drainage basin with relevant physical processes - see ref.3.

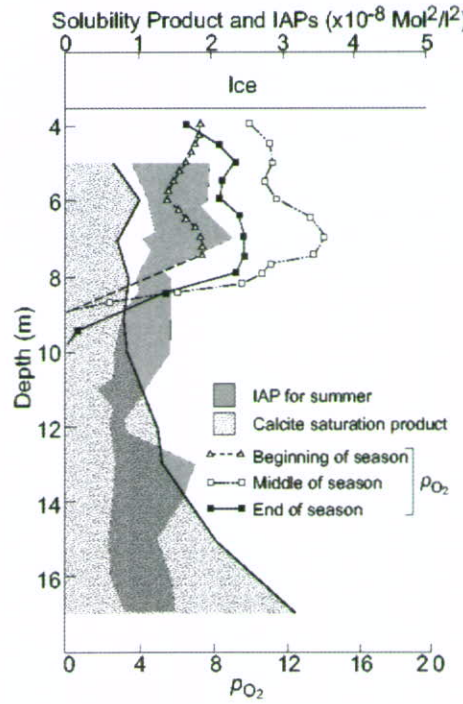

Figure 3. Lake Fryxell solubility profile. The stippled area shows the range where calcite is unstable; where the shaded zone exceeds the stippled zone, calcite can be precipitated. The lines are pO_2 profiles with saturation of O_2 above 9.5 m where algal activity is most vigorous - see refs. 4 and 5.

Lake Chemistry

Lake Fryxell is typical of many Dry Valley lakes in that it has a permanent ice cover and is thermally and chemically stratified. Calcium carbonate is currently precipitating from the water column. Biological activity also has an effect on the chemistry of the lake. The pO_2 data indicate that the lake has an upper euphotic zone and a lower anaerobic zone. The removal of CO_2 by algal photosynthesis increases the pH. This causes the precipitation of calcite when supersaturation with respect to calcite has been exceeded [shown as ion activity products (IAP), Fig. 3]. This occurs primarily in the lower euphotic zone (8–9 m) where algal activity is at its highest. The precipitated calcite, along with algal cells, settle out as a sediment rain, giving rise to the layered deposit common in Dry Valley lakes.[4]

Mineral precipitation can occur in the lakes on concentration as a consequence of evaporation (evaporitic concentration) when ablation rates exceed inflow. In Antarctica, evaporitic concentration can also occur under freezing conditions, as solutes are excluded from the ice that is formed.[4,5]

Alkaline earth carbonates (calcite, aragonite, or Mg-calcite) precipitate first from most Antarctic lakes, and their trace element content offers important clues to the composition of the lakes; further concentration precipitates gypsum. In an enclosed drainage, the less soluble carbonates are often precipitated at the lake margins where there is contact with more dilute waters, and gypsum closer to the centre.[6]

The next minerals to precipitate are more soluble ones. The final stages of mineral precipitation can occur at the surface of open water brine or within the sediment from occluded brine. Common products include halite (NaCl) and mirabilite ($Na_2SO_4.10H_2O$), which often dehydrates to thernardite (Na_2SO_4). In addition to halite, there are two more chlorides that occur in Antarctic conditions in the form of hydrohalite ($NaCl.2H_2O$) and antarcticite (calcium chloride; $CaCl_2.6H_2O$).[6,7]

Glaciology

Shorelines that mark high lake levels (strandlines) and minerals deposited by evaporation abound in Taylor Valley. Some of these formed in lakes dammed by ice sheets occupying McMurdo Sound, *e.g.* Ross Sea Glaciation, and others were formed lakes fed by inland ice, *e.g.* Bonney Glaciation (see Fig. 4). Our dating indicates an out of phase relationship between the advances of grounded Ross Sea ice from the east and expansions of Taylor Glacier from the west (Fig. 4). The expansion of the Ross Sea ice, caused by lowered sea level and lowered mean annual temperatures, would have resulted in a reduction in local precipitation in the Dry Valleys region and on the East Antarctic Ice Sheet. As storms would not have penetrated into the region as frequently as at present, the aridity would have been higher and caused a retreat of the Taylor Glacier and alpine glaciers. The expansion of the Ross Sea ice pushed ice tongues into valley mouths creating large proglacial lakes. The most recent such deposits are *Ross Sea Drift*, which is well dated (24–8 kA), and the earlier Marshall Valley Drift (130–182 kA); remnants of older drifts suggest several earlier glaciations.[8,9]

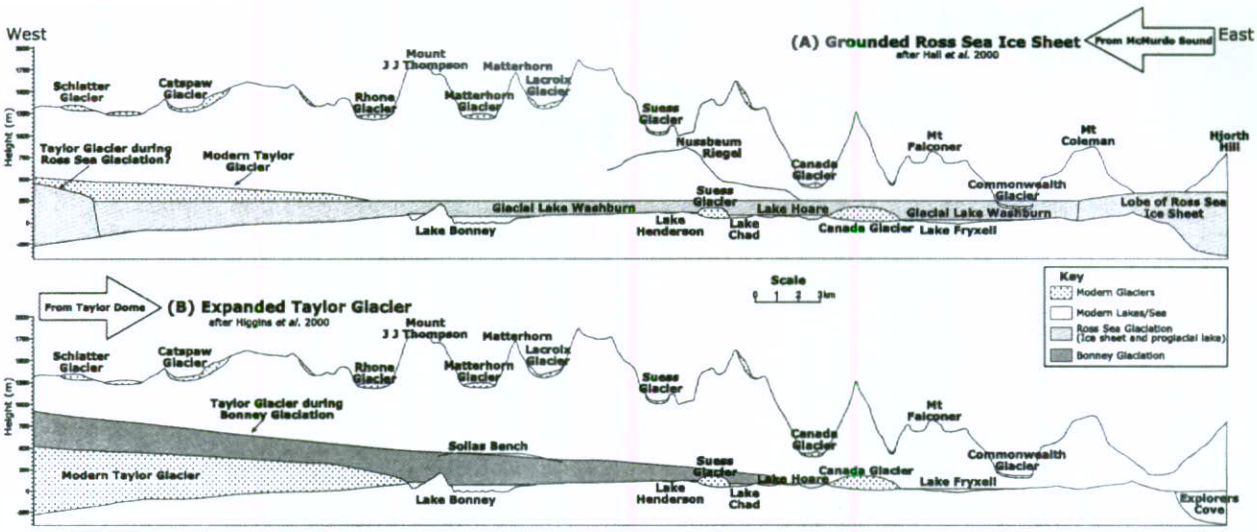

Figure 4. Opposing glacial advances into Taylor Valley. Upper: As sea levels lower an ice sheet builds in McMurdo Sound and dams the mouth of Taylor Valley trapping Glacial Lake Washburn; lower: Expansion of the East Antarctic Ice Sheet advances Taylor Glacier into the Lower Taylor Valley.

A reversal of these conditions during interglacial periods forces the Ross Sea ice to retreat from the Taylor Valley and the Taylor Glacier, and causes alpine glaciers to expand. Expansion of inland ice sheets pushed outlet glaciers down Taylor Valley, also creating proglacial lakes. The most recent deposit, *Bonney Drift*, is well dated (70–130 kA), with evidence of older drifts of 160–240 kA and 270–330 kA. There are at least three older deposits of glaciolacustrine sediments (*Nussbaum Riegel, Sollas Bench*, and *Pearse Valley*), that lie beyond the range of available dating techniques.[8,10]

Isotopic composition can be used to distinguish water originating from these two sources. Stable isotopes at or near natural abundance levels are commonly reported in the form of delta (δ) values, given in parts per thousand (or per mille; ‰). These are not absolute isotope abundances, but differences between sample readings and one or another of the internationally defined, and widely used, natural abundance standards, in this case the Pee Dee Belemnite where:

$$\delta = \left(\frac{R_{sample} - R_{std}}{R_{std}} \right) (10^3)$$

Ice from the snout of the Taylor Glacier has a mean $\delta^{18}O$ value of -42‰. In contrast, the waters from Ross Sea Ice Sheet were much less depleted, with $\delta^{18}O$ values of around -35‰.[11]

The project

The project has been to determine the conditions under which carbonate was deposited on the beds of three ancient lakes (Fig. 1) in Taylor Valley, when, and how. During the 2002/3 summer season the three areas (Nussbaum Riegel, Sollas Bench, and Pearse Valley) were sampled and photographs were taken, and the area mapped for the occurrence of carbonates (Fig. 5, upper). Subsequent laboratory analysis started by using XRD and SEM analyses (Fig. 5, centre and lower) that showed all three sites to be dominated by aragonite, sometimes also with calcite (Fig. 5, centre right); these Nussbaum Riegel carbonates contained abundant glass shards indicating the presence of volcanic ash (tephra) from an alkali basalt volcano such as Mount Erebus. The Sollas Bench deposits included both gypsum and carbonates in which halite could be seen under SEM (Fig. 5, lower left). Part of the field season was also spent coring the modern lakes to understand the processes of Antarctic lacustrine sedimentation (Fig. 5, centre left).

The origin of the salts in Taylor Valley has been a subject of contention since the discovery of saline lakes in the valley in the early 1960s. Numerous authors[12,13] agree that many of the salts in the valley originate from sea water and have been modified by processes such as (i) *leaching of soils* (which adds more soluble components, *e.g.* oxidation products and daughter products of radioactive decay), (ii) *precipitation of calcium sulfate and carbonates* (which results from concentration via evaporation and freezing, and finally leads to precipitation of sodium chlorides), and (iii) *addition of atmospheric aerosols* (which adds salts by the runoff of meltwater into the lake).

A seawater origin of the salts at the seaward end of Taylor Valley is easily explained by marine incursions during interglacial times; it is harder to explain at Taylor Glacier, at the opposite end of the valley. The origin of tens of millions of tonnes of salt in the Bonney Basin has been the subject of speculation. The presence of halite in the lacustrine sediments from Sollas Bench indicates that there was a substantial amount of salt in the basin prior to the dated Taylor Glaciations. The presence of brine, saturated in halite and gypsum, discharging from crevasses close to the terminus of Taylor Glacier indicates that at least part of the salts could be residing as evaporite deposits in a basin being over-ridden by Taylor Glacier.[13,14]

The source of the water from which the carbonate was precipitated can be determined using stable isotopes. Overall, the isotopic compositions of the lacustrine carbonates will reflect the nature of the water from which

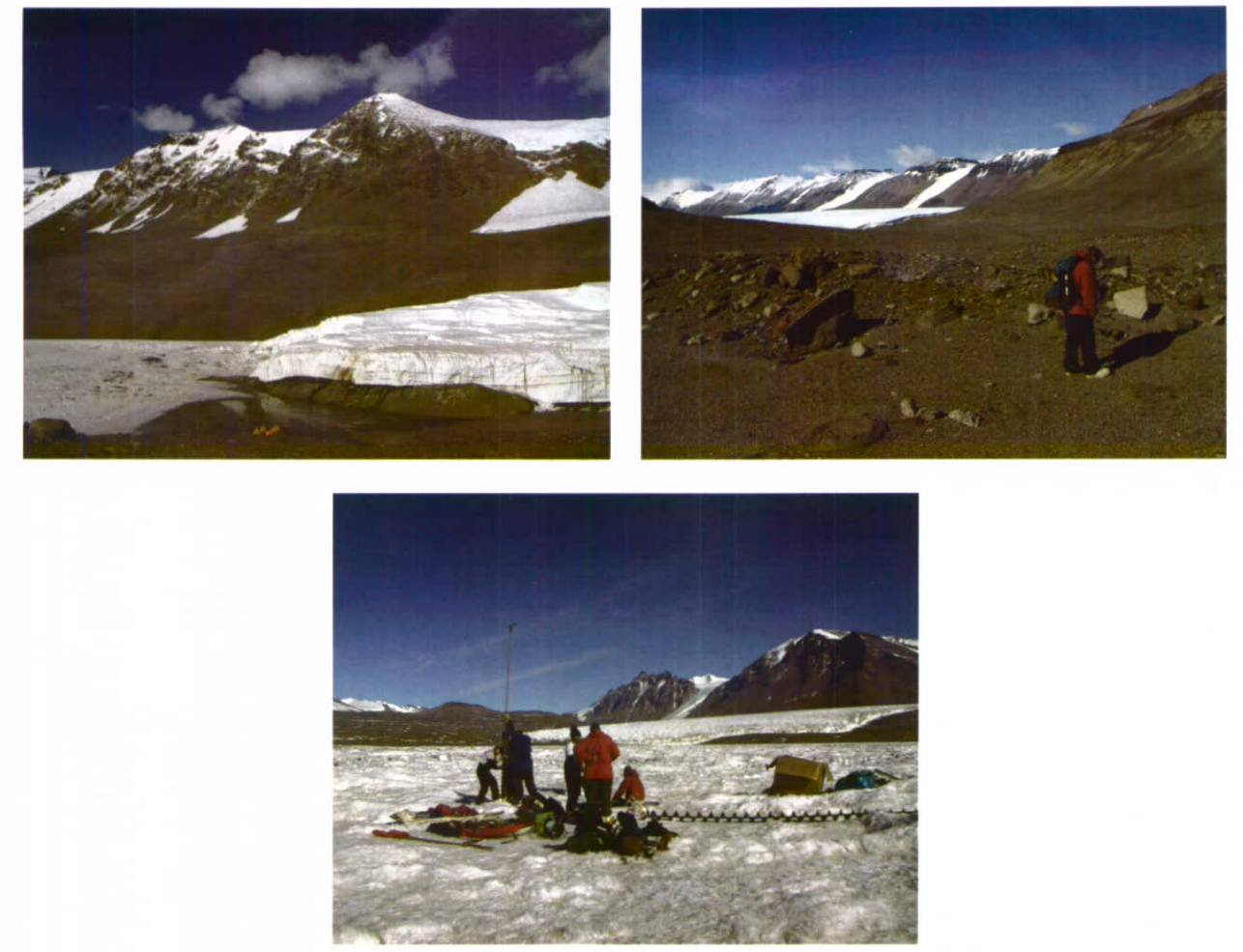

Figure 5. Upper left: Field camp site at the snout of the Taylor Glacier; upper right: carbonate sampling in the Pearse Valley; centre: drilling the 4 m ice cover of Lake Fryxell for coring; lower left: Nussbaum Riegel carbonates with glass shards; lower centre: Sollas Bench carbonates with radiating aragonite needles and halite; lower right: Pearse Valley carbonates with interlocking aragonite needles and calcite rhombs.

they were precipitated, and hence they can be used to determine the source(s) of the waters in the lake from which they were precipitated; Fig. 6 shows how this can be used for the Taylor Valley carbonates from ^{13}C and ^{18}O analyses.

The samples from Sollas Bench and Pearse Valley are more depleted in ^{18}O with $\delta^{18}O$ values of approximately -38‰ to -34‰; they were deposited from water sourced from the Taylor Glacier. Samples with less depleted values of -32‰ to 28‰ indicate that the source waters are from Ross Sea ice. The ^{13}C isotope reflects the nature of carbon dioxide cycling within the lakes. Strongly positive $\delta^{13}C$ values indicate low temperature equilibrium with atmospheric carbon dioxide—only possible with an ice-free lake surface and consistent with the presence of

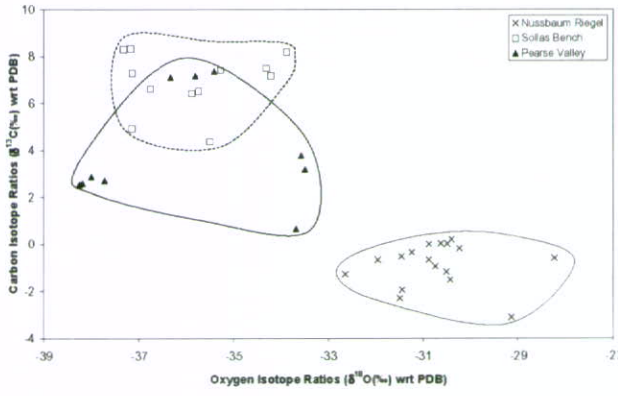

Figure 6. Stable isotope composition of Taylor Valley carbonates reflecting sources of water during precipitation.

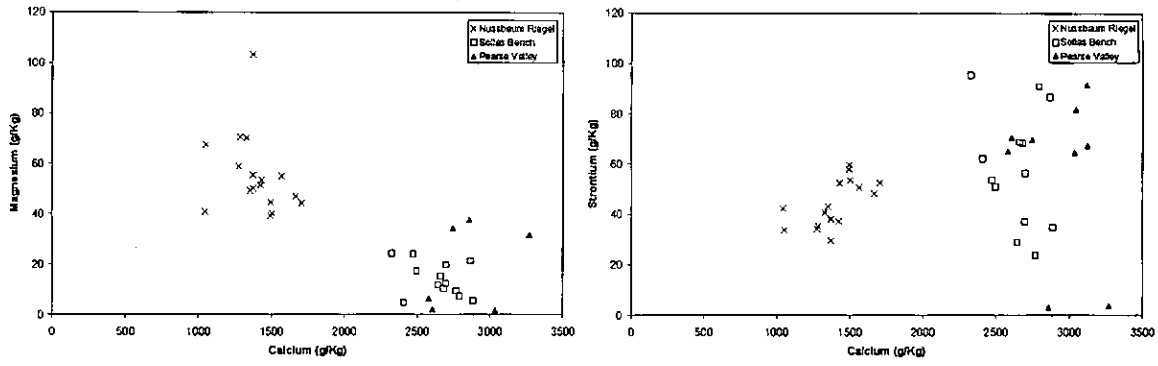

Figure 7. Magnesium and calcium (left) and strontium and calcium (right) carbonate composition in Taylor Valley.

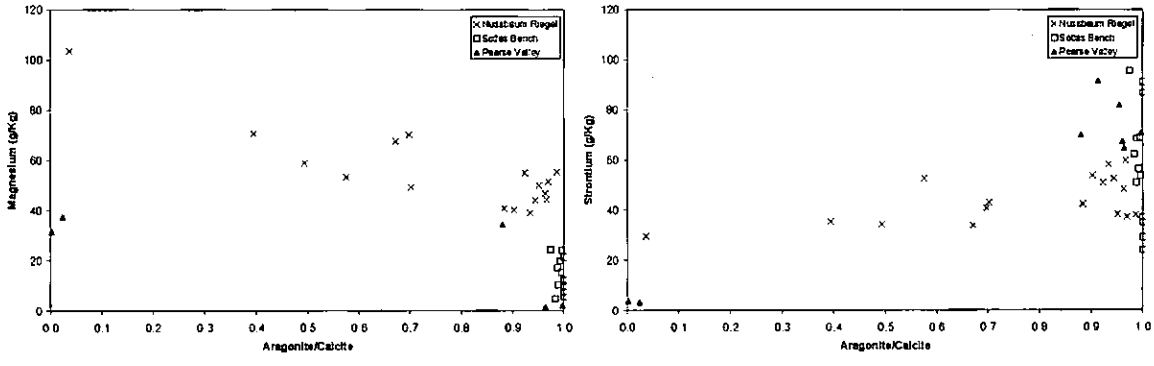

Figure 8. The effect of the aragonite/calcite ratio on magnesium concentration (left) and strontium concentration (right) in Taylor Valley carbonates.

halite—while the more negative values are likely caused by photosynthetic carbon cycling within an ice covered lake.

The trace element compositions of the precipitates are controlled by the carbonate mineralogy and the lake water composition. This is complicated by progressive concentration of trace metals in the remaining brine as evaporation proceeds and this results in increasing concentrations in the carbonates. Analysis of the carbonates shows similarities between Sollas Bench and Pearse Valley beds, but a distinctly different origin to the Nussbaum Riegel carbonates that are enriched in Mg but depleted in Sr (Fig. 7).

As aragonite has a larger, more open crystal lattice than calcite, larger cations, *e.g.* Sr^{2+}, fit more easily than smaller cations, *e.g.* Mg^{2+}. To check whether the mineralogy is controlling the trace element composition a plot of the magnesium and strontium concentrations against the aragonite/calcite ratio has been made (Fig. 8). This shows that although increasing calcite abundance results in increased magnesium and decreased strontium concentrations, the trendlines extrapolate to a different lake water composition. This is consistent with our model of proglacial lakes supported by opposing glaciations.

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Patent Proze

By John Landells and Helen Palmer

PATENTS AND FREE TRADE

The current international political climate is rife with free-trade talks and the Australian/American Free-Trade Agreement (FTA) has focused some attention on a possible New Zealand/American FTA. During the negotiation process for any trade agreement New Zealand's intellectual property legislation is likely to be closely reviewed. In the recently negotiated Australia/USA FTA, a whole chapter in the agreement was centred on intellectual property protection.

A particular point of concern for the United States would be issues involving the availability, pricing and protection of one of its primary exports, namely pharmaceuticals. The policies of the Crown entity Pharmac of essentially bulk-buying pharmaceuticals in order to negotiate lower drug prices from pharmaceutical suppliers will come under particular scrutiny. Pharmac's policies tend to result in the availability of a limited range of subsidized pharmaceuticals where the total spend is capped.

Other potential issues specifically surrounding patents include:
- New Zealand's lack of provision for pharmaceutical patent term extensions;
- New Zealand's anticipated blanket prohibition on patent protection for methods of treatment of humans; and
- the recently introduced patent infringement exemption for third parties seeking regulatory approval for a patented product before the expiry of the patent at issue.

The New Zealand Patents Act has been slowly progressing through a three-stage review, which includes the consideration for the provision of patent term extensions. A number of jurisdictions, including the European Union, Australia and the United States, provide for patent term extensions for pharmaceutical products for up to five years. You may ask why patent term extensions are desirable for pharmaceutical products. The answer lies in the length of time that it takes for a pharmaceutical product to get from the laboratory to the market place and through the regulatory approval process. For most pharmaceutical products this can be between 10 and 15 years. Although a normal patent term is 20 years, the effective patent life of a pharmaceutical product is usually no more than 5–10 years. Because of the expense of developing a pharmaceutical product — recent estimates suggest around US$1 billion — patent term extensions provide the pharmaceutical industry with a better incentive to invest in research and development. Although providing patent term extensions may result in increased investment in New Zealand by pharmaceutical companies, the trade-off is that such extensions may also slow down entry of cheaper generic drugs on to the New Zealand market.

Australia and the United States allow patent protection for innovations involving methods of medical treatment of humans. In contrast, the New Zealand Government has indicated that it does not intend to remove the exclusion from patentability in New Zealand of methods of medical treatment of humans. This exclusion from patentability is strongly supported by international patent law. We anticipate that New Zealand would come under pressure from the United States to align its legislation to provide patents for methods of medical treatment of humans. However, it is unlikely that retention of this exclusion from patentability would present much of an obstacle in a free trade deal.

Another point that is likely to receive close attention is the ability of manufacturers of generic pharmaceutical products to obtain regulatory approval in New Zealand prior to the expiry of the full patent term of a product under a patent infringement exemption. An amendment to this effect was brought into New Zealand's existing patent legislation two years ago and is likely to be retained in the pending Patents Bill. Such a provision essentially allows generic companies to prepare a generic product for launch into the market immediately after patent expiry, commonly termed "spring boarding". As the United States has done elsewhere, it is also likely to raise strong opposition to this spring-boarding provision, especially in light of our current lack of patent term extension, on the basis that the infringement exemption undermines patent protection.

In any trade negotiations the United States are sure to focus on ensuring New Zealand's patent laws provide strong patent protection for pharmaceutical products. Although strong patent protection may result in increased costs of pharmaceuticals, it also encourages further investment in research and development.

While much attention has been focused on the Australian/American Free-Trade Agreement (FTA), the New Zealand Government has also been quietly negotiating its own free trade agreement with China. It appears that New Zealand's soon-to-be-amended patent law may not require so many concessions in negotiations over a trade agreement with China.

Although an FTA is likely to provide an overall benefit to New Zealand, there is sure to be compromises made in any FTA negotiations. It will be interesting to see what compromises the New Zealand Government is willing to make in its trade negotiations to provide for a strong knowledge economy and to secure foreign investment for the high-tech industry sector.

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

Patent Proze
Baldwins
P O Box 852, Wellington.
Email: email@baldwins.com

John Landells

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Helen Palmer

IUPAC NEWS

Element 111 Is Named Roentgenium

Following the 80th Meeting of the Bureau in Bled, Slovenia, the name **roentgenium** for the element of atomic number 111, with symbol **Rg** was officially approved as of 1 November 2004. The IUPAC Council, at its meeting at Ottawa, Canada in 2003, delegated the authority to approve a name for the element of atomic number 111 to the Bureau.

In 2003, a joint IUPAC-IUPAP Working Party (JWP) confirmed the discovery of element number 111 by the collaboration of Hofmann *et al.* from the Gesellschaft für Schwerionenforschung mbH (GSI) in Darmstadt, Germany (*Pure Appl. Chem.*, **2003**, 75, 1601-1611). The most relevant experiment resulted from fusion-evaporation using a ^{64}Ni beam on a ^{209}Bi target, which produced a total of six decay chains of alpha-emitting nuclides following the presumed formation of ^{272}Rg + n (S. Hofmann *et al.*, *Z. Phys. A*, **1995**, 350, 281-282); S. Hofmann *et al.*, *Eur. Phys. J. A*, **2002**, 14, 147-157).

In accordance with IUPAC procedures, the discoverers proposed a name and symbol for the element. The proposed name was **roentgenium**, with symbol **Rg**. The Inorganic Chemistry Division Committee then recommended this proposal for acceptance and the provisional recommendation has now successfully passed expert examination and the prescribed period of public scrutiny. This proposal lies within the long-established tradition of naming elements to honour famous scientists.

Wilhelm Conrad Roentgen discovered X-rays on 8 November 1895, a new type of rays to which he gave this name in view of their uncertain nature. Their use has subsequently revolutionized medicine, found wide application in technology and heralded the age of modern physics, which is based on atomic and nuclear properties. In 1901, six years after their discovery, the benefit of X-rays to mankind was so evident that Roentgen was awarded the first Nobel Prize in Physics. Element 111 was synthesized exactly 100 years after Roentgen's discovery. To honor Wilhelm Conrad Roentgen, the name, roentgenium, was proposed for the element with atomic number 111.

Young Observers Going To Beijing

IUPAC is pleased to announce its call for applications for Young Observers to participate in the **40th IUPAC Congress being held in Beijing, China, 14-19 August 2005**. The theme of the Congress is "*Innovation in Chemistry*." To encourage young scientists to participate in this unique Congress, the organizers have established a program offering travel assistance.

In the spirit of innovation, IUPAC will also facilitate the participation of **Young Observers** in the concurrent General Assembly. The Young Observer program provides an excellent opportunity for young scientists to establish international collaborations, gain knowledge of global research activities, and participate in IUPAC activities. Some Young Observers from previous congresses have remained actively involved in IUPAC by joining and chairing subcommittees and task groups.

Awards will be offered by IUPAC to candidates from all National Adhering Organizations (NAOs) and Associate NAOs. Both the U.S. and U.K. NAOs will independently select and support the participation of young scientists from their countries as well. All successful candidates are expected to submit an abstract of a poster or paper to be presented at the Congress; such abstracts will be subject to adjudication as will all other submissions for presentation at the meeting.

For more details about these programs, including applications procedures, age limits, criteria for selection, and timelines/deadlines, please inquire to the IUPAC Secretariat Email: <secretariat@iupac.org>.

For details and updates about the IUPAC GA and Congress, visit <www.iupac.org/symposia/2005.html#140805>.

The Chemistry of Biosensors – Shedding Light on Antibody Interactions

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Introduction

The world biomedical diagnostics market is a multibillion-dollar industry that gives clinicians and scientists much clearer pictures of the physiological and pathological processes occurring in the human body. To date, this market has been dominated by systems that utilise the binding of an antibody to a specific target molecule or antigen, so called *immunodiagnostics*. These tests have predominantly been based around microtitre plate assays such as *e*nzyme-*l*inked *i*mmuno*s*orbent *a*ssays (ELISA). These utilise an enzyme label to catalyse a colour change and so indicate binding events either through inhibition assays (where sample target analyte blocks label binding) or sandwich assays (where the sample target analyte is simultaneously bound by immobilised and labelled antibodies).

The principal disadvantages with such assays are that they are practically restricted to use in a laboratory situation and often take from hours to days to give a result; they are labour-intensive and many of the signal development steps are inherently unreliable. Thus there has been a major move towards the development of biosensors, units that utilise a biomolecular interaction to detect a target by transducing that interaction into an electrical response. It is desirable that such sensors are able to be used on-site, be re-used many times, or be disposable and give a rapid and accurate result with minimal user interaction. Despite more than 10 years of intensive scientific study, the biosensors field has been largely unsuccessful in producing commercial biosensor systems. The only commercially successful on-site biosensor produced is the glucose monitor and it still has ongoing technological challenges to overcome.

The reasons for the failure to develop promise into reality come from several restrictions that biosensors have. In most cases they fail to achieve comparable detection limits to ELISA. Many of the recognition elements such as antibodies, enzymes and receptors, are intrinsically very easy to destroy. Most biosensor surfaces cannot be repeatably regenerated for a large number of cycles and need continual recalibration and recoating, and many biosensors struggle to make the transition from aqueous medium to the more complex biological media in which they must perform. Despite some very elegant sensory systems recently being presented, they seem to be unable to address these fundamental problems and liberate the antibody from the laboratory.

In order to make the next step in developing practical biosensors it is critical to have a fundamental understanding of the ways in which antibody binding is affected by a range of factors. These include the ways that antigen coatings are designed, how changing the medium in which the binding interactions occur affects the antibodies, and the type of labelling, if any, that is applied. All these will have a great bearing on the performance of any immunosensor system. Therefore, there is great scope for the chemist to apply knowledge of organic chemistry to solve some of the inherent problems of biosensing and shed some light on antibody interactions.

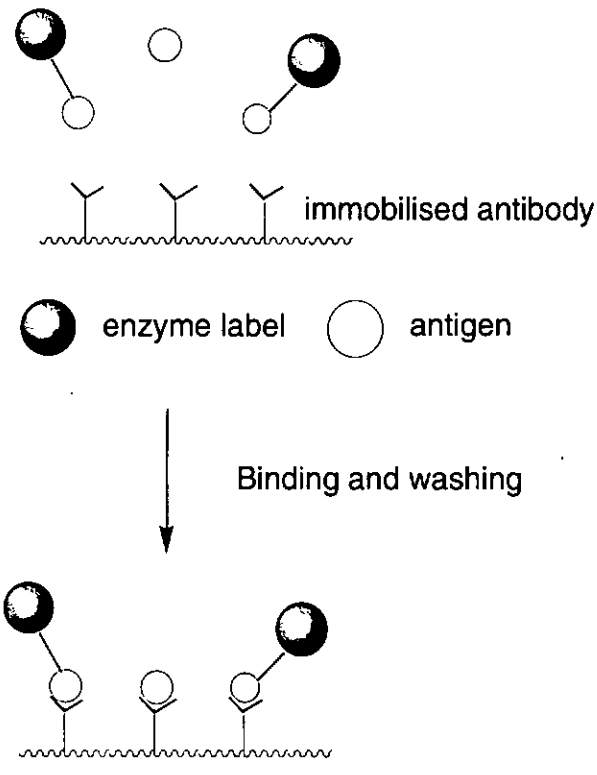


Figure 1. Competitive enzyme-conjugate based immunoassay of small molecules

Protein conjugation and the biosensor

Current work at the Bioengineering Sector of HortResearch and the University of Waikato has focussed on the study of small molecule antigens, particularly the reproductive steroid hormones such as progesterone. Progesterone is a good starting model as it is a key indicator of the oestrous cycle status of many animals, including the dairy cow, and is chemically similar to a range of other steroids of great importance to medicine and agriculture. Most immunosensors of progesterone have relied on enzyme conjugates of the steroid (Fig 1.). which have several inherent problems such as difficulties in purification and standardisation of production.[1] A potentially better system is to use protein conjugates of the analyte by attaching the analyte to a carrier protein by way of a chemical bridge.

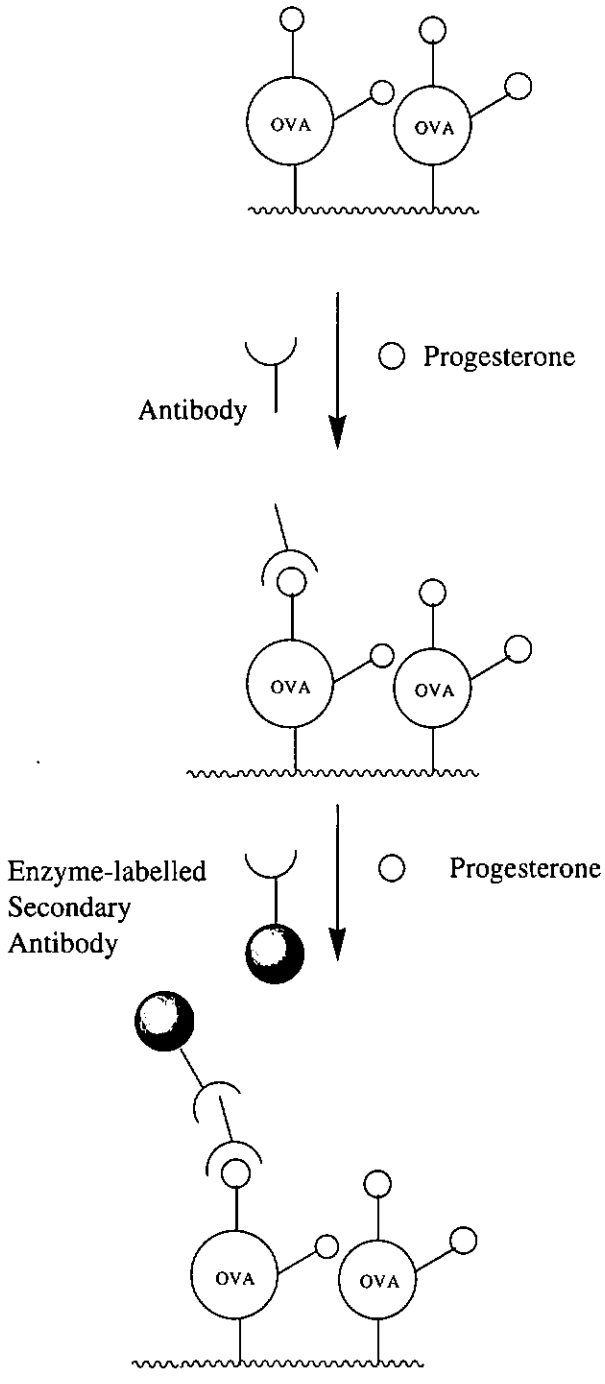
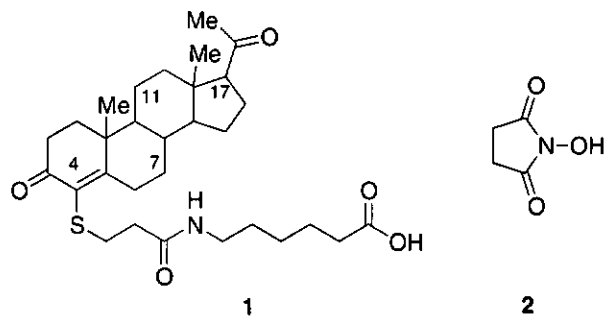


Figure 2. Protein conjugate based immunoassay using secondary antibody mediated enzyme labelling in a competitive format - see ref. 11.

Such systems are relatively understudied and so it is of great interest to assess the position of attachment and the length of the chemical bridge on the level of binding achieved in different biosensing formats. The intention here is to apply them as coating antigens in biosensors where the protein anchors the antigen to the surface (see Fig 2.).

Higher antibody binding leads to greater signal in the biosensor, which can lead to improvements in the detection limit of the assay. In the present studies the chemistry for attaching incrementally increasing linker lengths to progesterone to increase the spacing between the antigen and carrier protein was developed.[2] This is achieved by adding caproate units end on end through amide linkages,[3] and we have investigated the effects of different attachment positions on the level of antibody binding.[2] Conventionally, progesterone has been conjugated through positions 11 or 7 using existing functional groups, which can compromise antigenicity.[4] A potentially better approach is to produce a thio-linked conjugate at the 4-position, *e.g.* **1**, thus eliminating epimeric mixtures and still keeping the linker well away from the functional groups of the molecule.

The modified antigen **1** must then be conjugated to a carrier protein to act as the anchor and this can be done by activation of the carboxylic acid moiety with *N*-hydroxysuccinimide (NHS) **2** and reaction in an *N,N*-dimethylformamide-water solvent mixture. The NHS activation is critical to maintain repeatability of conjugation as it is not as sensitive as many other methods to the reaction conditions used. Repeatability and consistency of binding are critical to ensure such coating antigens can be produced commercially with the same number of haptens attached per protein molecule. This ensures that valid comparisons across conjugates can be made and that the antibody binding properties are not altered. MALDI-TOF spectroscopy provides an excellent means of characterising these conjugates and has shown a remarkably similar hapten number across 0, 1, and 2 caproate units; the carrier protein in these experiments is ovalbumin (OVA).



Such protein conjugates are potentially much more stable than antibodies as coating antigens, as their utility depends only on the stability of attachment and not on the conformation of an active site; if the protein is damaged slightly it will not greatly affect the binding. This extends not only to the ELISA-based assay but also to flow-through biosensors such as surface plasmon resonance (SPR). These modified proteins also have potential utility in delivery of drugs.

How do the linkers perform?

The answer to how linkers affect antibody binding and thus assay performance depends very much on the format used. We have found that in static assay systems in aqueous medium, where there is no flow-through of fluid over the conjugate coated surface, linker length is immaterial as the binding responses and the assay performance remain the same. This has been shown in ELISA where assay standard curves and binding curves are the same across 4-, 11-, and 18-atom linkers.[2] It is possible that this is due to the lipophilic linkers curling in on themselves rather than suspending the antigen in the fluid (Fig. 3). Furthermore, there are no distinct differences between attachments at either 4- or 7-positions.

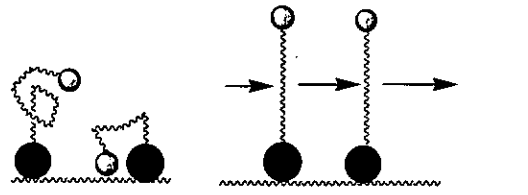


Figure 3. Stylised drawing of the possible configurations of immobilised protein conjugate in ELISA (left) and flow-through SPR (right).

The picture is very different when one considers rapid flow-through biosensors such as SPR where fluid is pumped over the surface; here the differences in binding are great. One sees that there is an increasing level of antibody binding in the aqueous medium as the linker length increases up to 18-atoms and, furthermore, there is much more binding with attachment at the 4-position rather than the 7-position.[2] This is shown in the binding sensorgrams that can be obtained with the SPR instrument. Speculatively, this may be due to the flowing fluid suspending the linkers in the aqueous medium and allowing for differences to appear on steric grounds whereas the longer linkers provide better spacing and thus improved binding (Fig. 3).

So what effect, if any, does this have on the performance of the assay? The answer is that as the linker length increases from 11- to 18-atoms, there is a significant reduction in the detection limit in the flow-through biosensor from 2.7 ng/mL to 0.7 ng/mL; this is most likely due to the higher binding signals obtained. Furthermore, the use of such conjugates in an SPR-based biosensor represents the first SPR biosensor for progesterone and provides excellent sensitivity over a broad range of concentrations from 0-50 ng/mL.[5]

Medium effects

An aqueous medium provides a good starting point but it does not accurately reflect the complex biological matrices in which biosensors are required to perform. Another limitation with immunosensing in general is that complex biological media usually have to be cleaned up extensively before they can be exposed to the sensing surface to give any kind of repeatable result. The problem with such clean-ups is that they fundamentally alter the composition of the medium. A classic example is progesterone in cow's whole milk. Progesterone is lipophilic and as such concentrates in the milk fat such that any attempt to 'de-fat' the milk will lead to distortions of the true progesterone concentration. Thus, it would be of great advantage to develop systems that work in complex media without the need for work-up. It is also interesting to consider the effects that another medium may have on the contribution of the linker to antibody binding.

Whole milk progesterone is a good indicator of the oestrous cycle status of the dairy cow and, as such, has attracted much interest as a target for on-line milk determinations in planning artificial inseminations. Now, these progesterone conjugates have been used to develop a novel ELISA system that requires no pre-treatment of the milk sample and has a wide assay detection region from 0.1 to 100 ng/mL. This represents a significant practical improvement in milk progesterone sensing by ELISA.[6] Previously, ELISA needed some form of pre-treatment or pre-dilution that greatly increased the labour content of the analysis, while many others only cover much narrower concentration ranges (of progesterone) and fail to allow for full profiling of bovine oestrous cycles.[7] With this new technique whole physiological profiles of hormone fluctuations can be prepared.

What is perhaps equally interesting is the effect that the milk medium has on the linker performance in ELISA. Whilst the linkers demonstrated no improvement for aqueous-based analysis, the picture is very different for the milk medium. By increasing the linker length to 18-atoms antibody binding significantly improved and the detection limit of the assay falls from 2.7 ng/mL for a 4-atom linker to 89 pg/mL for an 18-atom linker, *viz.* by a factor of 30.[6] Speculatively, this seems to be due to the lipophilic linker chains more effectively extending into the high lipid content of the whole milk than was observed in the aqueous medium. As our understanding of the factors affecting the often complex binding interactions improves, so also does our ability to understand the ways in which better immunoassays can be designed and better biosensors produced.

SPR biosensing

SPR is a quantum optical-electrical phenomenon of noble metals that has been utilised in biosensors composed of gold chips, whereby changes to the chemical environment of the gold surface produce minute changes in the refractive index that can be detected as a change in the incident angle, needed to achieve plasmon resonance. A schematic SPR sensorgram for a binding event is shown as Fig. 4. Flow-through biosensor formats such as SPR offer the possibility of developing on-line biosensors that can be incorporated in applications as wide-ranging as milking sheds, blood monitors, and on-line food analysis.[8] However, to date there has been no commercialisation of SPR-based biosensing beyond the lab. The main reason for this is that the surface stability is inadequate for the chips to be used repeatably in the field. The best existing surface chemistry is that used by Biacore AB (Uppsala, Sweden)

in their carboxymethylated dextran chips but this has not been applied on-site. Sensitivity of the assays is another important factor; SPR has much higher overall detection limits than the corresponding ELISA. For instance, milk progesterone SPR has a detection limit reported as 3 ng/mL compared to 0.089 ng/mL for our whole milk ELISA.[6,9] High sensitivity and low detection limit are very important in many potential medical applications such as detection of pathological markers in body fluids, where they are often present in very low concentrations. However, the poor detection limits of SPR methods block their use in many such areas. Work is presently underway at HortResearch to develop SPR-based systems with high sensitivity and low detection limits for important biomolecules, utilising organic chemistry to modify antigens and surfaces.[10]

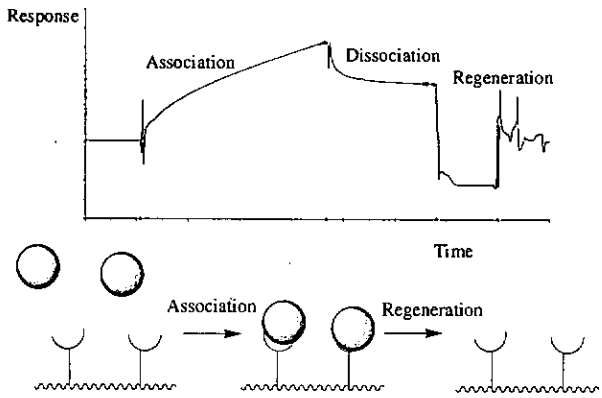


Figure4. Schematic of an SPR binding sensorgram and the corresponding binding event.

Expanding our understanding of biosensors

The work with progesterone as the model compound naturally leads to examination of a host of related small molecule targets and these are under active investigation for a range of quite different applications. Protein conjugates clearly provide some significant advantages over existing enzyme conjugates for ELISA and open the way to coating antigens on SPR sensor surfaces. The SPR technique offers great potential to develop on-site, portable, on-line biosensors for the measurement of a host of different antigens, and extensive work is underway on developing these systems as part of our biosensing platform. Thus far, the SPR systems, whilst demonstrating somewhat superior surface stability to many electrochemical alternatives, are largely restricted to laboratory based instruments such as those produced by Biacore AB, and also are not yet as sensitive as existing ELISA kits. The application of organic chemistry to solving some of these biochemical problems can open the way to more extensive use and commercial development, and this is one of the ongoing areas of focus in this work.

The key to developing biosensing systems for small molecules capable of overcoming the many fundamental problems encountered in the field, lies in an understanding of the ways in which the antigen may be chemically modified to improve the stability of the surface, the ability of the antibody to recognise the antigen, and, so that signal transduction elements may be incorporated into the antigen, to boost the signal. Linker technology, such as that illustrated above, plays a major role in improving antibody-binding performance.

Conclusions

It has been shown how important it is to have a fundamental understanding of the factors that affect antibody-antigen interactions if one is to logically develop biosensors with superior sensitivity, detection limit, and robustness for use in biological samples. The use of protein conjugates as coating antigens in immunoassay and biosensors has great promise and illustrates how organic chemistry may be used to improve detection limits. SPR-based biosensors are one of the most promising emerging areas in biosensor research. Work is ongoing to improve the detection capabilities of these systems for use on-site.

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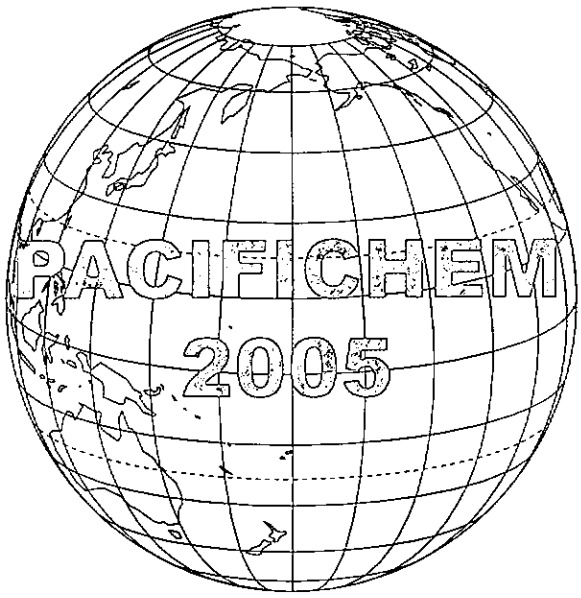

15-20 December 2005

Update

The dates are fixed, the programme is set, and Pacifichem 2005 now calls for papers. Abstract submission will open on the web on 18 January and close on 13 April 2005:

www.pacifichem.org

All delegates wishing to present a paper (invited or contributed, oral or poster) must submit an abstract online. Late submissions will not be accepted and every delegate will need to ensure that s/he complies with the requirements for the Technical Areas, and is aware of the type and limitation on audiovisual equipment and/or the poster board size provided. There will be a ***Student Poster Competition*** as at previous Pacifichem congresses and entrants will need to ensure that their abstract submission is designated for entry to this. Graduate student supervisors are particularly encouraged to select a PhD student from their group, or Departments to select a nominee for entry to the competition, remembering that New Zealand students have performed exceptionally well at past congresses.

The technical program is divided into the following areas: **Agrochemistry** (including agricultural, carbohydrate, cellulose, food, paper and pulp chemistry), **Analytical Chemistry** (including clinical, electrochemical, and trace analysis, and sensors), **Biological Chemistry** (including biotechnology, genomics and microbial chemistry, proteomics chemistry), **Chemistry and the Community** (including chemical education, chemical economics and business, chemistry and the law, public education and outreach), **Environmental and Green Chemistry**, **Inorganic Chemistry** (including geochemistry and nuclear chemistry), **Macromolecular Chemistry**, **Materials Chemistry and Nanotechnology**, **Medicinal Chemistry** (including pharmaceutics), **Organic Chemistry**, **Physical and Theoretical Chemistry**.

It will consist of some 225 symposia, spread through 658 half-day sessions; some symposia will also run evening sessions of which 95 have been assigned. Preliminary information on registration (opens 18 July 2005), visa issues, and hotels is provided on the website, and will be updated regularly as more details become available.

Additional to the above, ***Pacifichem 2005*** is again sponsoring a ***Young Scholars*** programme to encourage participation by up to 25 chemists from the developing regions of the Pacific Basin. These awards (for $US2,000 each + complimentary congress registration) are available to residents of the specified emerging countries (see website for details) that exclude New Zealand. Should you know of potential applicants then please encourage them to make application for one of these grants before the closing date of 15 January 2005.

Should anyone require assistance please do not hesitate to contact the NZIC Pacifichem representative:
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SCHOLARSHIPS AND FELLOWSHIPS IN EUROPE

Three European specialists with expertise in European researcher mobility programmes visited New Zealand in October 2004 to learn about research here, and to promote New Zealand's involvement in the Marie Curie scholarships and fellowships funded by the European Commission. They met some 275 scientists and technologists across the country.

The EU target for science is planned to grow from 2% to 3% of GDP by 2010, though attainment seems difficult. Researcher visits in Europe find difficulty in dealing with pension schemes, mother-tongue education for children, jobs for spouses etc., and the Marie Curie programme was designed to mitigate these effects.

Marie Curie funds are available for a spectrum of researchers, ranging from those without a PhD or 4 years research experience, through those with a PhD or more than 4 years experience, up to personal awards of roughly NZ$90k for individuals and greater amounts for research teams. PhDs can win international fellowships for two years. Slides of their presentations are available for download at: http://colab.rsnz.org/eu/ in Powerpoint and PDF formats.

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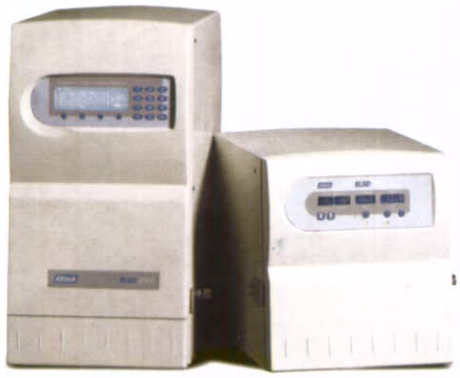

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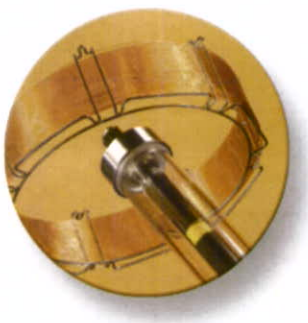

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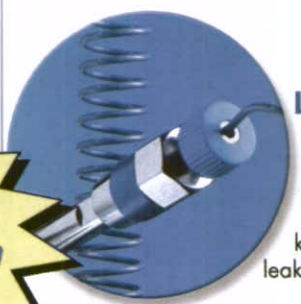

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