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Chemistry in New Zealand

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NZ Science Scene

NZ ASSOCIATION OF SCIENTISTS REQUEST FOR INFORMATION ON SCIENCE FUNDING

Recent science funding decisions by Government suggest a considerable shift in the nature and direction of the science funding and processes. In the absence of factual information about the possible impact of these changes on scientific institutions and on the skilled scientific workforce, NZAS is seeking information about positive and negative impacts of these changes. With this information, NZAS will act constructively to address problems in process and outcomes that may have arisen from this year's FRST funding round. Please send your comments to President, NZ Association of Scientists, Mike Berridge Email: mberridge@malaghan.org.nz, fax to 04 389 5095, or mail to NZAS, P O Box 1874, Wellington.

SYNCHROTRON HELPS BUILD TRANS-TASMAN SCIENCE LINKS

The New Zealand and Victorian Governments have announced that New Zealand will join the National Scientific Advisory Committee for the Australian Synchrotron project. A synchrotron is a large hollow ring about 60 metres in diameter that produces beams of very bright light, millions of times more powerful than the best conventional microscope. As a versatile analytical tool, it is used in biological and life sciences, mining, geoscience and to manufacture pharmaceuticals and new-age materials. The Australian Synchrotron will boost research and development in areas such as biotechnology and advanced manufacturing. The planning phase is well under way, and site preparation works are due to commence in September 2002, with the facility due to be fully operational in early 2007.

FUTURE DIRECTORS' AWARDS

The Ministry of Research, Science and Technology has announced the 2002 application round for the Future Directors' Awards. Places on the Institute of Directors "Company Directors' Course" are being offered to six scientists, technologists, or engineers who have both the capacity and interest in putting science and technology in the board room through directorship responsibilities. The Company Directors' Course is the Institute's premier course and covers all aspects of directing. It provides the individual with an intensive study of the duties, responsibilities and personal liabilities that arise from the diverse day-to-day activities of a company. Places on the course are available from 10-14 October 2002 and 21-25 November 2002. A full description of the course is on www.iod.org.nz For information and application guidelines see www.morst.govt.nz/funding or contact:
Diane.Gardiner@morst.govt.nz
Applications close at 5.00 p.m. on Tuesday 9 July 2002.

MASSEY AWARDED GRANT FOR SOLAR TECHNOLOGY AND RESEARCH

Massey University has been awarded a major grant from the Foundation of Research Science and Technology (FRST) for the development of solar technology and research. A project to build cheaper and more efficient solar cells and batteries will receive $3.2 million over the next four years. Led by Associate Professor David Officer, the $810,000 a year project will develop advanced materials for energy technology. Dr Officer says this is the first time a project of this type and breadth has been funded by FRST. The team, including Dr Simon Hall, Dr Richard Haverkamp, Dr Keith Gordon from the University of Otago, along with Dr Tony Burrell at Los Alamos and Dr Gordon Wallace from Wollongong, is developing integrated solar harvesting and storage technologies. These include existing titanium dioxide solar cells and nickel-zinc batteries developed at Massey University by Dr Hall's PhD student Michael Liu. The next generation technologies will use conducting plastic materials for the solar cells and the batteries. "One of the major problems with current technologies being used in remote rural areas is that as soon as the batteries die they create a large environmental problem. These new batteries won't use sulphuric acid or lead and will be much less expensive. The next generation of plastic cells and batteries will be even more environmental friendly," Dr Officer says. He says they are already looking at commercialisation opportunities for the nickel-zinc batteries but the plastic solar cells are further away from commercial realisation.

SCIENCE & TECHNOLOGY PROMOTION FUND OPEN FOR APPLICATIONS

Contestable funding has been made available by the Government of New Zealand to support activities that make people enthusiastic about science and technology and excite a desire to find out or experience more. Projects of all sizes seeking funding of up to a maximum of $100,000 (incl GST) are sought for the 2002-2003 round. This Fund offers the opportunity to develop innovative projects and will give priority funding to those trying new ideas that could be a model for others to follow. The fund is administered by The Royal Society of New Zealand, on behalf of the Ministry of Research, Science and Technology. Guidelines and application forms are available from www.rsnz.org/funding/

st_promotion or by contacting the Fund Co-ordinator at promotion.fund@rsnz.org For further information, contact The Royal Society of New Zealand, PO Box 598, Wellington, tel. (04) 472 7421. The closing date for preliminary applications is 9.00 a.m. on Monday 8th July 2002.

DR RICK PRIDMORE NEW CEO OF NIWA

The NIWA Board is pleased to announce the appointment of Dr Rick Pridmore as the new Chief Executive of NIWA to succeed Paul Hargreaves following his retirement. Dr Pridmore is currently Deputy Chief Executive (Strategic Development) and has played a major role in the successful development of NIWA since its establishment 10 years ago. Born and educated in the United States, Dr Pridmore holds a PhD in Zoology from the University of Otago and earlier worked with NIWA's predecessor organisations, the DSIR (Department of Industrial and Scientific Research) and the Ministry of Works and Development. He was NIWA's Research Director from 1993 until his appointment to his present position as Deputy Chief Executive in October 1999.

SUPER SPUDS SCIENTIFIC PROJECT WINS MAJOR AWARD

One of the country's top scientists, Dr Margaret Gilpin, has won the South Island section of the prestigious FiRST Scholarship Awards sponsored by Foundation for Research, Science and Technology. Dr Gilpin, who is a New Zealand Science and Technology Post-doctoral Fellow, and who works at Crop and Food Research in Christchurch, won the award for her poster in which she summarises the project she is working on - namely the development of potatoes that combine traits such as disease resistance, superior processing and strong appeal to consumers. Margaret Gilpin says that earlier this year her work was severely hampered when much of it was destroyed, but she's determined to continue with this important research. Her poster won the South Island section of the competition because the judges felt that it communicated innovative and high quality science in a clear, straightforward way. In addition to winning the South Island award, Margaret Gilpin also won the New Zealand Science and Technology Post-doctoral Fellowship category. She will now travel to Auckland where she will compete with the North Island winner to be the national winner of the FiRST Awards, to be announced by the Minister of Research, Science and Technology Pete Hodgson on 20 June. The FiRST Awards are designed to recognise excellence in science communication and a key criteria of the competition is that posters produced by entrant's need to incorporate quality scientific information and design to ensure that laypeople can understand the project and see the benefits that flow from it. The Foundation also wants to make sure that all New Zealanders can see and understand the importance of the exciting work happening in this country in science and technology. This year's FiRST Scholarship Awards have been judged by a panel of specialists with expertise in business, research, communication and design and science: Peter Maire, the President of Navman NZ Ltd, (winner of the 2002 New Zealand supreme exporter of the year award); Sir Gil Simpson, CEO of Christchurch-based Jade Software Corporation; Fraser Carson, a director of Wellington-based Fresco Advertising; and Kaa-Sandra Chee, last year's overall FiRST Award winner. All of the Judges commented on the high standard of the 27 South Island entries. Other South Island winners are:

Steven Kroening, a Technology for Industry Fellow, won the TIF category for his poster on Biodegradation and Composting Profiles of Woolscour Wastes.

Tracey Dale, of Crop and Food Research, won the Enterprise Scholarship for her Study of T-DNA Integration and Gene Expression in Transgenic *Pinus radiata*.

Sonia Whiteman of Lincoln University won the Top Achiever Doctoral Scholarship category for her Study of Petri Vine Decline in New Zealand.

Lucinda Robertson of Lincoln University was highly commended in the Top Achiever Doctoral Scholarship category for her poster on Inherited Ovine Cataract as a Model of Human Cataract Formation.

TYLER PRIZE FOR ENVIRONMENTAL ACHIEVEMENT

The John and Alice Tyler Prize is awarded to an individual or institution of any nation who has benefited humanity in fields associated with environmental science, energy or medicine. The University of California is administrator of the Tyler Prize and the Annual Award is $200,000 (joint winners share the cash prize). The closing date for nominations is 15 September 2002 and instructions on how to nominate may be found at www.usc.edu/tylerprize/

TERTIARY EDUCATION COMMISSIONERS APPOINTED

Six new Tertiary Education Commissioners have been appointed. The new members will join the current Chair and Deputy Chair of TTEC, Dr Andrew West and Kaye Turner, and it is intended that all will be confirmed in their roles once the Tertiary Education Commission is formally established by legislation. The Commission will comprise:

- Dr Andrew West (Chair) - appointed in August 2001.
- Associate Professor Kaye Turner (Deputy Chair) - appointed in August 2001.
- John Blakey, Chief Executive of the Forest Industries Training Organisation.
- Shona Butterfield, Chief Executive of The Open Polytechnic of New Zealand.
- Jim Donovan, Managing Director, Isambard Ltd and a member of the Government's ICT Taskforce.
- Andrew Little, National Secretary of the Engineering, Printing and Manufacturing Union.
- Tina Olsen-Ratana (Ngati Porou),

Manager of Te Kokiri Marae at Seaview and a board member of the New Zealand Qualifications Authority.

- Dr Ian Smith, Deputy Vice-Chancellor (Research and International) at the University of Otago.

NEW FOOD SAFETY AUTHORITY FOR NEW ZEALAND

The New Zealand Minister-designate for food safety, Annette King, has announced a plan to establish a New Zealand Food Safety Authority by July this year.

In announcing the plan for the new authority, Ms King said that she welcomed this new challenge. While, in New Zealand, responsibility for food issues had traditionally been shared between the health and agriculture portfolios, Ms King said that food safety was clearly a prime health concern.

"The work I have been doing in the past two years, particularly in relation to food labelling, has reinforced my interest across the whole spectrum of food issues," Ms King said.

"Establishment of the new Food Safety Authority represents good news for all New Zealanders. Its work will affect all our lives".

Ms King said the authority's minister would be advised by a 10 - member advisory board that would assess the authority's performance.

"This board will include consumer representation, as well as producer representation. It is essential that consumers' interests in food safety are effectively addressed.

"Until the authority is established, the Minister of Agriculture and I will remain responsible for our respective parts of the food administration system, and I will be working closely with Jim Sutton and the Ministers of Finance and State Services on legislation and communication and funding issues during the transition period," Ms King said.

Under the New Zealand treaty with Australia, ANZFA is responsible for developing standards for food labelling and composition for both New Zealand and Australia. The treaty, which governs the ANZFA relationship, specifically excludes food hygiene issues from the activities ANZFA undertakes for New Zealand and the food safety standards in the joint Food Standards Code do not, therefore apply in New Zealand.

NEW LABPLUS MANAGER

New Zealand's largest hospital laboratory, the Auckland District Health Board's LabPlus has a new leader with a vision to make the lab a leading New Zealand laboratory.

Don Mikkelsen, former laboratory manager of Health Waikato, has recently been appointed manager of LabPlus and already he has a clear plan for the future of the lab.

"I want to harness the strength of the LabPlus team and the lab as a whole, to recreate LabPlus as a leading laboratory in New Zealand," he says.

Mr Mikkelsen says he is excited about his new role at LabPlus. "Now that the teething problems have been sorted out, LabPlus is poised to do great things," he explains.

A recent International Accreditation New Zealand (IANZ) survey, has commended LabPlus after assessments conducted in December 2001. This follows the suspension of accreditation for the Virology/Immunology and Chemical Pathology (two of the nine LabPlus units) last year.

Since then staff have worked hard to restore accreditation. The latest IANZ report commended staff for the very significant progress achieved, and for the many quality enhancing initiatives evident at the assessment.

"The commendation is an absolute credit to LabPlus staff who have worked so hard to bring accreditation back to LabPlus," says Mr Mikkelsen.

He says now is the time for LabPlus to settle down, and get started on its business development. However, he believes the biggest challenge will be overcoming negative external perceptions of LabPlus.

"We will need to be proactive in promoting ourselves and work on improving our image and service," he explains.

Given his experience working for seven years as the manager of the laboratory at Health Waikato, during which time he greatly developed the lab's external markets, Mr Mikkelsen is well equipped for the task that lies ahead of him.

INTERNATIONAL SEARCH NETS INDUSTRY NEW ZEALAND DIRECTOR, BIOTECHNOLOGY SECTOR

Industry New Zealand has carried out an international search to appoint its new Director, Biotechnology Sector.

Peter Lennox is currently Director of Biotechnology Networks for Scottish Enterprise - the national economic development agency of Scotland.

Industry New Zealand Chief Executive Neil Mackay said the organisation was thrilled to have recruited someone of the calibre of Mr Lennox.

"Biotechnology is one of the three key sectors targeted by the Government in its Growth and Innovation Framework as offering huge economic growth potential, both in its own right and as an enabler for other sectors.

"It was therefore important to find a person of international standing for the Sector Director role," Mr Mackay said.

Mr Lennox says the job brings together all strands of his past experience. "I was originally a scientist, and I have extensive business and marketing skills gained through working with blue chip companies and key government officials in Europe, Asia and the USA."


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Working together with key scientists from research institutes, economic analysts, private sector companies, the media and the Scottish and UK governments, Mr Lennox and his team forged a dynamic biotechnology community. The team raised the profile of Scottish biotechnology worldwide so that it is now recognised to be at the forefront of new scientific discoveries.

"More than that, through our shared vision of doubling the size of Scotland's biotechnology cluster over four years, we moved science from the research lab into newly created companies," Mr Lennox said.

Mr Lennox has also held positions as Director North America for Locate in Scotland, aimed at attracting high value projects, and Director of Scottish Trade International, the government export agency, as well as being Director and Chairman of a number of public sector bodies and working in the food and drink industry, moving from scientific research through production to marketing positions.

He takes up the position in early to mid July.

STUDY INVESTIGATES INNOVATION FACTORS IN BIOTECHNOLOGY

A major survey of the biotechnology sector has been launched by Waikato Management School. Questionnaires have been sent to 150 organisations which may be involved in biotechnology, including businesses, CRIs, universities and other research organisations.The survey is an important stage in research begun three years ago by Waikato Management School Economics Department lecturer, Dan Marsh. This phase is investigating factors affecting innovation in biotechnology.The study has been endorsed by the New Zealand Biotechnology Association executive and will contribute to a better factual foundation for policy making.

In 2001 Mr Marsh worked with Statistics New Zealand and the Ministry of Research, Science and Technology to analyse the 1998/99 Biotechnology Survey data. For results from this and earlier work on the New Zealand biotechnology sector, see: http://ideas.uqam.ca/ideas/data/waieconwp.html

If any organisation has not been contacted and would like to participate in the survey, contact Dan Marsh (Email: dmarsh@waikato.ac.nz).

FELLOWSHIP OPPORTUNITIES

MoRST still has vacancies for Fellowships offered by the Japan Society for the Promotion of Science. Short-term Invitation Fellowships are available for periods of up to 60 days as well as Post-Doctoral Fellowships for periods of up to 2 years. MoRST acts as nominating authority for these Fellowships with the objective of furthering scientific relations between our two countries and encouraging highly qualified researchers to participate.
Email: Diane.Gardiner@morst.govt.nz
Or see http://www.morst.govt.nz

STUDENTS SELECTED FOR USA SPACE CAMP

Josie Spiller from Wellington Girls' College and Andrew Brown from Bayfield High School, Dunedin, have been selected by the Royal Society to attend the USA Space Camp in Huntsville, Alabama, USA in July. Josie and Andrew will join over 70 students from 35 countries in an action-packed 10 days which will include hands-on astronaut training, as well as learning about the mental, emotional, and physical demands astronauts must face. The trainees are also involved in leadership training and will experience 4 x g of lift-off force and actual weightlessness in the space simulator.

Josie is very interested in the physiological changes on the human body while in space and is looking forward to seeing the design strategies being applied for maintaining health, safety, and performance of the human body while in that environment.

Andrew has dreamed about attending the USA Space Camp ever since he heard about the programme 5 years ago and is absolutely over the moon that he has been selected. He has his own 60 mm telescope and has been a member of the Dunedin Astronomical Society where he enjoys going along to listen to presentations made at the observatory.

UNESCO NZ UNDERGRADUATE SCIENCE SCHOLARSHIPS FOR 2002

The UNESCO NZ Science Sub Commission, in association with the Secondary Principals' Association of New Zealand, has created an undergraduate scholarship scheme to recognise top secondary school science students in their first year of university. The scholarships are valued at $1500 each. The recipients of the UNESCO NZ Undergraduate Science Scholarships for 2002 are:

Rosalind Phillips

Rosalind attended Havelock North High School. In the 2001 NZEST examinations, she was placed 5th overall and was the top female student in the country. She followed this with a score of 460/500 in Bursary, achieving scholarship in all five subjects. She was school Dux in 2001. As a chemistry student, Rosalind demonstrated exceptional ability. She was selected as a member of four students to travel to India to compete in the International Chemistry Olympiad in July 2001. She is also a highly accomplished musician and was selected as a finalist for Young Hawkes Bay Musician of the Year. Rosalind is enrolled in the chemistry honours course at the University of Canterbury.

Mark Stringer

Mark attended Christ's College for 5 years. Academically, he is a very talented young man. He held a Somes Academic Scholarship and in his final year he was awarded Dux of the College. He achieved five scholarships in the Bursary exams. Mark is a capable athlete and has excelled in a variety of sports. He was captain of the 1st XI cricket team and squash team. Mark is currently studying at the University of Auckland. He plans to complete either a science or engineering degree.

BIOTECHNOLOGY TASKFORCE NAMED

Ten top biotechnology entrepreneurs, academics and business leaders have been appointed to the Government's new Biotechnology Taskforce.

The taskforce, established under the Government's Growth and Innovation Framework, will be looking at practical ways of stimulating the growth and international competitiveness of New Zealand's biotechnology sector.

"This is a highly talented group of people, selected because of their knowledge and practical experience of the biotechnology industry," said Research, Science and Technology Minister Pete Hodgson, who will be co-chair. "The taskforce will pick international trends on which New Zealand's biotechnology sector might capitalise, develop strategies for building high-value technologies, and identify areas where Government action might enhance the sector's development."

The taskforce will meet regularly over 12 months, after which it will be reviewed. It will be supported by biotechnology sector specialists from Industry New Zealand and officials from the Ministry of Research, Science and Technology.

The work of the taskforce will coordinate with the work on a national biotechnology strategy being led by the Ministry. The strategy is designed to ensure New Zealand keeps abreast of developments in biotechnology, while preserving essential social, cultural and environmental values.

The Innovation Framework announced by the Prime Minister in February identified biotechnology, ICT arid creative industries as key sectors in which the Government will focus efforts to lift New Zealand's international competitiveness. Taskforces for ICT, screen production and design have been announced.

The members of the Biotechnology Taskforce are:

- Bill Falconer, co-chair (Biotenz)
- Garth Cooper (Protemix Ltd)
- Diana Hill (Global Technologies Ltd)
- Elizabeth Hopkins (Neuronz Ltd)
- Claire McGowan (Northington Partners Ltd)
- Jim McLean (Genesis Research and Development Ltd)
- Bruce Munro (New Zealand Wool Board)
- Ray Potroz (Council of Trade Unions)
- Max Shepherd (Zenith Technology Ltd)
- Paul Tocker (Crop and Food Research Ltd).

NEW NEW ZEALAND - GERMAN COORDINATOR

German-born Auckland robotics scientist Dr Werner Friedrich is the new representative for New Zealand science and technology in Germany.

Dr Friedrich, a programme manager with the Crown Research Institute Industrial Research Ltd has an excellent record as a researcher and considerable experience in technology development and commercialisation. Born in Germany, but a New Zealand resident since 1983, Dr Friedrich has maintained close professional links with the research community in Germany. He is also New Zealand's representative on the International Advanced Robotics Programme and was awarded a Royal Society Science Medal in 1997.

In his new role as Coordinator of the New Zealand/Germany Scientific and Technological Cooperation Agreement Dr Friedrich will create opportunities for New Zealand researchers and technology based businesses to work with their German equivalents. He will also keep the New Zealand Government informed of science and technology developments in Germany.

"New Zealand enjoys a very constructive, and mutually beneficial, relationship with the German science and technology communities. Germany is a world leader in both basic and applied research and Dr Friedrich's efforts will ensure that New Zealand's innovators are well-connected to this important partner. His scientific background and record of working with industry make him well suited to keep relations between the two countries moving forward."

Contact: Dr Werner Friedrich
Phone: (09) 303 4116, Email: w.friedrich@irl.cri.nz

2002 ACADEMY MEDALS AND AWARDS APPLICATIONS AVAILABLE

Academy suite of medals and awards being offered for 2002:

* Hutton Medal: Animal Sciences.
* Sir Charles Hercus Medal: Biomedical Sciences and Technologies.
* Cooper Medal: for the best account of research work carried out in New Zealand in physics or engineering.
* Thomson Medal: in recognition of outstanding contributions in the fields of the organisation, administration or application of science and technology.
* Hamilton Memorial Prize for beginners in scientific or technological research in New Zealand.
* Hatherton Award for the best scientific paper by a PhD student at any New Zealand university in physical sciences, earth sciences and mathematical and information sciences.

The closing date for applications and nominations is 2 August 2002.

Electronic copies of the information and application forms are available from:
awards@rsnz.org or
www.rsnz.org/awards/academy_awards/forms.php.

COVER STORY

Expanding The Boundaries Of Elemental Analysis With Time Of Flight Mass Spectrometry

The latest major breakthrough in advancing elemental analysis with TOF mass spectrometry represents more than a 500% improvement on quadrupole ICP-MS. Analysis of every element is simultaneous and therefore a result for the full mass range is achievable in less than 30 seconds. Mass detection allows for rapid elemental fingerprinting of samples. Parts per trillion detection limits are easily achieved.[1]

The analytical community has long recognised the advantages of mass spectroscopy for trace analysis. During the last few decades there has been greater emergence of analytical techniques using this type of detection system. Some of these techniques are Liquid Chromatography Mass Spectrometry (LC-MS), Gas Chromatography Mass Spectrometry (GC-MS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Glow Discharge Mass Spectrometry (GD-MS).

These techniques share a common goal in enhancing what were thought to be matured techniques. The 'Time of Flight' (TOF) concept applied to ICP-MS achieves that same goal in advancing the elemental spectrometry technique. With significant advances in electronic device technologies, the components necessary for system control and high-speed data acquisition now enable the effective use of TOF in ICP-MS. However, orthogonal acceleration is required for truly effective ICP-TOFMS. So what are the advantages of this innovation and what else can you do with such a design?

The idea behind the development of orthogonal acceleration TOF is to improve resolution, minimize losses of low atomic weight ionised species, eliminate sample introduction noise and provide simultaneous measurement of ions reaching the detector. Seemingly high ideals but how are these goals achieved?

Resolution is defined as the ratio of the detected mass to the difference between this mass and the nearest neighbour mass ($R = M/\Delta M$). How well two adjacent masses (mass channels) are resolved depends on what conditions are imposed on the ions from the moment they are ejected from the plasma ion beam to reaching the detector. On-axis Time of Flight requires the ions to be bunched or collected then pushed out, or accelerated, in the same direction towards the detector. This approach increases the probability of collisions and repulsions between ions resulting in what is referred to as mass-charge interferences. Ions may be deflected away from the detector, this leads to reduced resolution for the entire mass range and decreased sensitivity for low atomic weight ions.

The orthogonal (o) approach does not bunch up the ion beam but rather uses a high frequency push out accelerating the ions perpendicularly to the ion beam from the plasma. By carefully forming a ribbon beam with the ion optics prior to the acceleration zone the ICP-oTOFMS minimizes the mass-charge interferences and less low atomic weight ions are deflected away from the detector. Non-charged molecular species that pass through the ion optics are trapped in a collector on axis with the ion beam. The resolution is further increased by use of a Reflectron that accelerates the ions in the opposite direction and on to the detector. The Optimass 8000 can achieve a resolution (R) of up to 2000. This is a significant improvement on quadrupole ICP-MS, which typically achieve a value of up to 300.

Since the lighter masses reach the detector first and the heaviest masses, ^{238}U last, all within 32 msec, each push out gives a simultaneous detection of all mass channels. Strictly speaking it is pseudo-simultaneous detection but this is as close to true simultaneous detection as is practically possible for the ICP-MS technique. Repeating this at 30,000 Hz gives a very high temporal resolution, ideal for chromatographic type data acquisition where transient peaks are generated from samples such as for electrothermal vaporization sample introduction.

As the plasma conditions are the same for all masses detected the plasma noise is minimized. Compare this with a quadrupole ICP-MS where sequential peak measurement, peak hopping, is required. Simultaneous mass determination is ideal for ratio determinations of isotopes, elimination of isobaric interferences and rapid screening of samples. Incorporating a mass ejection system called SmartGate™ allows elimination of unwanted masses such as Ar species and other polyatomic interferences without the need of a collision cell. Parts per trillion detection limits are easily achieved.[1]

The simultaneous mass detection allows rapid elemental fingerprinting of samples. For example, for a quadrupole ICP-MS to determine 24 elements in a sea water sample can take 5 minutes. While aspirating the sample there can be problems with torch injector tube blockages due to the high dissolved solids load. With the Optimass 8000 the same analysis is performed in less than 30 seconds for all masses from AMU of 5 to 238. Fingerprinting is ideal for the analysis of environmental, forensic, biological, clinical, soil and geochemical samples.

GBC Scientific Equipment has spent the last fourteen years developing and refining the ICP-oTOFMS technique and is now realising the full potential of this patented technology. For more information contact GBC at gbc@gbcsci.com, telephone +64-9-3600928 or visit the website at http://www.gbcsci.com

circle number 1 on the reader reply card

References

1. Sturgeon, R.E., *J. Anal. At. Spectrom.*, **2000**, *15*, 607-616

NEWS

Call for Nominations

Nominations for President, First Vice-President, Second Vice-President, Honorary General Secretary and Honorary Treasurer for 2003 are called for.

Nominations can be made by Branches, or by any six members, and must be forwarded to the Honorary General Secretary by 31 October 2002.

Notice of Annual General Meeting

The Annual General Meeting of the New Zealand Institute of Chemistry will be held on 6 November 2002 in Wellington. Details of the time and place will be posted on the website www.nzic.org.nz and sent to Branch Secretaries at a later date.

Grant Boston
Honorary General Secretary

Chemical Education Trust 2002 Distribution

Applications are invited from secondary school chemistry teachers (senior chemistry teacher via Head of Science) for grants from the NZIC Chemical Education Trust to promote the teaching of chemistry in their school. For the 2002 distribution grants of about $400 are envisaged, but this does not rule out the possibility of applying for a greater or lesser amount.

Applications should be received no later than 1 September 2002 and addressed to:

Professor Leon Phillips
Department of Chemistry
University of Canterbury
Private Bag 4800
Christchurch

NZIC Branch News

AUCKLAND

The Auckland Branch hosted a lecture by Corday-Morgan Award winner **Professor Chris Hunter** from the University of Sheffield on Monday 15 April 2002. Professor Hunter's talk, which was entitled "Quantitative Approaches to Molecular Recognition", was well received. Earlier in the day, Chris presented a talk about the "Assembly of Complex Supramolecular Architectures" at the Department of Chemistry.

The University of Auckland

Congratulations to **Shen Vun Chong**, the Auckland Branch NZIC Student representative in 2000, on being awarded his PhD at the recent The University of Auckland Autumn Graduation. Shen's thesis entitled "Interactions of Oxgenated Organic Molecules on the (111) Surface of a Uranium Dioxide Single Crystal" was awarded The University of Auckland best doctoral thesis and the Department of Chemistry's L H Briggs Memorial Prize for best doctoral thesis.

Congratulations also to **Hima Madhavaram** and **Norrie Pearce** for attaining their doctorates. The Faculty of Science graduation ceremonies were held on Monday 29 April 2002, with close to 80 chemistry graduands in attendance.

Cancer Society Research Centre

Three recent arrivals in the chemistry section of the Auckland Cancer Society Research Centre (ACSRC) are **Dr. Shannon Black** (University of Bath); **Dr. Adrian Blackburn** (Trinity College, Dublin, and University of Bristol); and **Dr. Brent Lindsay** (an Auckland graduate with postdoctoral experience at the University of Utah).

CANTERBURY

The 2002 Canterbury Branch Committee is:

Jan Wikaira (Chair)
Cassandra Hinton (Treasurer)
Kristin Hoskin (Secretary)
Rob Lake
Kevin Sutton
Michael Edmonds
Rebecca Hurrell
Chris Sumby
Meryn Bowen
Jonathan Morris
Geoff Groves

The NZIC Canterbury Branch year started with a barbeque at the University of Canterbury Staff Club on March 11. Aimed at students (and other prospective members) the event attracted about 40 people, including some undergraduates and chemical engineers. The food was plentiful and well received, and the Branch President, **Jan Wikaira**, spoke about the role of NZIC and outlined the planned activities for the year.

This was followed on 16 April 2002, by a seminar from **Professor Chris Hunter** of the University of Sheffield entitled "Quantitative Approaches to Molecular Recognition". This proved to be a fascinating account of the development of tools to understand and model non-covalent interactions between aromatic groups. The story began with the development of model compounds to quantify these interactions as inputs to molecular mechanics force fields, with the ultimate goal of predicting the base stacking interactions that determine sequence dependent structural properties of DNA.

The May meeting will consist of talks from the Science Outreach Programme. This highly successful programme for high school students is intended to enhance science education and to encourage people to study more science. Two presentations from the programme were the basis for a popular Branch meeting last year that helped to publicise the programme and demonstrate the quality of the material.

University of Canterbury

The 2001 NZIC Conference provided recognition for students from Canterbury. **Chris Sumby** won the student seminar prize, **Richard Payne** was 2nd in the poster competition, and **Mary Gower** was highly commended in the same. Prizes were also awarded by the Chemistry Department at the end of last year to outstanding students: C.E. Fenwick Prize for 400-level Chemistry: **Richard Payne**; Haydon Prize for 300 level Chemistry: **Timothy Heaton-Burgess**; Institute of Chemistry Prize for 200-level Chemistry: **David Pearson**.

Recent and current Chemistry Department visitors include: **Professor Chris Reed**, from the University of California at Riverside, on 12 April 2002 with a seminar titled: New Superacids for Organic and Inorganic Chemistry Strong but Gentle" where he described some of their investigations of carborane superacids; **Dr. Thomas A. Newton** from the University of Southern Maine (collaborating with **John Blunt** and **Murray Munro** on the isolation and characterization of biologically active materials from fungi); **Professor John Cannon**, from Brigham Young University, Provo, Utah, is spending a half-year sabbatical working with **Ward Robinson** and observing the modus operandi of the X-ray laboratory. **Carol Taylor** from Institute of Fundamental Sciences, Massey University, visited in April to give a talk on "Hydroxyproline: Molecular Hinge & Fine-Tuning Device".

In further Departmental news, **Jan Wikaira** and **Richard Hartshorn** have each received a Teaching and Learning Committee Conference Grant to attend the RACI Chemical Education Division 2002 Conference in Melbourne. **John Blunt** has been granted Erskine leave for the period 5 May till 24 June, which he will spend at the National Cancer Institute. **Greg Russell** is also away and will be working at the University of New South Wales until 28 June as part of his study leave. **Peter Steel** is also on study leave this year and is in currently in Sweden at Uppsala University. Prior to that he was at the University of Oxford. Later in the year he will be visiting James Cook University in Townsville to investigate various techniques for the stereoselective synthesis of ruthenium complexes.

There has been an exodus of postdocs from the Department in the last few weeks. **Dr. Sylvia Urban**, who has been part of the Marine group for the past three years, has returned to Australia before heading to Italy to get married in May. **Dr. Wilford Lie** who was collaborating with John Blunt on NMR techniques for proteins has also departed and **Dr. Mark Humphries** who was working with **Andrew Abell** has left after a two-year stint.

Jonathan Morris has also seen two of his students recently complete their studies for a PhD. **Christopher Bungard** finished his PhD. last year before taking up a postdoc in Philadelphia. Another PhD. student, **Regan Anderson** completed his PhD. on the "Total Synthesis of Variolin B" in April and has now taken up a postdoc in the Department. Several masters students have recently finished their time in the Department with **Tim Harwood** and **Hsin-I Chang**, who were both working on natural product isolation, and **Mark Lewis** who worked with **Richard Hartshorn**, completing Masters degrees.

MANAWATU

The April meeting of the branch was a joint meeting with local high school chemistry teachers on the theme *Chemistry at the Interface with Biology*. The meeting started at the New Zealand Dairy Research Institute (see note below) with **Grant Boston** giving an instructive introduction into the corporate structure of New Zealand Dairy Research Institute and was followed by a tour. **Euan Cant** showed the 'chemical tourists' the spaghetti-like array of stainless pipes and cauldrons in the factory scale section designed for the batch making of new food sensations. A novel feature for the detection and analysis of odours of dairy products was ably illustrated by **Justin Bendall**. On the outlet of the GC was a special nose fitting that allowed a trained 'smeller' to detect individual odours as they came off. **Colin Hughes** (analytical) and **Tim Coolbear** (microbiology and biochemistry) gave an insight into their respective sections. Thanks go to all the staff at New Zealand Dairy Research Institute who assisted with the very interesting tour. The dinner which followed at the Massey University staff club, Wharerata, included, of course, generous amounts of dairy products. Replete, the group had a few minutes to exchange news and ideas with fellow chemists and teachers before hearing a talk on the enzyme chymotrypsin by **Trevor Kitson** (Massey University). The mechanism of action of chymotrypsin was illustrated using stopped flow analysis. The final session included a quick look at the refurbished chemistry research laboratories and trialing of possible school-level experiments with **Tony Wright** (Massey University) and **Adrian Jull** (Massey University). These experiments used chemicals that can be obtained in the supermarket. Decomposition of hydrogen peroxide by iodide ion was used to measure the amount of Vitamin C in a consumable item, fruit juice. In the presence of bleach, food dyes progress through a range of colours before going completely colourless. The time taken for the bleaching reaction was deemed to be well within the attention span of a high school student!

The May meeting was addressed by **David Bibby** from Industrial Research Ltd, Petone on the topic, *The Chemistry of the Future*. The lecture made the point that in the 21st century three things will happen that have never happened before and these will result in major changes to society: (a) Mankind's impact on the biosphere will be global and detrimental. (b) The world population will peak and 'grey'. (c) A new form of intelligence will emerge. David Bibby discussed these points, emphasizing the opportunities for chemistry and chemists.

Above: **Sir Neil Waters**, the previous Vice-Chancellor of Massey University cutting the 75th Anniversary Cake. Sir Neil, a Fellow of the NZIC, is now an Honorary Research Fellow in chemistry at Massey's Albany Campus. Standing next to Sir Neil are **James McWha**, the present Vice-Chancellor and **Sir Allan Stewart**, the first Vice-Chancellor. (photo credit - Massey University News).

Above: As part of its 75th Anniversary celebrations, Massey University opened the new chemistry laboratories to the public. Here some "young chemists" enjoy paper chromatography. (photo credit: Massey University News).

Molecules for Life Conference Chairman **Mike Boland**, reports that the meeting at Napier in December 2001 was financially successful and has returned $15,000 to each of the participating societies – the New Zealand Institute of Chemistry, the New Zealand Society for Biochemistry and Molecular Biology and the New Zealand Biotechnology Association.

New Zealand Dairy Research Institute

NZDRI has changed its name to *Fonterra Research Centre* (FRC) from the beginning of June. Chief Executive **Allan Anderson** said that the name change would identify the organisation with Fonterra, both within the local community and with Fonterra's customers and associates. The new name of *Fonterra Research Centre* reinforced the organisation as the central R&D capability of Fonterra and widened its focus from purely dairy-based research. **Mike Boland** has been appointed Executive Manager Science of *Fonterra Research Centre*. Mike's role is to help FRC preserve and develop the quality of its underpinning science and to ensure that the right science is accessible or being developed to support the dairy industry's on-going requirements. Mike has recently attended the 16th Brunner Symposium at Michigan State University, USA where he delivered an invited paper. **Nick Robinson** has been appointed Section Manager of the Food Science Section at FRC. Nick is a graduate of Waikato University and has worked with **Alastair MacGibbon** in the Milk Lipids Group at NZDRI since 1995.

Massey University

This year Massey University is celebrating its 75th Anniversary and as part of this the Massey chemists are holding a reunion of chemistry graduates. The event - *Chemistry@massey* - will be held 4 – 7 July 202 in Palmerston North. The opening mixer, with quizmaster, **Trevor Kitson**, will be a trivial pursuits evening with questions ranging from chemical knowledge to who's who in the history of *Chemistry@massey*. The after dinner speaker will be **Geoff Malcolm** who was the first chemistry professor at Massey University. If you are a Massey chemistry graduate who has not been contacted about this celebration please contact **Andrew Brodie** (email A.Brodie@massey.ac.nz or phone 06 356 9099 extn 3536) as soon as possible.

Emily Parker, has welcomed two new postdoctoral fellows into her group recently. **Dr. Matthias Rost** comes from the University of Jena in Germany. His background is in synthetic chemistry and he will be involved in the synthesis of some novel enzyme substrates, inhibitors and reaction intermediates. There are also plans to tempt him with the delights of enzyme chemistry during his two year stint at Massey. **Dr. Linley Schofield** has joined the group to sort out the challenges of protein purification! Linley is planning to purify and functionally characterise the host of enzyme mutants (created by **Dr. Charlie Matthews**) of the first enzyme of the shikimate pathway. **Wayne Campbell** has successfully defended his PhD thesis on "Porphyrins for Surface Modification." His supervisors were **David Officer** and **Tony Burrell**. Wayne is now working in the Nanomaterials Research Centre before deciding his next move. **Trevor Kitson**, **Al Nielson** and **Tony Wright** were recently awarded distinguished teaching awards as recognition of their efforts in 200-level chemistry classes. PhD student, **Daina Grant**, has received a RSNZ Science and Technology award to attend the International Conference on the Science and Technology of Synthetic Metals in Shanghai. Massey Scholarships are awarded to the top 5% of students who have completed their first degree. This year chemistry did particularly well with the scholarships being awarded to **Sam Brodie**, **Adrian Chaplin**, **Ross Knudsen**, **Nikki Meyer**, **Anne Mahon**, **Patricia Shields** and **Celia Webby**.

"Massey University's developing research expertise in the field of organic synthesis, electrochemistry, material characterisation and nanotechnology has played a large part in the successful selection of Victoria University's MacDiarmid Institute for Advanced Materials and Nanotechnology as one of the nation's Centres of Research of Excellence," reports *Massey News*. The Nanomaterials Research Centre (NRC), opened in July 2001 by the 2000 Chemistry Nobel Laureate **Professor Alan MacDiarmid**, will link its expertise to that offered by the team at Victoria, led by former Massey Professor of Physics **Professor Paul Callaghan**. NRC Director, **Associate Professor David Officer**, says that the NRC's research strengths in the development of new materials for solar cells, batteries, sensors and other applications critical for New Zealand's future, have been recognised by its participation in the MacDiarmid Institute. "Participation in the Centre of Research Excellence has already created significant research opportunities for Massey staff and students. A number of the Institute's projects will involve collaboration between Alan MacDiarmid and Massey people. NRC researcher **Dr. Warwick Belcher** will visit Professor MacDiarmid's laboratory at the University of Pennsylvania during May." One of the real advantages of being part of the research group will be access to equipment, facilities and expertise at the six other CoRE sites and their international collaborators, says Dr. Officer. NRC research leaders **Drs. Simon Hall** (Chemistry - IFS) and **Richard Haverkamp** (Institute of Technology and Engineering) will both be involved as Principal Investigators in key projects within the CoRE research programme and anticipate receiving significant funding for both research student support and equipment. **Dr. Keith Gordon** at the University of Otago, who is also an NRC research leader, has a key role to play as a Principal Investigator in a number of the NRC-related projects.

Peter Kovacic, San Diego State University, recently spent 3 weeks at Massey University. He gave six lectures to the 700-level chemistry students and two seminars. It is also rumoured he and Geoff Jameson wrote a paper. Other visitors who have given seminars recently are **Chris Reed**, University of California, Riverside on *New Superacids for Organic and Inorganic Chemistry: Strong but Gentle*; **Han Vos**, Dublin City University on *Synthetic and Supramolecular Aspects of Ruthenium Polypyridyl Chemistry*; **David Hulmes**, Institute de Biologie et Chemie des Proteins, CNRS, Lyon, France on *Building Collagen Molecules, Fibrils and Supra-Fibrillar Structures*; and **Anthony Killard**, Dublin City University, on *Electrochemical Immunosensors*.

Dr. Anita Sharma has been appointed as a Postdoctoral Fellow in the Institute of Technology and Engineering. She will be starting in July and working with **Richard Haverkamp** on anodic reactions in high temperature molten salts. She comes to us from Auckland having studied in India and Canada and has recent experience as a scientist at Pacific Lithium Ltd. It has been a busy month for **Aaron Marshall.** In April he completed an MTech (Chemical Technology), got married then left for Norway with his new wife to study for a PhD at the Norwegian University of Science and Technology (NTNU) in Trondheim with **Professor Georg Hagen**. His work will be on electrocatalysis in PEM electrolysis of water. The supervisor for Aaron's masterate, **Richard Haverkamp**, through his collaboration and regular travels to Norway was able to facilitate the fully funded PhD award. "It is great to see one of our top students get this opportunity. Aaron will do well and I hope he will be the first of many students to exchange between the two Universities." says Richard.

OTAGO

The first branch outing of the year involved a trip to the Portobello Marine Aquarium, where talks were given by **Professor Mike Barker** and **Dr. Mark Lokman**. The evening was enjoyed by all, with the possible exception of **Dr. Lyall Hanton** who has swom never to ride in a bus again.

Scott Dickie who completed his BSc(Hons) at Otago last year has started a PhD with **Jim McQuillan** on surface chemistry in paint pigment dispersions. Scott was awarded an Enterprise Bright Futures Scholarship funded by Technology NZ/Resene Paints. **Dave Warren** has moved south from his teaching position at Wairarapa College, Masterton to start a PhD with **Jim McQuillan** on IR spectroscopy of reactions at photocatalyst and fuel cell electrocatalyst surfaces. Dave's scholarship is funded by Johnson Matthey, UK.

Dr. James Moffett, a graduate of the University of Otago Chemistry Department, has recently been promoted to Senior Scientist in the Department of Marine Chemistry and Geochemistry at the prestigious Woods Hole Oceanographic Institute (WHOI), Woods Hole, Massachusetts. WHOI is the largest privately-funded oceanographic research institution in the world, and leads the world in many areas of marine research (e.g. the famous submersible Alvin which explored the wreck of the Titanic). Jim graduated B.Sc. (Hons.) in Chemistry from the University of Otago in 1981. Following that, he studied for his Ph.D. in Chemical Oceanography at the Rosestiel School of Marine and Atmospheric Science, University of Miami, graduating in 1986. His thesis Title was "The Photochemistry of Copper Complexes in Seawater". He was then appointed to a post-doctoral position at WHOI, subsequently joining the tenured research staff in 1988. His research interests include metal geochemistry and cyanobacterial ecology, speciation and redox chemistry of trace elements in natural waters, with emphasis on transport processes and catalytic processes, characterization of biologically produced chelators, effects of protozoans on chemical fate and metal contaminants in harbours.

Dr. Udo Beckmann (PhD with **Professor Karl Wieghardt** at the Max Planck Institut für Strahlenchemie) joined **Associate Professor Sally Brooker's** group, Brookers Bunch, as a Marsden Postdoctoral Fellow on May 1.

Dr. Kate McGrath gave the inaugural seminar of The MacDiarmid Institute for Advanced Materials and Nanotechnology entitled "Pattern Control Through Surfactant Self-Assembly" by video conference on May 3rd. Her talk in front of a live audience in Dunedin was simultaneously seen by audiences in Christchurch and Wellington. Thanks to the success of this talk, further video conference seminars to the Institute are planned.

WAIKATO

Dr. Richard Coll has accepted a position at the Institute for the Advancement of University Learning at the University of Oxford and left Waikato on 21 June 2002. His position as Waikato Branch Chairperson has been taken over by **Bob Wilcocks** and the officers of the Branch are:

President:	**Bob Wilcock** (replacing Richard Coll)
Treasurer:	**Michael Mucalo**
Secretary:	**Shane Burggraaf**
Branch Editor:	**Michele Prinsep**
Branch Delegate:	**Bob Wilcock**

The annual "start of year BBQ" went well with a good turn out of students and staff from Ruakura and around Hamilton. There were a number of new people who signed-up for membership, which was pleasing.

The other Branch activity consisted of **Nick Kim**'s talk at the Exscite Centre. Nick entertained the audience with a talk on the examination of forensic evidence. As Nick pointed out, lawyers are quick to challenge legal issues in court and some well-established practices such as alcohol breath and blood testing, but loathe to entertain arguments around other issues like gun shot residues. It seems that the presence of such residues are taken as proof that the accused was the perpetrator. Nick's studies show that this may not necessarily be the case, especially with old guns that can spray residues in different directions to the end of the barrel. The talk fitted in nicely with the Forensic Exhibition at Exscite. Members were much impressed with the talk and enjoyed the interactive exhibits at Exscite.

Above: Inside the "Mystery Cafe" the scince for Exscite's "Whodunnit?" exhibition.

Above: Nick Kim telling the Waikato Branch about the gunshot residues.

Richard Coll took the opportunity to present **Karen Love** with the **JE Allen Memorial Chemistry Prize** for the best performance in second-year chemistry at Waikato University. Karen, a third-year BSc(Tech) student, chose as her prize a book on industrial chemistry.

Above: Karen Love receiving the J E Allen prize for best second year chemistry student at th University of Waikato from Richard Coll.

Richard Coll has just returned from two conferences in the USA. The first, the annual conference held by the USA-based National Association for Research in Science Teaching, was a large 850-delegate conference. It is interesting to note the proliferation of studies in chemical education and greater interest in education research at the tertiary level. Richard presented some findings from **Jacinta Dalgety's** work on the development of the Chemistry Attitudes and Experiences Questionnaire (see, *Chemistry in New Zealand*, **2001**, *65*(3), 42-47) and the work was very well received. The other conference was on Cooperative Education, *i.e.* work-based learning, which is an important part of Waikato's Science and Technology offerings. Richard presented studies on the internationalisation of work-based learning and contributed to a workshop on research design and methodology in education research.

Bill Henderson has just commenced a three-year term as Chairperson of Department. Bill and **Brian Nicholson's** PhD student, **Corry Decker** is currently completing her thesis on Electrospray-friendly ligands, in between swimming across Lake Taupo, and, that not being enough of a challenge, Cook Strait. **Dion Tupara**, also a joint student between Bill and Brian, recently completed his MSc, submitting a thesis on applications of electrospray mass spectrometry in inorganic chemistry, concentrating on highly charged metal complexes and complexes of cyclophane ligands. Bill, along with ex-Waikato PhD student **Scott McIndoe**, now at Cambridge University, are planning to write a book on applications of electrospray mass spectrometry in inorganic chemistry. The 6th Edition of Mackay, Mackay and Henderson "Introduction to Modern Inorganic Chemistry" has recently been submitted. Along with two undergraduate students (**Carol Goss** and **Daniel Van de Pas**) currently doing their Special Topics research projects with Bill this year, he should be able to keep busy!

Over the summer we enjoyed brief visits from ex-students **Nick Goodwin, Maarten Dinger** and **Scott McIndoe** who were escaping the winters of Bristol, Amsterdam and Cambridge, respectively. All seem to be highly successful and enjoying their research work. **Maarten Dinger** has moved from a postdoc in Florida to a postdoc at the University of Amsterdam, looking at metathesis catalysis. **Nick Goodwin** continues postdoc work with **Professor Neil Connelly** at Bristol, and **Steve Alley**, who submitted his thesis on ferrocenylphosphorus compounds in 2001, is hoping to get a postdoc in Dublin, where he is currently coaching rugby. **Rebecca Taylor** (MSc 2000) continues with her PhD at ANU (**Professor Martin Banwell**) and has just been awarded a scholarship from there. **Karen Murphy** (PhD in porphyrin complexes in forensics; with Bill, Nick Kim and **Tony Cartner**) continues with her postdoc with **Dr. Nick Long** at Imperial College.

Waikato inorganic chemists were out in force at the excellent NZIC Conference at Napier in December, and a good time was had by all. Congratulations especially to **Nick Lloyd** for winning the best student poster competition. **Brian Nicholson** won the "Driver-of-the-Conference" award for taking the 2.90 m high rental van through the motel entrance with the 2.85 m high beam...

The inorganic lab in 2002 is active. **Cameron Evans** submitted his PhD thesis on electrospray mass spectrometry of metal carbonyl clusters in January and has now successfully defended it at the oral examination. He is now looking overseas for his next chemical adventures. The two manganese carbonyl PhD students **Wade Mace** and **Victor Fester** have set up "The Gentlemen's Club" in the C-block labs, adding a note of refined culture (and very good coffee) to the otherwise spartan environment (as befits a politically correct university, "gentlemen" in this context is not gender-specific). Amongst the second-year MSc students, **Nick Lloyd** continues to produce ever-more-complicated NMR spectra of his tin complexes, and **Sam Whitley** is successfully unravelling the chemistry of aryl-mercury oxides and hydroxides. First-year MSc students **Nicole Addison**, who is working on metal carbonyl clusters synthesised using vile-smelling phosphines, and **Susanna Thwaite** who is investigating gold chemistry has joined them. Susanna has been awarded a DAAD scholarship to spend part of her MSc research time with **Professor Hubert Schmidbaur** in Munich later this year.

Brian Nicholson is enjoying life without (much) administration, after passing on the Chairpersonship of chemistry to another inorganic chemist, **Bill Henderson**. This means that inorganic chemists have been in charge of chemistry at Waikato for all but four years out of the last twenty! Brian is taking some leave in the second semester of 2002 and will be spending the main part of it in Adelaide, renewing his collaboration with **Michael Bruce**'s group.

It is with regret that **Dr. Richard Coll** is leaving Waikato in June. Richard has accepted a position at Oxford University in the chemical education area. This has increasingly attracted more and more of Richard's time and, while we lament the transfer of an inorganic chemist to another area of chemistry; we wish Richard all the best in his new position.

Local Non-University News

The official opening of the Riverlea Road Campus by the Minister of Agriculture, **Jim Sutton** took place on Wednesday May 8. The campus is comprised of Livestock Improvement's Milk Analysis Laboratory, Animal Health Laboratory, Genemark DNA Analysis Laboratory, and Dexcel's Milk Characteristics Laboratory, which provide services to the dairy industry.

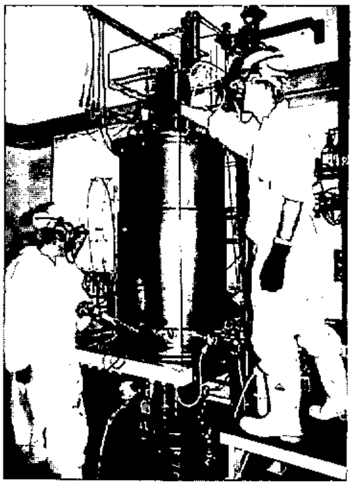
Branch Editor's Note: The Waikato Branch would like to take this opportunity to publicly acknowledge the assistance provided by Richard Coll in gathering and providing the Waikato News for *Chemistry in New Zealand*. **Michele Princep** replaces him and she knows that he will be a hard act to follow! We wish him well in his new venture.

WELLINGTON

The March meeting saw a return visit to the Branch of **Professor Ian Shaw**, the Food Safety Programme Manager of ESR Christchurch. Ian gave an illuminating discourse on "Natural Toxins–Ingenious Assassins" that held the audience captive. From LD_{50} values of recognised poisons [ethanol 10,000 mg kg^{-1} to tetrodotoxin (Japanese fugu or puffer fish) 0.00001 $mgkg^{-1}$], the impact and action of snake venoms and the Botulinum toxin led to seratonin – the audience was fascinated. Discussion on the decrease in male sperm count related to 17β-estradiol and the current (at the time of speaking) zucchini controversy ended a most successful evening.

On April 5 2002, the Council of the NZIC met at Victoria University under the auspices of the School of Chemical & Physical Sciences.

The April Branch meeting of the consisted of a presentation **"Human Pharmaceutical Production in New Zealand" at Industrial Research Ltd (IRL)** by **Dr. Max Kennedy** followed by a "walk-around" of the nearly completed extensions to the bio-pharmaceutical facility at IRL. The procedures used by the Biopharmaceuticals Division of IRL in the development and contract manufacture of active pharmaceutical ingredients, mainly for clinical trials, for biotechnology and pharmaceutical industry clients in New Zealand and overseas were outlined. The production, which excludes protein syntheses, involves fermentation, solvent extraction and purification but, of necessity, must comply with the rigours of ISO 9001/14001 registration etc. and follow current Good Manufacturing Practices in accordance with US Food and Drug Administration Code of Federal Regulations. The facilities for strictly contained fermentation and solvent extraction are used in the manufacture of small solvent soluble molecules of microbial origin. These include anti-infectives, immune modulators and anti-cancer agents, and examples of the products manufactured include brefeldin, rapamycin and ansamitocin. The costs of the new facility, which will be fully under remote control mount into several millions of dollars.



In May **Dr. Greg Lynch**, a partner in the intellectual property firm Baldwin Shelston Waters (and known to readers for his regular column with Jane Calvert "*Patent Proze*" in *Chemistry in New Zealand*), told members **"What Chemistry Researchers Should Know About Intellectual Property".** Greg followed a PhD in chemistry from Otago and postdoc work at Oxford with a stint at IRL before becoming a registered patent attorney in New Zealand and Australia, and a Barrister and Solicitor of the High Court of New Zealand. His address covered: Intellectual Property -what is it? Why do you need to know about patents in particular? What is important and what do chemistry researchers need to know? Recognising that the cornerstone of any business that relies on scientific research is often the technology it has protected by patents. We were treated to aspects of the highly expensive Kodak versus Polariod case. Patent issues relating to the definition of an alkoxy group (-OR), and the extent of patent cover one can reasonably expect, were illustrated by the claim that $-OCHF_2$ cannot reasonably be expected as included in a generic claim for the alkoxy group –Oalkyl. The fascinating discourse was followed by an extensive question and answer session and those that attended were well satisfied with another first-rate Branch meeting.

Industrial Research Ltd (IRL)

"SCIENCE IS MAGIC" - the front-page headline of the Saturday April 6, 2002 *Dominion* newspaper. The eye-

catching picture was of the son of one of IRL's staff, **Jeffrey Evans**, looking at "elephant toothpaste" made by IRL's **Dr. Mark Waterland**, during a visit by the children of staff members to the Gracefield site.

The new CEO of Industrial Research Limited is **Dr. Nigel Fitzpatrick.** He comes from Unilever in Switzerland and will have arrived at Gracefield at the end of May. The reshuffle of senior managers in June/July of last year saw a new General Manager, R & D Operations (**Dr. Sunil Vather**) appointed at Gracefield. In December, the Applied Inorganic Chemistry, Materials Physics, and Ceramics teams were combined under manager, **Dr. Bob Buckley,** with the new name of the *Materials Technology Group*. **Dr. Neil Milestone** will be acting as a NSOF (Non-Specific Output Funding Manager-advisor) as well as assisting with the new science thrusts and the bids to the Foundation. **Dr. Ian Brown** has responsibilities in the commercial funding area. The new structure is intended to provide flexibility around project areas, some of which reflect a move into new aspects.

Work continues apace on IRL's cGMP pilot plant for the synthesis of potential drug candidates. The 300 m^2 flameproof facility is designed to carry out concurrent cGMP processes and will include a 250 L glass-lined reactor, 50 L Buchi Rotavapor, 50 L hydrogenator/cryogenic reactor, 100 L filter dryer, and a single fluid Heating/Cooling system rated from –70 to +200 °C. Forming an integral part of this facility is the recently purchased HEL SIMULAR reaction calorimeter, which will enable the safe translation of potentially hazardous laboratory scale chemical reactions through to the facility. The facility, coupled with the IRL expertise in calorimetry will provide a unique resource in New Zealand, and is designed to help facilitate the development of candidate drugs from a research level to the production of multi-kilogram cGMP quantities for up to and including FDA approved Phase I clinical trials.

Dr. Catherine Dickson, recently travelled under an ISAT award to Melbourne and successfully initiated some joint research work on (the new cement and concrete buzz word) geopolymers with CSIRO colleagues.

Dr. Tim Kemmitt is currently in Lyon, France at the Université Claude Bernard, through a BRAP award, working on metal organic precursors suitable for use in film preparation. One of the novel compounds he and student **Hana Robson-Marsden** (VUW) produced in the titanium alkanolamine system, analysed by **Dr. Graeme Gainsford**, is on the front cover of a recent *Acta Crystallographic, Section C.*

Research student **Gabriel Ossenkamp,** (VUW/IRL) is writing up his PhD thesis on surface treatments of silica.

Dr. Steve Bagshaw recently hosted **Professor Mike Anderson** from UMIST as they developed a collaborative project to obtain details on the super-microporous materials that Steve has prepared. **Uli Wolf**, our German student returned to Germany in March.

The Carbohydrate Chemist Group has gone through a period of expansion growing from 18 members to 28 in the last year. Included in these recent staff additions is **Dr. Graham Caygill** as an NZ S & T postdoctoral fellow (the 4th in the Carbohydrate Chemistry Team in the last 8 years) to install, validate, and run our new HEL reaction calorimeter. Also with regards to postdoctoral fellows, in the last few months one Marsden grant conceived and written by **Dr. Richard Furneaux** has wound up and another successfully prepared by **Dr. Peter Tyler** on the "Secrets of Longevity" has recently begun.

Victoria University

Professors Brian Halton and **John Spencer** left the School of Chemical and Physical Sciences in mid-May for periods overseas. Brian departed for a two-month period in Europe in Norway (University of Bergen) and at the Max Planck Institute for Polymer Research (Mainz, Germany) while John has had two and a half weeks at the University of Pennsylvania in **Professor Alan MacDiarmid**'s laboratory. In late July **Dr. Peter Northcote** will take a six-month sabbatical leave.

2002 New Zealand Chemistry Olympiad Team

Peter Lau (Mount Roskill Grammar), **Gemma Mason** (Burnside High), **Kelvin Peng** (Auckland Grammar), and **Andrew Yearsley**, (Avondale College) have been selected as the 2002 New Zealand Chemistry Olympiad team to compete in the 34th International Chemistry Olympiad to be held in Groningen, The Netherlands, from July 5-13. Kelvin's sister, Irine, won a Bronze Medal in Beijing, China at the 1995 Chemistry Olympiad. The non-travelling reserves are **Alan Chan** (Westlake Boys' High) and **Paul Cheng** (Maclean's College). They are to be accompanied by **Dr Robert Maclagan** (University of Canterbury) and **Dr Suzanne Boniface** (Queen Margaret College, Wellington) as mentors, and **Dr Sheila Woodgate** (University of Auckland) will attend both as an observer and a member of the International Steering Committee. The students were selected after a training and selection camp held at the University of Auckland in early April that involved assessment over four exams and tests lasting a total of eight hours. The New Zealand government provides *no* support to the NZ Chemistry Olympiad Trust, which has organised New Zealand's participation in the International Olympiad. Financial assistance has come from New House Publishers, Crescendo Enterprises, ABA, Unilever, Bayer, Thermoplastic Engineering, School Supplies, Biolab Scientific, Gough Technology, the Faculty of Science at the University of Auckland, and the Department of Chemistry at the University of Canterbury.

Cosmetics In A Chemist's Career

By C. L. H. Stonyer

Only a small proportion of my 50 plus years as a chemist in manufacturing industries was formally devoted to cosmetics. However, if a cosmetic is a decorative preparation applied to the body that can be removed once its period of usefulness has passed, then my introduction to cosmetic chemistry was in 1945. That was the year I joined Vacuum (now Mobil) Oil Co. in Wellington, with no idea of what I would be doing - not that they had much idea of what I could do. Expecting some oil-associated activity, I was surprised to learn that one of my projects would involve sheep on a farm at Porirua, 20 km north of Wellington. The product concerned was a sort of paint for branding sheep and it had to last a year, then when the sheep were sheared, the brand had to be completely and easily scoured from the wool. The existing product was a sticky mess of red iron oxide, rosin oil and a solvent. Rosin oil is natural gum rosin, plus an assortment of fatty and rosin acids derived from trees. Exposure on the wool meant oxidation to compounds that the mildly alkaline scouring liquors could not remove. Customers were complaining!!

The development of better products in a range of colours was one of the most interesting projects of my cosmetic career. It involved pleasant trips to Windley's farm at Porirua, where we not only branded sheep, but also gave lots of sympathy to Mr. Windley about how terrible it was that "they" were going to cut his farm in half to build a motorway, thus ruining the place for farming. In the laboratory we made cute little scouring baths with Meccano mechanism. We made an exposure accelerator from a round one gallon tin and the inside bits from a mercury vapour lamp. We got lots of samples of pigments which the suppliers said would not fade, and we had trips to the top floor of the (now historic) building where the Department of Agriculture had set up their own testing laboratory. I also visited the CSIRO labs in Geelong where they were doing similar work (I was on holiday - Mobil would not have considered it cost effective to send me). After this visit I discovered the importance of publication. We had developed an inverted emulsion formula (later discarded), and I must have revealed enough of the details for the CSIRO to copy it because they issued a bulletin to Australian manufacturers giving them this formula with no mention at all that it was not all their own work! Of course Mobil chemists, in common with most other industrial chemists, never published anything.

The project ended with the Department of Agriculture, approving all our products - not that the company made much money from them as all branding fluids were banned a few years later. Some years passed before I was in touch with cosmetics again, unless house paints are considered to be cosmetic products - which largely they are.

Tasman Vaccine Laboratory, despite its name, branched out into many and varied products from about 1960. There were products that turned the saturated fat in sheep and cattle into polyunsaturated fat. There were resins that absorbed protein from aqueous solutions. There was construction of a radiation plant. There was work on turning an unused animal by-product into a steroid precursor, and there were plenty of interesting things to do.

Most of these developments eventually moved off-site but what did not move were the large propeller stirred mixers used for blending our liquid products. Using these, with only minor modification, we made a cream for applying to cows udders. It was used to prevent teat cracking and it contained an antiseptic to help with the mastitis problem. The formulation was easy; I took a hand cream formula from a Union Carbide booklet and added trichlorocarbanilide (TCC), an antiseptic that was being used in human deodorant soaps. It superseded hexachlorophene that had been the wonder drug until its drawbacks became apparent. Compared to DDT, TCC was great for a year or so but when a farmer in the South Island complained that his cows had sunburnt udders, we realised nothing was perfect.

Still, the cream was well liked and some customers wanted it with or without the TCC. Adding a bit more Paraben, we continued selling it. Our office girls also liked it although they somehow got the impression that we were making a special product for them. At a Christmas function when we revealed its true function there were shrieks (of horror) but we could get no volunteers for proper field tests on humans.

A contract from ICI for their antiseptic cream and liquid products expanded our knowledge of cosmetic chemistry rapidly. Not long afterwards other companies also engaged us to make their products which helped in improving our quality control methods. By this time we even felt confident enough to suggest improvements to some of the products we made for others.

The limitations of our mixers were becoming more apparent for several reasons. Most cream formulations are thin when first emulsified and hot, but at the lower temperatures needed for addition of perfumes and some preservatives they are usually much thicker. Because of this, the poor mixing efficiency we had was a worry.

Another concern was minimum batch size. The wide, shallow vessels had a minimum batch of not much less than their maximum, a source of great anguish to many. I had been agitating for some time for a purpose-built cream mixer with counter rotating dual stirring, good heating and cooling, and with strength to take a vacuum. Eventually, as part of a project to move our "human" product production away from the "animal" area, such a vessel was designed.

What a problem this turned out to be! Costs of the move started to rise, unforseen difficulties arose, and an obvious solution was to cut the cost of the new mixer (it was very expensive). The design engineer produced alternative designs almost weekly. Being convinced that nothing was as good as counter-rotating stirring, I rejected everything except the original design, making myself very unpopular.

Finally, the vessel was built and I am pleased to say that it made excellent creams for many years.

Sales staffs, who often seem unwilling to make estimates of their annual needs, frequently request small batches, but there is also the pressure to hold minimum inventories of raw materials and to use raw materials from several sources. If you have a costing system that allows for the cost of clean-ups, the cost of changing filling and packaging machines, the value of product lost in the mixer and the testing cost of a new sourced raw material, you may be able to discourage small batches. Those production managers who are insulated from sales pressures by a production-planning department are indeed lucky.

For seasonal sales variations our farm servicing staff had learnt to live with the problem but those on the "human" side had to learn the hard way when we started making sunscreen products. After a dull summer, not only did we have unsold stock of finished goods, but there were raw materials in stock that would have to wait over a year to be used.

A note about water, its quality and the quality of production staff. There was a time when New Zealand water supplies in many places were consistently more than satisfactorily pure. Overseas formulations inevitably specified deionised water but to my knowledge a lot of cosmetics were made with tap water, perhaps filtered to remove particulates. My personal share of this infringement of the rules must amount to thousands of kilos of cream and millions of litres of liquid. However, one of my colleagues, discovering that his plant had a deioniser, decided to use it when making a batch of cream. The finished product had to meet a bacteriological standard and to his amazement, never having had a batch fail, it showed gross contamination. The fault was soon traced to the deioniser resin beds which, not having been used for many months, had happily grown lots of undesirable organisms. Any one of a number of people could have prevented the problem arising, but through ignorance or indifference failed to do so. I have seen great faith put in manuals of procedures, but unless all staff are alert, well motivated, adequately trained and suitably experienced, such things will happen.

In 1980 a move to Auckland and to self-employment was a complete change of lifestyle. Although this was most enjoyable, a cheeky letter of about fifty words had me becoming an employee again. Smith Biolab was an unusual firm to say the least. It seemed that they could not believe that my predecessor was really leaving, so I had a whole two days to learn what the job entailed, where all the gear was, what procedures were followed, where I fitted into the organisational structure and so on. My formal career as a cosmetic chemist had started with a great leap forward!

The cosmetic factory of Smith Biolab came into being as a result of a careful measured expansion of an old importing company, S. A. Smith. They had bought into two firms, Biological Laboratories Ltd., and Scientific Equipment, in the mid-1960s when it appeared that import restrictions would reduce their profits from foodstuff importing. This started them on the "Health" and associated business. The seasonal nature of their biological business led them to seek agencies for the local manufacture of imported products. One of my long time chemical acquaintances, Ron Learnan, joined the company about 1960 (he joined the Institute of Chemistry in 1970 - I became a member in 1946). Ron had a more unusual time after graduating than most of us - he became a competitive motor racing driver in England and pictures of the sausage shaped cars of that era adorned his office.

Production was in the basement of one of their buildings and wax crayons, chlorine-releasing tablets for babies bottles, and sundry medicinals were made by Paul Thompson, a pharmacist who had joined in 1972. It did not make for a good manufacturing environment. A move into more suitable premises near the main office in Northcote was prompted by the purchase of yet another company. This was a Tauranga firm, Australasian Chemical Company, which in 1976 had an agency from a US drug company to make a very profitable drug. The name must have appealed because it was promptly painted on the new building, and they traded under that name for the next decade.

By the late 70s several more overseas agencies had been acquired and a number of health related products, including shampoos and creams were being made. This was done under the control of Paul Thompson, with some assistance from Ron Learnan, now Technical Director (he was also on the Board) who was about a quarter of a mile (~1/2 km) away. In 1978 Paul Thompson was made sales manager of the products he had been making and his period as factory manager, foreman, chemist, purchasing officer and quality controller ended with the appointment of a chemist and a factory manager. They reported to him separately, thus creating at least the appearance of good quality management.

My arrival in 1981, as mentioned above, was probably as big a shock to them as it was to me. I had come from multinationals with reasonably good systems and protocols, to a place with a much more relaxed attitude - even the fairly rigid instructions of the multinationals whose products we made were sometimes regarded as flexible. Of course, not all the overseas experts who came to see us were as good as they purported to be. One came to watch us making his products and made such stupid comments and remarks on how another of their plants did it that we could barely refrain ourselves from commenting on him.

In 1983 the factory manager suddenly left, leaving the foreman, the office assistant and me to run the plant. I think we did it very well for the few days it took before the aforesaid Ron Learnan came to take charge - we must have done because a couple of years later when Ron retired because of his health, we took over again and no-one was sent to take charge. During the period that Ron was there he provided me with useful technical assistance for I had discovered, soon after my arrival, that I was the only person on the staff with any knowledge of the industrial chemical world - I became a consultant to various departments (acting, honorary, and unpaid as in the army).

What did I do? After rewriting some of the laboratory methods, refining some of the systems for sampling raw materials and redesigning the batch sheets, I decided that the most interesting thing was product development. There was no lack of requests from the sales department and with new cosmetic raw materials promoted by suppliers at frequent intervals, product development was a major function.

There were the usual plant problems, some due to mistakes or misinterpretations of the plant operators, some because of inadequate or unsuitable plant and some because the originators of the product were not specific. Most of the overseas companies that we made product for were very good, but there was one product not made for any principal that gave us a lot of trouble: babies teats. These had been made for many years before I joined, the information having come from a latex supplier. The plant was very crude and obviously made at the lowest possible cost. The dipping bath had no temperature control and the drying heat-treatment ovens had no fans and only elementary thermostats. The reject rate was always more than anyone liked and I wondered why we kept making them. Towards the end of my stay I tried to do some statistical experiments, varying operating conditions in various ways. I also obtained more recent information from the latex suppliers and this helped a bit. Finally I decided that a lot more work was needed, as well as improvements to the plant.

As I became more of a cosmetic chemist I discovered what a huge mine of information there was on formulation of cosmetics and on new raw materials. Product development was really a question of making choices from all this. My basic criteria were:

1. What will the product cost?
2. Can our plant make it?
3. How well does it meet the marketing department's needs?
4. Do we have all the raw materials, and if not, what do any new ones cost?
5. Can we do all the QC tests ourselves?

Much of this was in a talk I gave to a Cosmetic Chemists Conference in 1983 - "The Manufacture and Quality Control of a Facial Moisturiser" [reprinted in *Chemistry in New Zealand* as "To Make a Cosmetic, Take ..." – see **1983**, *47*(3), 57-61].

These Cosmetic Chemists conferences were very intensive gatherings, much more so than a lot of other conferences I had attended. Starting after lunch on a Friday, they gave papers until lunch on Saturday, interrupted only for the official dinner on Friday night. I gave a paper every year that I was in the business. One may have been a bit baffling because it was hurriedly written in case a scheduled speaker could not come (for good reasons). He didn't and I filled in on a subject totally different from his!

One of these conferences provided the classic after-dinner speaker of all time (the speech was given before the dinner for some reason, but that is a minor detail). One Geoffrey Palmer, now an eminent retired politician, spoke at length and in great detail about the imminent introduction of GST (Goods and Services Tax). Most of the New Zealand listeners and all of our Australian guests were baffled as to its effect on cosmetic chemistry. We found out much later that Geoffrey's minions had prepared two speeches, one for us and one for the conference of pharmacists that was scheduled for a week or so after our meeting and that he had given us the wrong one! Did anyone ever find out what ours was about?

During my five year stint we could not escape dealings with the Health Department. My work at Tasman Vaccine, both before and after ICI bought the company, had made me familiar with their basic philosophy and whether the regulations were likely to be enforced. Fortunately we did not make any products for internal use, so their demand for factory and laboratory improvements were not unreasonable. The operator of a small plant not 100 km from Auckland may be telling this tale himself, but it shows how absurd literal interpretation of rules can be. There was a well equipped laboratory, a good small manufacturing plant and adequate written protocols. However, the manager, the foreman, the chemist and the quality controller were all the same person. The Health Department took a dim view of this and forced him to employ a chemist, who worked in the lab and who in theory had the power to prevent any product being made or sold if he was not satisfied with anything. Profits went down a bit and the shareholders, the next level up, were not too pleased. Still, there were two people to take the blame if anything went wrong.

The Salmond Smith Biolab (as it was now called) Laboratory was equipped with only the most basic gear: a p*H* meter, a good viscometer, a balance, a refractometer, hydrometers, stirrers and all the usual glassware, ovens and a waterbath. I improvised a few others like a wetting test. I knew we should have an infrared spectrophotometer, but the management of the time could not be persuaded. Not long after my departure the Health Department virtually forced the purchase of one.

Much more costly and probably overdue, was the more serious attention paid to Codes of Good Manufacturing Practice that resulted in the complete revamp of the whole factory with modern wall and floor coatings, a better layout and greater security against any passing person wandering into the factory. The chemist who succeeded me, and the manager who had followed Ron Learnan did a great job!

All chemists will know how easy it is to waste money and hope that they are not responsible for it. I offer the following tale as a warning to others. It was a very expensive episode for which I was responsible.

We used our colleagues at Biological Laboratories, just up the road from us, for microbiological tests on our products. Being part of the same firm it cost us nothing and saved me a lot of time - not that I wanted to do any microbiology. Most of the work was straightforward and in some cases our overseas principals had supplied methods to be used for their products. The Biolab staff had been very helpful in the work needed for another paper we wrote jointly, and presented to another Cosmetic Chemists Conference. "Preservation of Shampoos".

Unfortunately I did not realise that because of the limited range of products they made, they did not have a graduate microbiologist, and that their knowledge of microbiology was limited in depth compared to that of the staff I worked with at Tasman Vaccine. I knew something of the importance of storage time, multiple challenges with a variety of organisms and neutralising the active ingredient, when a new antiseptic or preservative was under investigation. Regrettably, not enough testing was done when we decided to make a new, emulsified product. The result was that one of the essential emulsifiers, over the course of time, combined with the preservative and consumers had a faulty product containing micro-organisms that while not pathogenic, gave it a rather peculiar odour.

Another lesson I learned from this was that manufacturers' claims should be studied for what they did not say as much as for what they did. For example, an ester which makes a cream or lotion absorb faster on the skin can be highly recommended by its makers but they never tell you anything about the effect on the consistency of the product, nor about how much is too much.

Then there is a well-known antibiotic marketed for many years by a multinational, and heavily promoted in booklets and similar expensive publications. Reading these you can believe that it is the answer to everyone's prayer, but unless you look up all the references they quote, and look carefully at the range of micro-organisms that it is effective against, you can get into big trouble.

The same company markets a cheaper product of the same type, developed some years after the first one when they had discovered which part of the molecule was the active one. However, efforts to get the company to admit that the cheaper product can be used to replace the expensive one always fail.

Another total waste of money, not only in the form of my wages, but also in the large fees paid to consulting analysts (we did not have the necessary, costly, "black boxes" to do the work), occurred over a product development.

I was given a list of active ingredients wanted in two cough syrups and for tablet versions of the same. All I had to do was to find good sources for all the raw materials, formulate the syrups and discuss with a tablet manufacturer what could and should go into the tablets. The tablet maker had once tried to make a syrup and informed me that it was a very difficult task and would take me a long time. However, I formulated the two syrups, he produced hundreds of pills and I set about arranging suitable long term storage tests with the help of the Health Department. An initial set of samples was sent to the analysts, who reported on the content of every active ingredient. At regular intervals another set of samples was sent and finally, after many months, we were able to report to our sales people that we would be able to get Health Department approval. To our chagrin and horror we were told that they no longer wanted the products! How many thousands of dollars were spend on this project were never calculated, but it was many.

I left this exciting but demanding life about the same time as the Health Department was becoming more insistent about protocols, better identification of raw materials and better environments in factories. Because of this, and the demise of import licensing, many one-chemist factories had closed and their products were being imported, often from Australia. The survival of the Smith Biolab factory, trading as Formula Products, is thus a tribute to the abilities and innovative skills of the staff.

Not wanting to abandon work entirely, I found some consulting jobs. It would be too insulting to reveal anything about my sojourn with a chemist who was convinced that only people with PhDs could do really useful work and who had an unfortunate experience as a result. Another strange man was the one who imported lots of shampoos and conditioners from England. He knew that freight on these watery products was costing him plenty, and he didn't have an international brand name as a selling aid, or an extensive advertising budget. The products were good but not outstanding and I found him a local contract manufacturer and said that I would supply all the formulas he needed. What happened? He decided to go on importing!

Looking back on the cosmetic content of my career I realise how lucky I was that most of my time was devoted to work of a chemical, or at least technical nature. For today's chemist I suspect that protocols, recording data and writing up what happened occupies more than he or she really wants. Tough!

This personal account was written at the request of the N.Z. Society of Cosmetic Chemists, and included in their private publication *Cosmetics in New Zealand 1946-1996* published in December 1996. Permission from the Society to reprint it here in edited form is gratefully acknowledged.

About the author

In the course of 50 years, Lester Stonyer has run a paint plant, managed other factories and laboratories, formulated and developed many products from cosmetics to sheep branding fluids, besides analysing these and others like explosives, oils, gelatine and vaccines. He has written articles, protocols, lecture notes and a lot of miscellaneous material – see for example "What is an Industrial Chemist?", *Chemistry in New Zealand,* **1997**, *61*(6), 3-8; **1978**, *42*(3), 108-111; (with I. D. Rae) "New Zealand Chemists in Australia's Munitions Industry in the Second World War" *Historical Records of Australian Science*, Canberra, **1992** *9*(3), 223.

His first job after leaving Timaru Boys High School was as a lab boy in the Davis Gelatine Factory in Christchurch. He fought his way through Canterbury College to a degree and was almost in the Air Force in 1941 when the manufacture of explosives took him to Australia together with 28 other New Zealand chemists. Back in Wellington in 1945 he was with Mobil Oil until 1960, thence to Tasman Vaccine Laboratory's Waikanae subsidiary Premier Products to make paint and some agri-chemicals. A transfer to the main plant in Upper Hutt brought a variety of chemicals and management work, ending in 1980 a short time after ICI bought the company. Moving to Auckland, he mixed consulting with a few years of making cosmetics for Smith Biolab until, 10 years later, the lure of Wellington proved too strong.

Now being seriously retired and living in Paraparaumu, he confines himself to his hobbies, reads books on almost any non-fiction topic that involves technology, occasionally writes to the paper, and gives simple talks to Senior Citizens on Science and Technology.

Research On Advanced Ceramic Materials In New Zealand

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Introduction

At first sight, the existence of a significant research group in Wellington working on the development of advanced ceramic materials may raise a few eyebrows, since New Zealand has a very small technical base, with few manufacturing industries investing in basic research. Yet, over the past decade the Gracefield research group has become internationally renown for its fundamental work on sialon materials (silicon aluminium oxynitrides) leading to the development of a New Zealand export industry. Its research has led to the development of new and improved hard materials (cermets) for agricultural and forestry cutting tools, it has developed electroceramics for use in fish-finding radar and other sensing devices, and has carried out research on dense bioceramic oxides for joint replacements. Scientists of the group collaborate with overseas research institutes such as the German Aerospace Centre and the Tokyo Institute of Technology in basic research on fibre-reinforced metal oxide composites for lining the combustion chambers of gas turbine engines and porous ceramic materials for catalysts and humidity control. In addition, the Gracefield campus is the national focal point for solid state NMR, being home to two solid state spectrometers (including the highest field superconducting NMR magnet in New Zealand, namely 11.7 T), and is an acknowledged centre for the application of NMR to inorganic materials. Research and teaching links with the New Zealand Universities are also an important ingredient for success. Moreover, the recent strengthening of the association between IRL and Victoria University in the area of materials science by the awarding of a Centre of Research Excellence (in Materials Science and Nanotechnology) is both an acknowledgement of this fact and a blueprint for future developments.

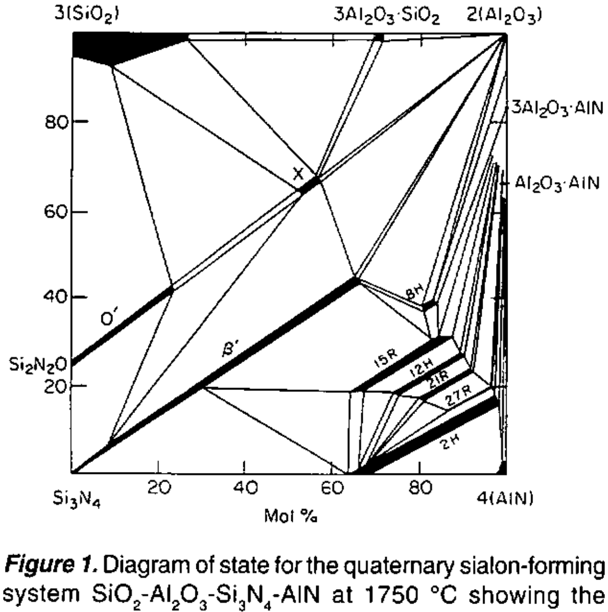


Figure 1. Diagram of state for the quaternary sialon-forming system SiO_2-Al_2O_3-Si_3N_4-AlN at 1750 °C showing the stability fields of the principal compounds β-sialon, O-sialon and X-sialon. The α-sialon phases which contain a third metal fall outside this diagram.

There are several reasons why high-quality basic research is being carried out in New Zealand on advanced ceramics:

i) The work provides essential underpinning for the development of new technologies and products for manufacture, either in New Zealand for use here or for export, or for manufacture overseas under appropriate licensing arrangements. It also has the potential to spin-off small new high-technology companies.

ii) It enables New Zealand technologists and engineers to stay at the forefront of new developments in materials and facilitate their transfer to New Zealand as appropriate.

iii) It allows us to train and maintain the expertise of a pool of scientists, engineers and technologists experienced in developing, manufacturing and handling new-generation materials.

iv) It raises the profile of NZ ceramics research internationally, and provides us with access to a greatly expanded range of expertise, new ideas and potential new products.

In order to be a fully functioning member of an international research team, we need to be able to contribute expertise not readily available elsewhere. Many of our successful collaborative projects have involved the application of multinuclear solid state NMR to fundamental research on ceramic systems,[1,2] including sialons, ceramics synthesised by sol-gel or mechanochemical processes, inorganic geopolymers, fibre-reinforced composites and porous ceramics. This paper briefly describes recent work in some of these internationally recognised areas.

Sialon ceramics

Sialons (silicon aluminium oxynitrides) can be prepared with a range of compositions, crystal structures, and physical properties, making it possible to tailor the material to conform closely to the requirements of a particular application. The diagram of state for the quaternary system SiO_2-Al_2O_3-Si_3N_4-AlN (Figure 1) shows the stability fields for some of the most important structural types; β-sialon is isomorphous with β-Si_3N_4, O-sialon with Si_2N_2O, and X-sialon with mullite ($Al_6Si_2O_{13}$). The formula of β-sialon is $Si_{6-z}Al_zO_zN_{8-z}$, where z is 0 (pure Si_3N_4) to 4.3. O-sialon is $Si_{2-x}Al_xO_{1-x}N_{2-x}$, where x is 0 (pure Si_2N_2O) to 0.4. X-sialon has the nominal formula $Si_{12}Al_{18}O_{39}N_8$.

Although not shown in Figure 1, the area in the top left-hand corner of the diagram contains a region of glass-forming compositions while the bottom right-hand corner contains a series of polytypoid sialons isostructural with AlN. The addition of alkaline and rare earth oxides stabilises a further series of sialons isostructural with α-Si_3N_4. Some sialons, especially α-sialon, have extremely high fracture toughness, making them superbly suitable as high-speed cutting and machining tools. Others, *e.g.*, β-sialon, are particularly suited to being formed into intricate shapes, allowing them to be used for engine parts such as turbocharger rotors or formed into light and porous but strong components suitable as biomedical implants. Others still, *e.g.*, O-sialon, which show superior resistance to oxidation and attack by molten metals find application as refractories in metal smelting operations.

Of the various methods available for synthesising sialons, one of the most versatile is carbothermal reduction/nitridation (CRN), in which a highly pure clay such as New Zealand halloysite is mixed with finely divided carbon and heated at >1400 °C in an atmosphere of purified nitrogen:

$$\underset{\text{kaolinite}}{3Al_2Si_2O_5(OH)_4} + 15C + 5N_2 \rightarrow \underset{\beta\text{-sialon }(z = 3)}{2Si_3Al_3N_5} + 6H_2O\uparrow + 15CO\uparrow \quad (1)$$

The composition of the product depends on the Si:Al ratio of the original clay, but can be modified by the addition of SiO_2 or Al_2O_3. This is important in the tailoring of sialon ceramics to specific applications, since sialons with high z values are more easily sintered, whereas sialons of low z have higher fracture toughness. Since the CRN reaction is particularly appropriate to the New Zealand situation, we have extensively studied it using a variety of techniques including solid-state ^{27}Al and ^{29}Si NMR to establish the fundamental chemistry, physics and thermodynamics[3-6] necessary for scaling-up the process. Factors to be taken into consideration in scaling-up include uniformity of mixing the solid components, the effect of heat transfer and thermal gradients in the furnace, uniformity of gas distribution to the reactants, and the effect of gas flow rate on the removal of CO and SiO species. Typical of the problems encountered with such solid-gas sialon synthesis is the vapour-phase formation of an amorphous wool-like material which is removed from the reacting mass and re-deposited in the cooler parts of the furnace (Figure 2). This was found by NMR to be a mixture of SiC, SiO_2 and elemental Si (the latter two species resulting from the disproportionation of gaseous SiO), together with a potassium feldspar formed from the small amount of impurity K in the clay, concentrated in the vapour phase.[7] These findings were verified by an analysis of the process thermodynamics.

During the course of our CRN research, an alternative synthesis route was developed, using elemental Si powder instead of C as the reducing agent.[8-9] The silicothermal process was found to be particularly appropriate for the synthesis of X-sialon and the silica-rich compound O-sialon:

$$\underset{\text{kaolinite}}{3Al_2Si_2O_5(OH)_4} + 6Al_2O_3 + 6Si + 4N_2 \rightarrow \underset{\text{X-sialon}}{Si_{12}Al_{18}O_{39}N_8} + 6H_2O\uparrow \quad (2)$$

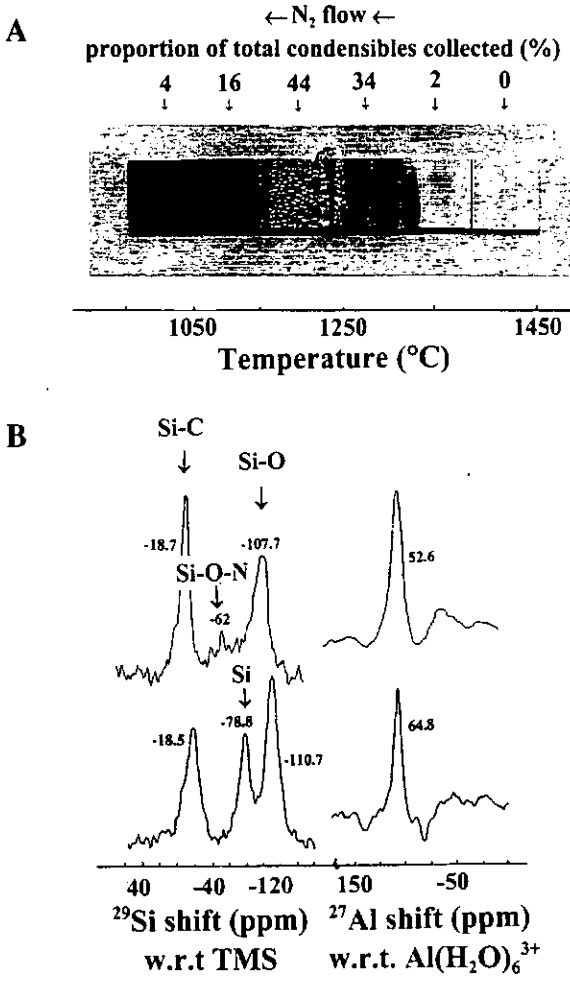
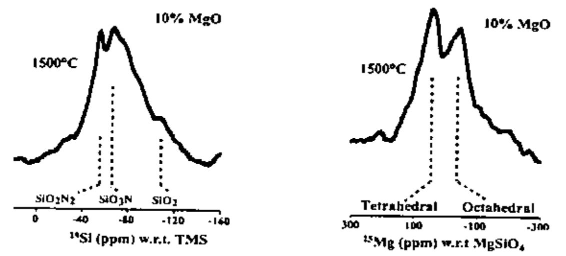


Figure 2. **A)** A sequence of alumina plates placed in the cooler part of the furnace temperature gradient downstream of a carbothermal sialon synthesis experiment, showing the proportion of material deposited from the vapour phase as a function of distance from the hot zone. **B)** ^{29}Si and ^{27}Al solid state magic angle spinning (MAS) NMR spectra of the amorphous vapour-phase deposits showing the various Si-containing species present. The ^{27}Al spectra are characteristic of tetrahedral Al in a feldspar-like matrix. Taken from ref. 7.

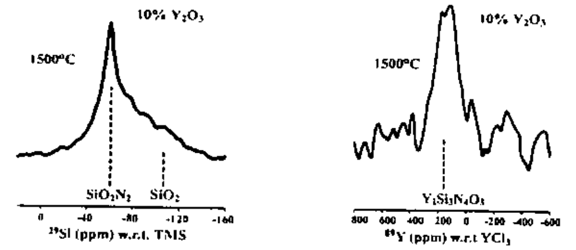
The addition of various metal oxides was found to influence the course of this reaction, MgO and Y_2O_3 being particularly beneficial. Both these cations (and Si) could be studied by solid state NMR,[10-12] which indicated differences in the constituent silicon oxynitride units, and revealed the presence of amorphous or glassy oxynitride phases responsible for the enhancing effect of these oxides (Figure 3).

The fabrication of practical components from sialon powder involves shaping by pressing or slip-casting, followed by sintering at typically 1500-1750 °C to form a hard, dense material. The latter step is difficult since the sialon system at high temperatures does not readily form a molten phase through which material transport can occur. Some of our research has focussed on the addition of various metal oxides to assist sintering by forming such intergranular phases.[10-12] As was found for silicothermal synthesis of X-sialon (above), the oxides of yttrium and magnesium were found to exert the most beneficial effect on its sintering at 1500 °C (Figure 4). Cerium oxide was also found to be an effective sintering agent for this sialon.



^{29}Si spectrum at 1500°C is typical of X-sialon but with more SiO_2N_2 structural units.

At 1500°C the Mg is in both octahedral and tetrahedral sites. The glassy phase formed probably contains nitrogen.



The product is rich in SiO_2N_2 units, which are structural units of both X-sialon and N-melilite ($Y_2Si_3O_3N_4$).

The main peak is in the region charactistic of N-melilite.

The broad spectrum suggests the yttrium is in an amorphous oxyynitride phase.

Figure 3. A selection of solid-state MAS NMR spectra of X-sialon prepared at 1500 °C by silicothermal synthesis in the presence of 10 mass % MgO (upper spectra) and Y_2O_3 (lower spectra). The ^{29}Si spectra provide an indication of the principal Si-O-N units present, while the ^{25}Mg and ^{89}Y spectra are typical of amorphous or glassy compounds, suggesting that X-phase formation is enhanced at 1500 °C by improved diffusion and mass transport through the molten Mg- or Y-containing phases. Adapted from ref. 12.

Our exploitation of silicothermal synthesis for the production of O-sialon, has led to the development of composites of O-sialon with silicon carbide.[13] These materials have proved to be particularly resistant to attack by molten metals such as aluminium and its alloys, and commercial production has now begun in New Zealand of specialised refractories in a variety of complex shapes for aluminium smelting, utilising our silicothermal process.

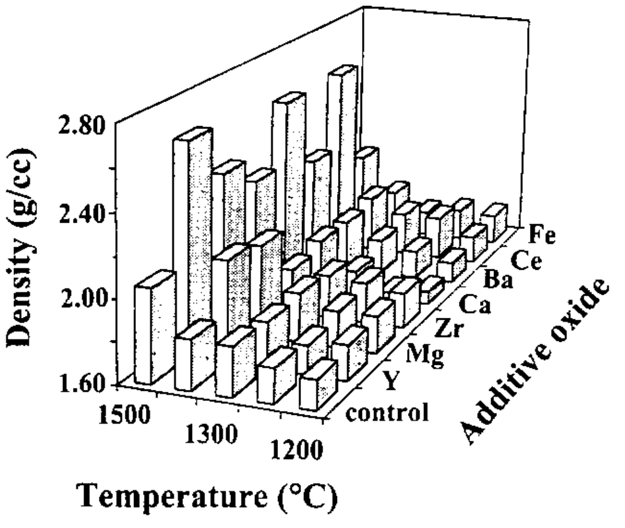


Figure 4. Bulk density of X-sialon pellets sintered with 3 mass % of various metal oxide additives as a function of sintering temperature. Taken from ref. 11.

An interesting spin-off from the silicothermal synthesis work was the discovery of a new form of sialon, shown by solid-state NMR to be a previously unknown low-temperature form of O-sialon[14] (Figure 5). Subsequent electron microscope studies confirmed the identity of this phase and established its structural relationship with the high-temperature form of O-sialon (Figure 5).[15,16]

Since the production of sialon ceramics is a high-temperature energy-intensive process, developments which lower the processing temperature are being actively researched. One such possibility investigated in collaboration with researchers from the University of Hokkaido is the use of fluoride additives to lower the sintering temperature.[17] Another interesting project currently in progress is the use of mechanochemical processing (high-energy grinding) to homogenise the starting materials and lower the subsequent synthesis temperature. The results so far, obtained in collaboration with the Tokyo Institute of Technology and the University of Warwick, have shown that grinding promotes the formation of sialons at temperatures well below those required for reaction in unground reactant mixtures (Figure 6), in some cases causing reactions to occur which otherwise would not have occurred under these conditions.[18]

A drawback to the use of sialon ceramics is their tendency to oxidise in air at elevated temperatures. In collaboration with the Institute of Geological and Nuclear Sciences, the surface oxidation processes of sialons have been studied by advanced techniques such as Particle Induced X-ray Emission (PIXE), Particle Induced Gamma Emission (PIGE), Rutherford Backscattering Spectrometry (RBS) and Nuclear Radiation Analysis,[19-21] as well as solid state

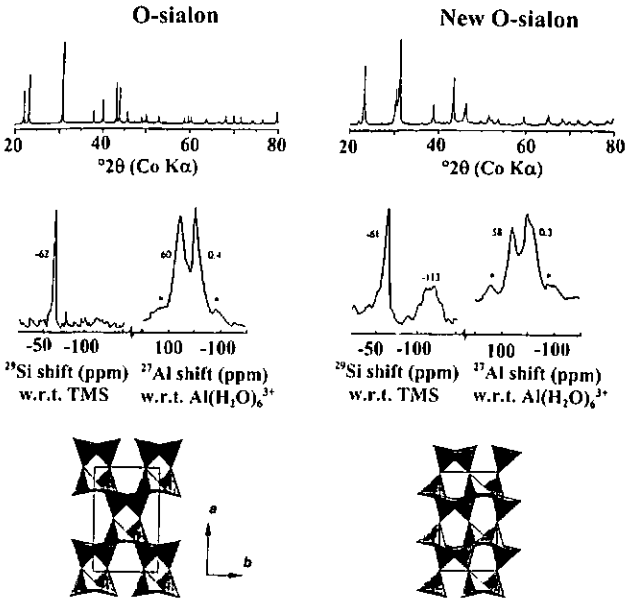


Figure 5. X-ray diffractograms and ^{29}Si and ^{27}Al MAS NMR spectra of O-sialon and an newly-discovered low-temperature form. Although the XRD powder patterns (upper) are significantly different, the NMR spectra (centre) indicate that both forms contain Si-O-N units (–62 ppm in the ^{29}Si spectra) and similar tetrahedral and octahedral ^{27}Al spectra, in which the peaks marked with asterisks are spinning side bands. The broad feature at –113 ppm in the ^{29}Si spectrum indicates the presence of free silica. The structural relationship of the two forms is shown above. Adapted from ref. 15

NMR.[22] PIXE provides surface analyses of Si, Al and Y to a depth of about 3 mm, while PIGE gives analyses of ^{16}O and ^{14}N to approximately the same depth. RBA was used to determine detailed depth profiles of Y, Si, Al and O in the outer micron or so of the sample, and NRA provided the same information for ^{14}N, using the ^{14}N (d,α_1) reaction (Figure 7). The results indicate that the oxidation process in X-sialon and α-sialon is controlled by oxygen diffusion up to 1280 °C, but in O-sialon, diffusion is the rate-controlling step up to 1450 °C. NMR studies of changes in the bulk composition of the sialon confirm that O-sialon is significantly more resistant to oxidation than X-sialon or β-sialon.[22] A combination of solid-state NMR, thermogravimetry and electron microscopy has also been used to determine the bulk oxidation mechanism, kinetics and activation energies of the various sialon types in both powder and sintered compacts (Figure 8), and in humid atmospheres.[23-26]

Ceramics produced by sol-gel processes

A key strategy in designing energy-efficient processes for producing advanced ceramic materials is the use of homogeneous precursors in which the atoms are intimately mixed on an atomic scale. Such precursors often transform to the desired monophase crystalline products at temperatures several hundreds of degrees lower than in mixtures of the discrete reactant powders. Since the gel precursors are usually X-ray amorphous, solid-state NMR is the technique of choice for studying the thermal transformation mechanisms of such materials. In conjunction with the German Aerospace Centre, we have studied the formation of the important engineering aluminosilicate mullite ($Al_6Si_2O_{13}$) from precursor gels.[27,28]

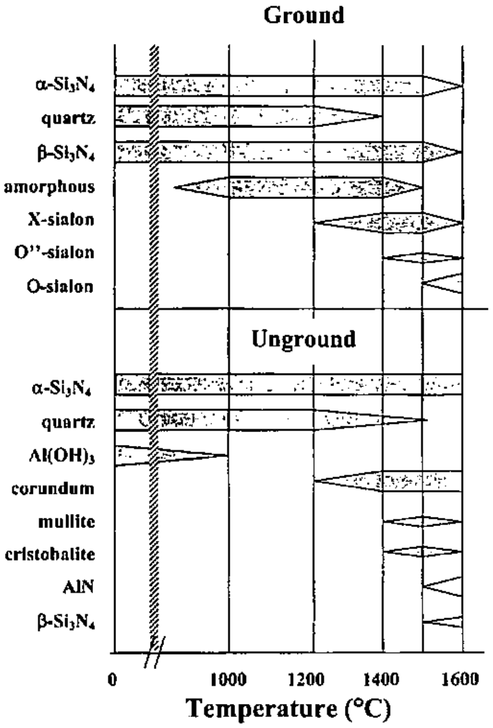


Figure 6. Semi-schematic representation of the effect of mechanochemical treatment (high-energy grinding) on phase formation in a mixture of SiO_2 (quartz), Si_3N_4 and Al_2O_3 of O-sialon composition, as a function of post-grinding heating temperature in flowing nitrogen. Note the formation of sialon products in the ground mixture but not in the unground control. Taken from ref. 18.

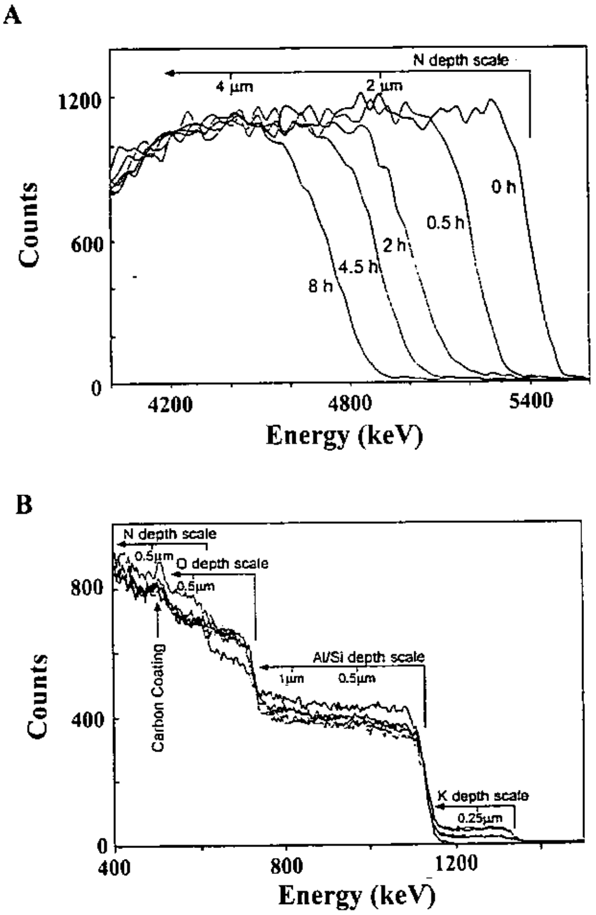


Figure 7. A) ^{14}N(d,a$_1$) nuclear reaction analysis (NRA) profiles of O-sialon samples oxidised at 1400 °C for varying times. The sample is irradiated with a deuteron beam, and the energy of the α-particles emitted as a result of interaction with the N atoms depends upon their depth thereby providing nitrogen depth profiling information. B) Rutherford backscattering (RBS) profiles of O-sialon samples oxidised at 1400 °C for varying times. The energies of $^4He^+$ particles elastically scattered off the sample nuclei depend on the mass and depth of the target nuclei, providing both compositional and depth profile information.

MAS NMR of ^{27}Al has been used to monitor the way in which the aluminium environment of the gel changes during its thermal transformation to crystalline mullite (Figure 9A).

Since these are hybrid gels made from a combination of organic and inorganic reagents, elimination of the organic by-products is an important feature of the thermal treatment, and has been studied by dynamic mass spectroscopy of the evolved gaseous products (Figure 9B) to allow the firing conditions to be optimised.

Mullite is a promising candidate material for components to be used in a new generation of economic and ecological aircraft gas turbine engines. With the aim of reducing the fuel consumption, NO_x emissions, weight, and noise of these engines, ceramic components for use as combustion chamber shingles, liners and diffuser rings are contemplated (Figure 10A).

The most important properties of these materials are oxidation resistance for >10,000 hours, high thermal stability and thermal shock resistance, good mechanical stability and strength, good damage tolerant fracture

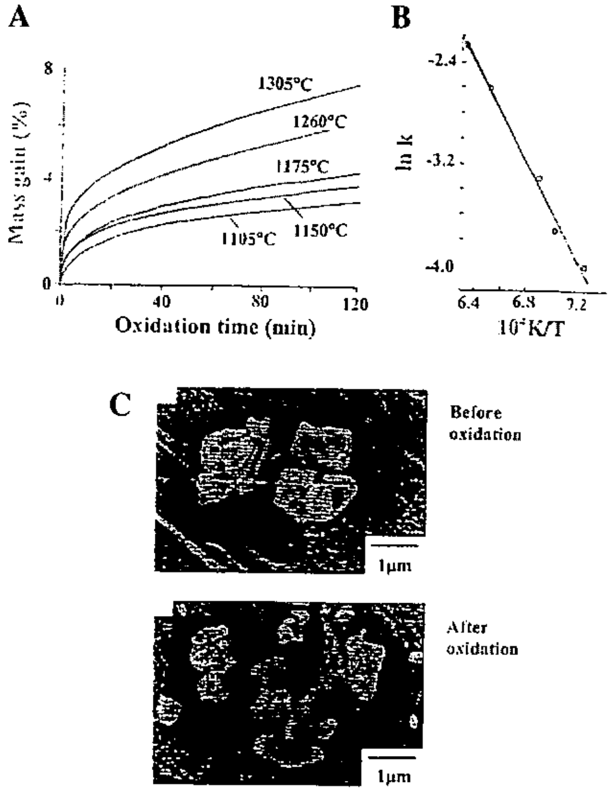


Figure 8. A) Mass-gain kinetic curves for the oxidation of carbothermal β-sialon powder, leading to the Arrhenius plot shown in B. C) Scanning electron micrographs of the β-sialon particles before and after oxidation at 1000 °C. Adapted from refs. 23 and 24.

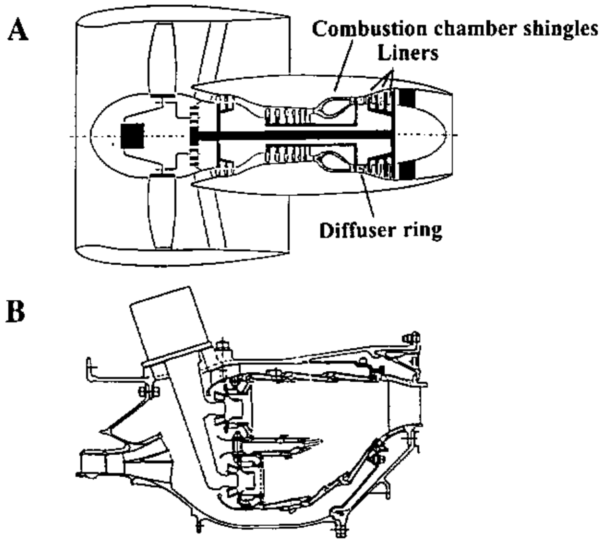


Figure 10. A) Schematic diagram of an aero gas turbine engine showing the combustion chamber shingles, diffuser and liners which could be made from mullite fibre-reinforced composites. B) Diagram of a current aircraft turbofan engine design. The combustion areas shaded in grey could be lined with an advanced ceramic material to improve performance.

behaviour, and the ability to be fabricated in complex shapes. The thermal shock resistance of mullite combustion chamber liners of gas turbine aero engines operating at temperatures up to 1400 °C (Figure 10B) must be sufficient to withstand rapid heat-up and cool-down conditions. These can be achieved by reinforcing the mullite ceramic with mullite fibres, which must, however, be prevented from bonding to the mullite matrix.[29]

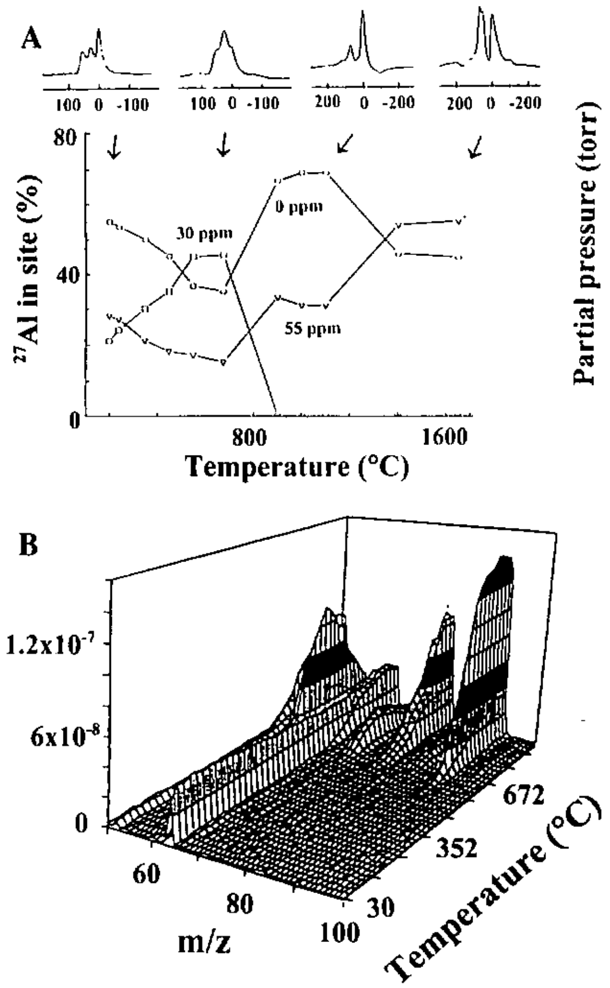
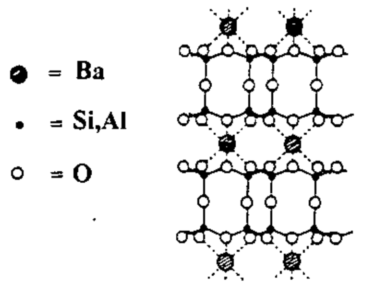


Figure 9. A) Changes in the ^{27}Al MAS NMR spectra (upper) of mullite precursor gels during thermal conversion to crystalline mullite. The spectra provide information (lower) about changes with heating temperature in the relative numbers of tetrahedral and octahedral Al atoms (the peaks at 55 and 0 ppm, respectively) and of a purported 5-coordinated Al-O species at 30 ppm. B) Dynamic mass spectroscopic analysis of the gaseous species evolved during heating of a hybrid (organic/inorganic) mullite precursor gel. The organic species of *m/z* 56-58 and 90-93 (hexane-heptane and substituted benzenes, respectively) are unexpectedly thermally stable and may have formed catalytically during the long period of thermal pretreatment at 350 °C applied to this gel. Taken from ref. 27.

As part of this project, we have used solid-state NMR to investigate the sol-gel production of several possible fibre coating materials including celsian ($BaAl_2Si_2O_8$)[30], yttrium aluminium garnet ($Y_3Al_5O_{12}$),[31] lanthanum hexaluminate ($LaAl_{11}O_{18}$)[32] and calcium hexaluminate ($CaAl_{12}O_{19}$)[33] (Figure 11). These studies have provided interesting insights into the formation and thermal behaviour of a purported pentacoordinated Al-O species, assisted by collaboration with the NMR laboratories at the Universities of Oxford and Exeter in an in-depth study using newly-developed multiple-quantum and cross-polarisation NMR techniques to determine the Al environment in these species (Figure 12).[34]

In addition to conventional aluminosilicate mullite, interest is growing in a little-known class of aluminate materials with the crystal structure of mullite but which do not contain Si. With colleagues at the Estonian Academy of Sciences (at Tallinn) and the University of Warwick, we have made double rotation NMR measurements at several magnetic fields to determine the details of the structural sites of the Al and Na atoms[35] in the mullite-structured compound $NaAl_9O_{14}$ (Figure 13), and we are currently studying a series of aluminium borates with similar mullite structures. Double rotation NMR (DOR) is a method for removing the quadrupolar broadening and improving the resolution of an NMR spectrum by spinning the sample about two axes simultaneously.[2]

A. Celsian



B. Lanthanum hexaluminate

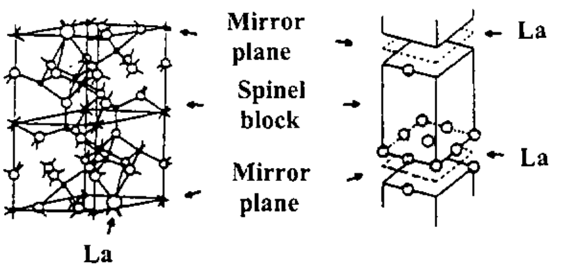


Figure 11. Crystal structures of two compounds investigated for their potential use as fibre coatings to prevent fibre bonding in fibre-reinforced mullite composites. A) Celsian (a feldspar) undergoes a polymorphic phase change at 300 °C with an associated volume change leading to mechanical instability on thermal recycling which would minimise interfacial bonding and facilitate fibre pull-out. B) Lanthanum hexaluminate contains blocks of spinel structure separated by mirror planes containing the La atoms, along which cleavage readily occurs. Taken from ref. 29.

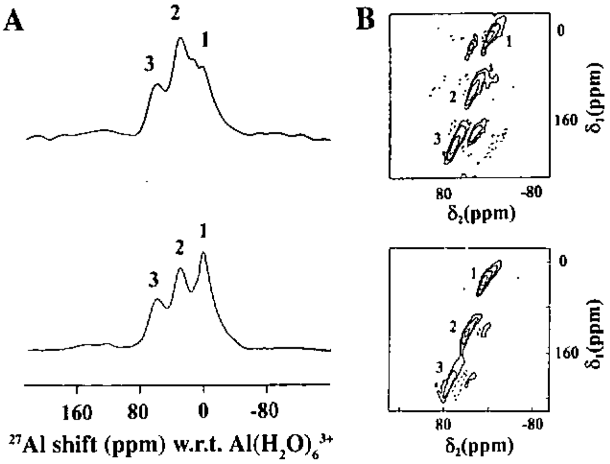


Figure 12. A) ^{27}Al MAS NMR spectra of mullite precursors derived by sol-gel methods. Note the outermost tetrahedral and octahedral peaks enclosing the central peak ascribed to either 5-coordinated Al-O species or distorted tetrahedral Al-O tricluster units. B) The corresponding 2-dimensional multiple quantum NMR spectra, showing the improved resolution of these three sites by this method. Adapted from ref. 34.

Inorganic geopolymers

By their nature, ceramic materials require heat energy in their production, but the ultimate energy-efficient eco-friendly ceramic would be produced at room temperature. Such materials have recently become a reality with the development of inorganic geopolymers, which, although formed and hardened at room temperature, possess all the characteristic properties of ceramics *viz.* durability, physical and chemical stability at high temperatures. These properties may find applications ranging from large prefabricated building panels and heat-resistant insulation for electrical wiring looms used in the automotive and aerospace industries to materials for immobilising toxic chemical waste or radioactive waste in storage.

We have worked on the development of three-dimensional aluminosilicate geopolymers based on sialate, sialate-siloxo or sialate-disiloxo structural units:

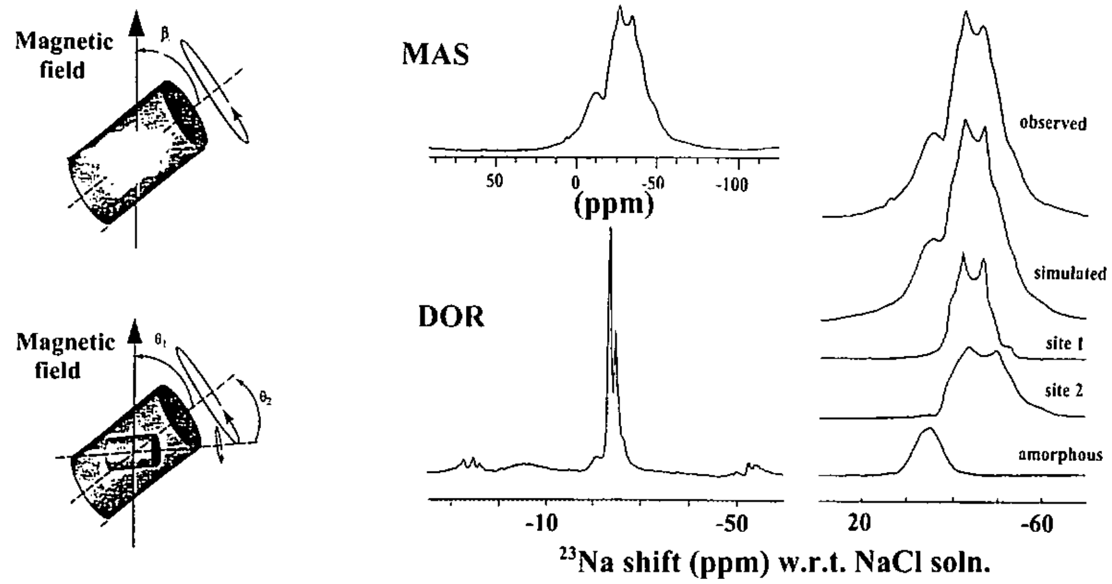


Figure 13. Comparison between the conventional ^{23}Na MAS NMR spectra of mullite-structured $NaAl_9O_{14}$ and the corresponding double rotation (DOR) spectrum. The improved resolution of the DOR spectrum reveals the unexpected presence of two Na sites in the structure and allows the simulation of the MAS NMR lineshape (right). Adapted from ref. 35.

(-Si-O-Al-O-)$^-$M$^+$ sialate
O O

(-Si-O-Al-O-Si-O-)$^-$M$^+$ sialate-siloxo
O O O

(-Si-O-Al-O-Si-O-Si-O-)$^-$M$^+$ sialate-disiloxo
O O O O

These units can be formed from a reactive aluminosilicate such as dehydroxylated kaolinite and are condensed with sodium silicate at the appropriate stoichiometry under highly alkaline conditions to give chain or ring polymeric structures. Solution NMR has been used to monitor the polymerisation process, which was found to depend critically on the water content.[36] These geopolymers remain essentially X-ray amorphous up to their melting point, as high as 1400 °C in some cases, but solid-state NMR has revealed a framework structure of tetrahedral Si and Al, with charge balance provided by the alkali metal ions (Figure 14).[36] These geopolymers also have proved to be suitable matrix materials for composites containing ceramic powders such as alumina, silica, mullite, β-sialon, ironsand, and typical waste materials such as crushed rock or crushed demolition brick (Table 1). In some cases the addition of ceramic fillers does not affect the strength of the composite too adversely (Table 1), and it can reduce the tendency of the polymer to crack during curing or drying. The addition of a small amount of glycol similarly was found to reduce microcracking.

Porous ceramics

Layer-lattice clay minerals such as kaolinite have structures consisting of alternating tetrahedral Si-O and octahedral Al-O sheets. This inherent structural architecture can be exploited to produce materials with tightly constrained pore size and shape, by selectively leaching out either the silicon or the aluminium, under conditions that leave the layer structure intact.[37-40] Working in collaboration with the Tokyo Institute of Technology, we have used solid state NMR to study the structure and porous properties of the silicas obtained by acid leaching a number of different layer-lattice clay minerals (Figure 15). Silica produced in this way from kaolinite was found to contain very small slit-shaped micropores with a radius of 0.6 nm and hydrophilic surface properties,[41] unlike zeolites which have cylindrical pores with either hydrophilic or hydrophobic surface properties. Leaching with KOH solution under controlled conditions removes the silica component from the clay, leaving an intact γ-alumina structure with a narrow unimodal pore radius distribution of 2-3 nm of potential use as a catalyst support for the Claus Process, in petroleum refining, or in automobile catalytic converters. The spent leaching solution may also be put to good use, since amorphous potassium aluminosilicate may be precipitated from it.[42] This material has a potential application as a cation exchanger with excellent ammonia adsorption properties. Composites can also be formed between γ-alumina and the amorphous potassium aluminosilicate, with the interesting ability to simultaneously exchange both cations and anions, making them potentially useful materials for treating waste water by removing the two most common pollutants, ammonium and phosphate ions.[43]

Table 1. Physical properties of polysialate-siloxo geopolymer containing 50 mass% of inorganic filler.

Geopolymer composite filler (Mpa)	Density (g/cm^3)	Compressive strength
unfilled	1.40	54
crushed brick	1.65	19
crushed stone	1.62	26
kaolinite	1.62	30
ironsand	2.06	21
corundum	1.90	8
β-sialon	1.79	15

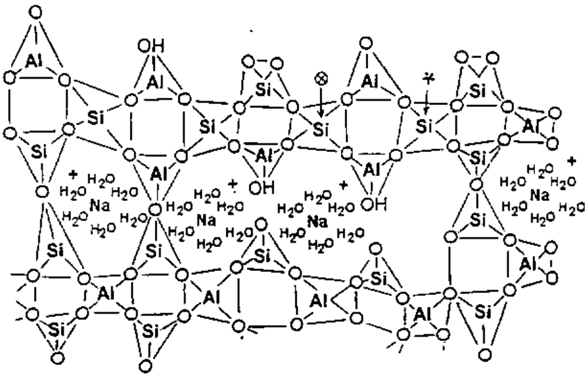


Figure 14. Possible structure of the sodium sialate-siloxo geopolymer suggested by its ^{27}Al, ^{29}Si and ^{23}Na solid-state NMR spectra. Taken from ref. 36.

Conclusions

Despite the small size of New Zealand's technology base and its limited resources for materials research, these examples serve to illustrate the active and ongoing participation by the Gracefield ceramics group of Industrial Research Limited in fundamental research on a wide range of potentially useful materials. Two of the keys to this success lie in our ability to augment our own expertise and facilities by collaboration (to mutual advantage) in the fundamental research of a number of overseas laboratories, and a willingness to make a unique contribution to these collaborations, especially in the areas of our own considerable experience such as solid state NMR. If we maintain these associations and seek to develop new links appropriate to our research directions, we will continue to be in the forefront of new developments in advanced ceramics, to the ultimate benefit of New Zealand.

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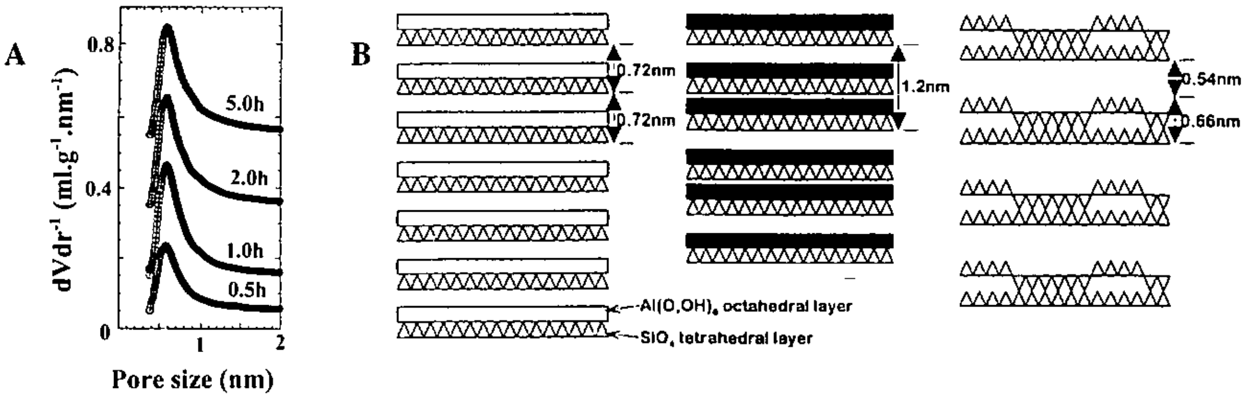

Figure 15. A) Pore size distribution derived from the argon adsorption-desorption isotherms of silica derived from dehydroxylated kaolinite (metakaolinite) by selective acid leaching for the indicated times. Note the sharp pore size distribution of about 6 nm. B) Schematic model for the development of microporous silica from metakaolinite by selective acid leaching. Taken from ref. 41.

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Crystals Great And Small

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"All crystals great and small" (to parody a well-known hymn line) have provided crystallographers with both physical beauty and intellectual satisfaction for centuries. At the turn of the 20th century, Roentgen (1901), followed by Laue (1914) and the Braggs (1915) developed new diagnostic tools for the chemist based on X-ray diffraction, earning Nobel Prizes for their discoveries in the years shown. Since then there have been many other notable advances in the techniques some recognized, *e.g.* Hauptman & Karle (Nobel Prize 1985), and some much utilized, *e.g.* Patterson, of the Patterson method. From today's viewpoint it is clear that many projects at Industrial Research Limited (IRL) depend on these tools to elucidate both chemical properties and structural information essential to the commercial development of new materials and processes.

Although the underpinning laws of diffraction may be unchanged, advances in the power and resolution of both X-ray sources and detectors over the last 5-15 years, coupled with the automation and development of new algorithms, means that a much wider variety of chemical structure and analysis problems can be now be tackled. The topics in this article, chosen to illustrate these advances,[1] are taken from recent research and development programmes based at IRL, Wellington.

Crystals unstable in air

A series of titanium complexes have been prepared by Dr Tim Kemmitt's group incorporating a tridentate *N*-methyldiethoxoamine (MDEA) ligand with chelating diolate ligands as part of their program to develop new precursor compounds and study their Metal Organic Chemical Vapour Deposition (MOCVD) properties. All these compounds are unstable in moist air, many hydrolyzing rapidly from solids into a sticky pool of liquid. Fortunately, collection of data under a cold stream from the boil-off of liquid nitrogen allows good diffraction data to be collected. Indeed, the collection of data at low temperature has become standard practice in recent years with both increased intensity and lower vibrational parameters expected, let alone if the conditions are a requirement to prevent decomposition as in this case!

Four complexes: $Ti(MDEA)(O\text{-}O)]_2$
where O-O = $OC(CH_3)_2C(CH_3)_2O$, **1**
$OC(C_2H_5)_2C(C_2H_5)_2O$, **2**
$OC(CH_3)_2CH_2CH(CH_3)O$, **3**
$OC(CH_3)_2CH_2C(CH_3)_2O$, **4**

were shown to exist as dimers in the solid state. However, in the vapour phase complexes **3** and **4** dissociate into monomers. The X-ray crystal structure of **1** (Figure 1) shows the dimeric structures, with one arm of the aminodialkoxy ligand μ-bridging two titanium centers. Further characterization by variable temperature ^1H and ^{13}C NMR spectroscopy, thermogravimetric and differential thermal analyses, and high temperature mass spectrometry was carried out, giving additional information on the structural behaviors in solid, solution and gaseous phases.

The Ti-O (non-bridging) bonds range from 1.824(2)-1.877(3) Å. The bridging oxygen of the MDEA ligand is asymmetrically bound to the two titanium atoms (averages 1.998, 2.103 Å). A survey of six-coordinate oxygen-bridged titanium compounds of this type (26 hits[1c]) shows this to be consistent with previous observations. The asymmetry has been related to the relative influence of the *trans* alkoxide ligands in a series of β-diketonate complexes.[2,3] In the current case, constraints provided by the chelating tri-dentate MDEA ligand possibly have a larger influence on the asymmetry, where the length of one side of the bridge is restricted by the chelate ring. Across the series **1** – **4**, the Ti – Ti bond distance increases from 3.295(1) to 3.382(5) Å, while the average Ti-O bridging bond length increases from 2.030(2) to 2.066(5) Å. Clearly, the complexes with the longer bridging bonds more readily dissociate in the vapour phase.[4]

Unraveling disordered materials / crystallite diffraction using synchrotron radiation

Organic molecules that give rise to large second-order non-linear figures of merit (μ-β) consist of electron donor and acceptor groups that flank a π-conjugating bridge.[5] Several organic chromophores with potential as 'right-hand side' non-linear optical (NLO) compounds have been prepared by Dr Tony Woolhouse's team at IRL and studied by X-ray diffraction in order to determine both conformational and the extent of bond length alternation (bla).[6] The basic requirement of this class of molecule is that they be polarisable in an asymmetric (non-linear) manner, a condition that is met in molecules that contain conjugating π-electron bridges that are flanked by donor and acceptor functionalities (D-π-A). One of the compounds studied crystallized in multiple and highly twinned blocks as the iodide salt with formula $C_{23}H_{27}N_2O_2I$. From a close inspection of the reciprocal lattice plots, *i.e.* the observed diffraction, measured on a CCD detector using the advanced programs RLATT & GEMINI[7] at the University of Canterbury Crystallography Laboratory, a unit cell and dataset was extracted from data collected at 168 K of a crystal about 0.4 mm in size. This led to a poorly resolved structural solution confirming the chemical makeup but not giving sufficient resolution for further study - the conventional *R* factor[8] was 27%.

The crystal batch from which this multiple "crystal" was mounted was then shown by X-ray powder diffraction at IRL Gracefield laboratory to contain at least two crystal forms. It was thought that the other phase(s) were crystal forms with different amounts of water of crystallization. Some careful crystallization confirmed the phase identified in the abnormally-twinned crystal studied was the target NLO material. At this point, the project stalled since the crystallites of "almost pure" phase were too small to give sufficient observed diffraction from standard laboratory X-ray generators.

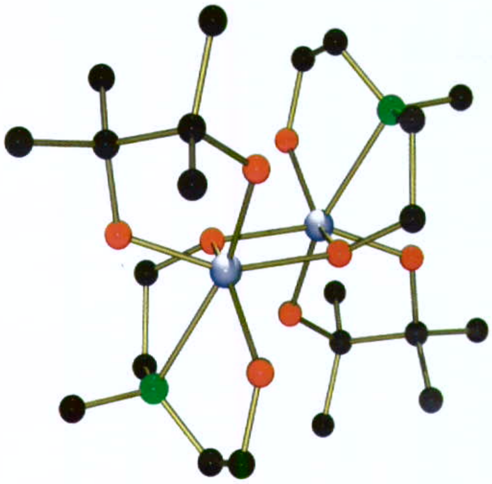

Figure 1. [Ti(MDEA)(OC(CH_3)$_2$C(CH_3)$_2$O)]$_2$ centrosymmetric dimmer (see refs. 1a and 1b). Hydrogen atoms have been excluded for clarity. Atom colours (arbitrary radii) in order of increasing darkness are Ti, N, O, and C.

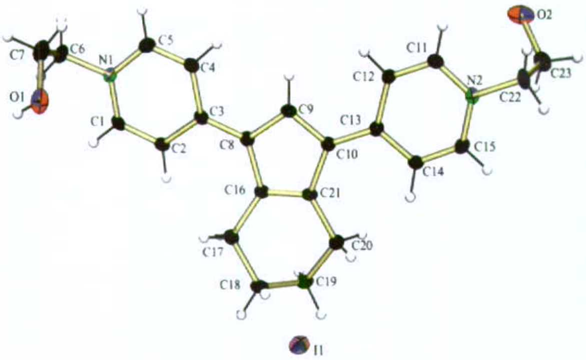

Figure 2. $C_{23}H_{27}N_2O_2I$ asymmetric unit cell content (see refs. 1a and 1b).

Fortunately, the author was able to obtain some time on the National Synchrotron Light Source's (NSLS's) X9B beam line while at the Brookhaven National Laboratory (BNL). A small plate fragment, about 0.15 x 0.10 x 0.003 mm, was mounted using "protein-loop" technology and diffraction data collected at wavelength 0.92 Å and 100 K. The resultant structure now was completely resolved (Figure 2) with no partial ordering of the saturated six-membered ring and gave a final *R* factor on all data of 2.6%. Figure 3 illustrates how the molecules are packed in the cell where there are hydrogen bonds linking the end hydroxyl units at each end to the two iodide anions.

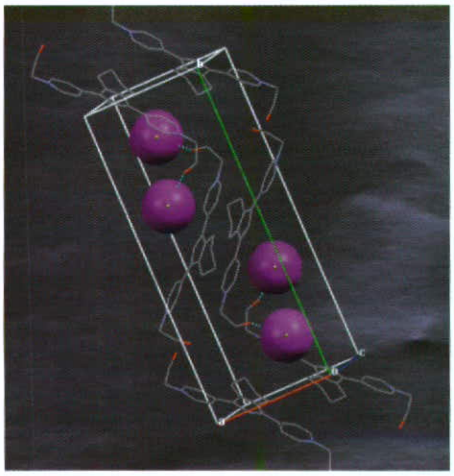

Figure 3. Unit cell packing (see ref. 1d) of the $(C_{23}H_{27}N_2O_2)^+I^-$ molecules with iodide anions shown as balls, hydrogens omitted and the O-H…I hydrogen bonds dotted

When do crystals become "crystalline" powders (the power of synchrotron radiation!)?

The development of new antibiotics is essential for continued human and animal health. A class of carbohydrate-based enzyme inhibitors[9] called Immucillins have been generated through collaborative research between IRL and the Albert Einstein College of Medicine (AECoM, Yeshiva University, New York). These interact strongly with *N*-ribosyl transferases and have potential as anticancer agents, antiparasitics, and as agents to ameliorate autoimmune disorders. Human clinical trials of one of these, Immucillin-H, for T-cell leukaemia treatment have begun in the USA under the stringent FDA regulations.

Transition state analysis of mammalian purine nucleoside phosphorylases (PNPs) at the AECoM by Professor Vern Schramm's group led to the design of five carbohydrate-based molecules inhibitors (Immucillins), which were synthesized at IRL by members of Dr Richard Furneaux's team and evaluated at AECoM. With dissociation constants at the 20 to 100-pM range, these are the five most powerful inhibitors known for human and malarial PNPs. Even at these extraordinarily low concentrations binding of the Immucillins has been shown to cause considerable unpredicted structural changes (folding) in bovine PNP. Identification of numerous transition state inhibitors supports the transition state stabilization hypothesis for enzymatic catalysis. Thus, by examining the structure of different Immucillins, and then determining the structural changes that occur when they are bound to their target enzymes in combination with advanced computational analysis of the free and bound molecules,[10] it is hoped to be able to explain both the selectivity and strength of the Immucillin-enzyme interactions.

Unfortunately, the Immucillins usually crystallize as powders or as very thin, often twinned needles. Diffraction data has been collected from one of these larger needles and a unique dataset from one of the twins isolated.[11] In a recent International Science and Technology Linkages Fund (ISAT)/BNL/IRL sponsored trip,[12] data was collected on a "nearly invisible" crystallite, after several "large needles" (0.25 x 0.2 x 0.05 mm) had been shown to be twins. One of the BNL NSLS division staff, Dr K R Rajashanka, mounted a crystal 0.075 x 0.063 x 0.005 mm and a triclinic dataset was collected.

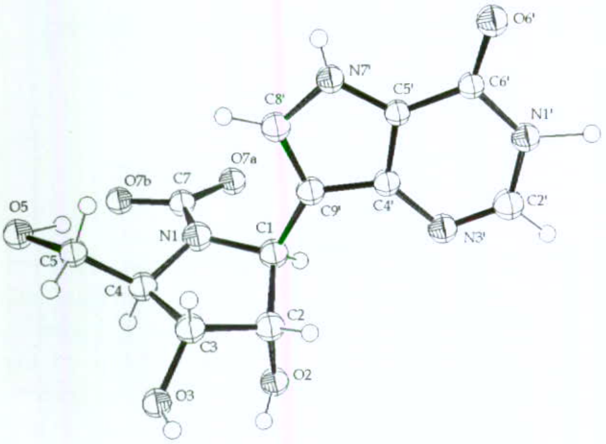

Figure 4. One of the two independent Immucillin-H anions (see ref. 1a).

As the sample was enantiomerically pure, the space group had to be the less usual noncentrosymmetric triclinic P1 with two independent molecules - structural solution was therefore also not easy! A partial structure was identified from one of the maps produced by an SnB run[13] and so the structures of the two independent molecules were located and refined. Both the quality of the data, and the subsequent algorithms coded in SnB, are symbolic of what can be done with the quality data from the intense focussed synchrotron X-ray radiation and the fast readout image plate detector technology. The final *R* factor (on all data) was 4.5% and the structures of the two ($C_{12}H_{19}N_4NaO_{11.5}$) (Figure 4) represent the first Immucillin-H determined in an anionic form (as a sodium salt, see Figure 5).

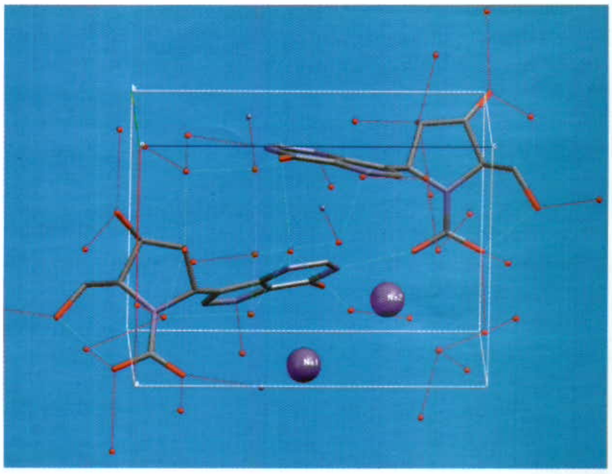

Figure 5. Unit cell packing (see ref. 1d) showing Immucillin-H anions, sodium cations and water molecule oxygens; hydrogen bonding interactions are shown by dotted lines.

Is the crystal chosen representative?

During attempts to synthesis new inorganic/organic composite layered compounds with interesting magnetic properties, members of Dr Jeff Tallon's team at IRL prepared several tungstate salts based on the $[W_{12}O_{42}]^{12-}$ anion. Compounds were identified by a combination of (conventional) single crystal and powder diffraction experiments.[14] Two crystallites were examined using the NSLS synchrotron facilities. In one of the "powder" batches there were, literally, a few crystallite fragments (<1% of the product); given the fact that the previously identified salts had not been the anticipated layered compounds, it was decided to examine one of these.

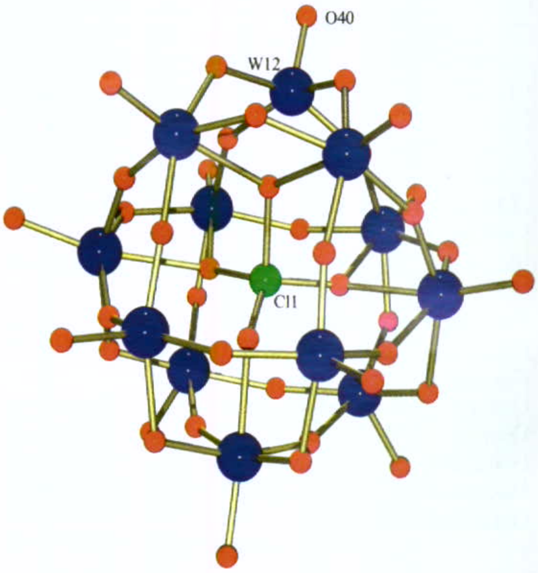

Figure 6. The unusual anion $[W_{12}O_{36}ClO_4]^{n-}$ found in a non-representative crystallite fragment (see refs. 1a and 1b); atom colours in order of increasing blackness are Cl, O and W.

The anionic entity in the structure of the 0.088 x 0.075 x 0.008 mm fragment is shown in Figure 6. A novel tungstate has been formed with a bound perchlorate anion at its center giving an overall composition of $[W_{12}O_{36}ClO_4]^{n-}$ with the usual charge balance expected to be provided by ammonium cations. This structure has not been fully characterized so water and ammonium cations cannot be easily distinguished. However, it was not unexpected to find that the bulk powder diffraction shows effectively no sign of this entity but just the parent $[NH_4]_{12}[W_{12}O_{42}].xH_2O$ salt. So "commonsense" prevailed, although this does sound a warning for the unwary investigating non-homogenous reaction products!

Hydrogen bonding … a crystallization driver?

Hydrogen bonding is perhaps the most interesting and most common lattice binding interaction that has been

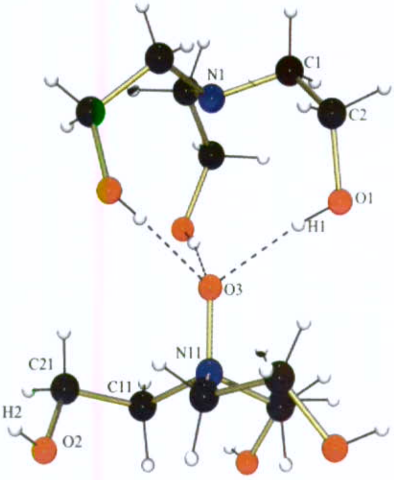

Figure 7. Trigonal hydrogen-bonding (dotted bonds) in a [triethanolamine] [triethanolamine-oxide] complex (see refs. 1a and 1b); a complementary set of hydrogen bonds link to adjacent molecules via three symmetry-related H-2 atoms (see Figure 8). Atom colours in order of increasing blackness are H, O, N and C.

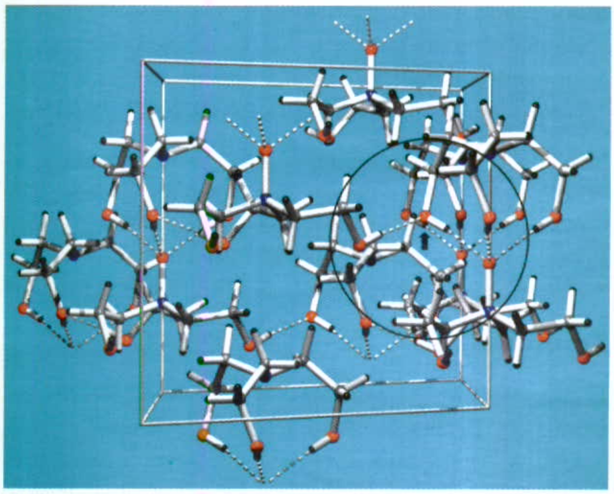

Figure 8. Partial unit cell contents showing hydrogen bonding (dotted bonds) in a [triethanolamine] [triethanolamine-oxide] complex (see refs. 1b and 1c). The arrow within the black circle indicates a representative oxygen with the two different hydrogen bonds. Atom colors in order of increasing blackness are C, O, N and H (as bond caps).

extensively examined in recent years. The positive conclusion from the earlier debate,[15] namely that C-H...O interactions do exist and, though weak, do influence the final crystal packing in solids, has spurred investigations and widened the view on such interactions to almost all accessible members of the periodic table.[16] Indeed, in a recent example both the directionality and importance of phenyl ring C-H ...I^- hydrogen bonding was observed.[17] This last example comes from a few crystals from a metal oxide triethanolamine complex synthesis that had been set aside by Dr Tim Kemmitt.

Analysis of one crystal which crystallized in the trigonal space group R3 showed that it contained pairs of triethanolamine and triethanolamine-oxide molecules in which the amine oxygen is acceptor to a trigonally-related set of ethanolamine hydrogens (H...O 1.7 Å, O-H...O 156°, see Figure 7). The amine-oxygen is therefore 4-coordinate as it fits into this "H-bond cap"; such coordination is rare.[16] A further trigonally-related set of H-bonds (H...O 1.8 Å, O-H...O 177°) to the triethanolamine oxygens completes the unique and rather elegant three-dimensional polymeric structure (shown in Figure 8). It appears that the driving force for the crystal formation came from the unique and strong hydrogen bonding. Only this example has been previously presented.[18]

Conclusions

The intention of this article has been to show results from quite recent structural studies that demonstrate the breadth and power of today's diffraction techniques and equipment, and how these have been applied to IRL projects. Inevitably, the examples highlight the increasing importance of access to synchrotron X-ray facilities with chemical projects ranging from new drugs and precursor chemicals to advanced magnetic materials. Some New Zealand X-ray crystallographers, particularly those involved in protein and macromolecular studies, have been using overseas synchrotron facilities for many years. We all now look forward to the planned synchrotron construction in Australia (in Victoria), which will bring physical access much closer, hopefully at reasonable cost. It is certainly an appropriate time to consider a funded program for future access to such facilities for all science disciplines within New Zealand, perhaps modeled on the successful Australian Synchrotron Research Programme.

In overview, New Zealand continues to be well served by its existing conventional diffraction facilities. I acknowledge here particularly those at the University of Canterbury (Professor Ward Robinson and Dr. Jan Wikaira) and at IRL (Dr. Ian Brown, Mr Martin Ryan and Dr. Mark Bowden).

Acknowledgments

Professor G.M. Sheldrick, University of Gottingen, Germany. Bruker Software (SMART software (1996), Siemens Analytical X-ray Systems Inc., Madison, Wisconsin, USA. SAINT software (1994-1996), University of Canterbury X-ray Crystallography Laboratory. Dr Jon C. Hanson and the Brookhaven National Laboratory, Chemistry Department and the National Synchrotron Light Source, Upton, New York, USA.

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Chemistry On Stamps (Chemophilately[1])

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> ***"The only science is physics. All the rest is stamp collecting"***
> *E. Rutherford Nobel laureate in chemistry (stamp 22)*

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Stamps and specific postal cancellations are issued to commemorate events and to inform and educate the public. Due to their universal circulation, stamps are rapid, powerful, and effective messengers which may raise curiosity in or enhance or degrade the image of our profession in the public eye.

Collecting chemistry-related philatelic material enables the collector to combine a hobby with professional interest, to study in a non-systematic but delightful way the history of chemistry, to learn about unknown chemists from remote countries who received fame both professionally and non-professionally, and to learn about family and student-teacher relationships in an arbitrary chosen group of professional brothers. It enables one to look with amazement, anger, or a feeling of superiority on the liberties taken by stamp designers and on the errors that they make in designing chemical formulas on stamps.[2]

Stamps can be educational tools, display the periodic table and minerals or activities of famous chemists, and even explain details in the oxygenation of haemoglobin.[3] Papers in the *Journal of Chemical Education* and occasionally in other journals cover some of these aspects, chemophilatelic exhibitions are shown in ACS meetings, and a modest journal, *Philatelia Chimica et Physica,* enters its 14th year.

Consequently, once in a quarter of a century there is a place for a paper on chemophilately in *Accounts of Chemical Research,* a journal whose first editor once wrote a paper in verse form.[4] The topic is so rich and diverse and the space so limited that any choice of material must be arbitrary. This paper reflects a personal outlook on a few sub-topics that the author finds informative, interesting, and sometimes amusing.

Chemical Societies

Jubilees of large, old, and prestigious chemical societies are sometimes commemorated by stamps. The 75th and the 100th jubilees of the ACS were commemorated by stamps 1 and 2 (Figure 1), which differ not only in the 4.3-fold increase in postal rate. The brown stamp of 1951 displays a chemical distillation apparatus and the smoke-producing chimneys of a chemical plant, which today will be regarded as reflecting the negative side of chemistry. The 1976 stamp is much more light-hearted and colourfully displays simple laboratory tools. In contrast, the British Royal Society of Chemistry chose a different approach on its 100th jubilee stamps issued in 1977. They colourfully commemorate British achievements in chemistry as exemplified by activities of Nobel laureates related to chemicals known to the general public. The cholesterol structure honours D. H. R. Barton's conformational analysis (stamp 3); a vitamin C model honours its first synthesis by N. Haworth (stamp 4); starch chromatography honours A. J. P. Martin and R. L. M. Synge, who pioneered its use (stamp 5); and the NaCl crystal structure honours W. H. and W. L. Bragg, who determined it (stamp 6). Likewise, a 1990 stamp from Berlin (not shown) commemorates the 100th anniversary of the German Pharmaceutical Society by showing a model of aspirin.

Contribution Of Small Countries

Although smaller chemical societies usually have to be satisfied only with special postal cancellations, small countries sometimes achieve great original chemophilatelic accomplishments, as shown by the following three examples. How much time does it take a trained scientist's eye to recognize the unusual philatelohydrocarbon produced in Monaco (stamp 7)? It is not a tetrahedral CH_4, as was presumably intended, but tetrahedral tetravalent hydrogen HC_4.[5]

Grenada's list of elements is displayed together with Jöns (John in Grenada) Jacob Berzelius on stamp 8. The semi alphabetical order, *e.g.* Cd, Ca, Cf, C, Ce, Cs, Cl, Cr, follows the complete spelling of the elements' names; the appearance of elements such as Cf, No, Es, and Md, whereas more important elements such as Al, Hg, As, Sb, and Ne are missing, is puzzling. Luckily, the elements discovered by Berzelius himself do appear in the list.

Comoro Island issued stamps displaying Nobel laureates in several disciplines. The chemistry stamp (stamp 9) displays Ramsay (chemistry prize, 1904), but also the non-chemists Banting and Hench (medicine prizes, 1923 and 1950) and Perrin (physics prize, 1926), as well as Mary Curie (with "1913" rather than "1911" - chemistry prize). Amazingly, a half-filled horizontal beaker suspended in air without support is stirred by nobody without spilling a single drop.

Both Sides Of Chemistry

Both positive and negative contributions of chemistry are represented on stamps. The positive role is exemplified by drug-related stamps, especially by a British stamp (stamp 10) showing an African nurse treating a baby on a background of 17 drugs used in Africa against various diseases. Vitamin C (stamp 4), penicillin, quinine, and insulin (stamps 85-87) (Figure 2) are other examples.

The uglier side of chemistry is demonstrated on two Dutch stamps. Stamp 11 displays a seal, an endangered species, emphasized by the black margin, on a background of biphenyl molecules, which symbolize the pollutant chlorobiphenyls. Stamp 12 from 1988 shows formulas of


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ETAT COMORIEN 200F
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17P
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70
NEDERLAND
12
13
A.I. VIRTANEN
1,80
SUOMI-FINLAND
14
500
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Kein ALKOHOL im Straßenverkehr
DEUTSCHE 80 BUNDESPOST
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ANTIGUA 1c
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SVERIGE 20
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Figure 1.


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Figure 2.

environmentally hazardous air pollutants related to gasoline [NO_x, CO, C_xH_y, and PAK (polyaromatic hydrocarbons)], the words "lead-free gasoline" in Dutch, and a "Pb" crossed out with red X.

Changing attitudes with the passing of time are demonstrated in Scandinavia. In 1945 the Finnish chemist Virtanen (Finnish stamp, stamp 13, 1980) received the chemistry Nobel Prize for preservation of green fodder which involved acidification to $pH < 4$. However, the effect of acidity on vegetation was so alarming in 1986 that Sweden issued a stamp symbolizing trees on a first day cover pleading "stop acid rain" in many languages and showing HNO_3 and H_2SO_4 on the first day cancellation (I, Figure 3). Another example is EtOH, one of the first structures displayed philatelically. It appears on a 1948 Japanese stamp (stamp 14) commemorating the government monopoly for its production. Forty years later the fight against drunken drivers is displayed in the command "Kein Al-kohol" on a German stamp (stamp 15).

Both sides of chemistry merge in the personality of Fritz Haber (stamp 27), whose ammonia-forming process increased food production via fertilizers but who also introduced chemical warfare in the First World War.

Chemistry Nobel Laureates

Many chemists appear on stamps. Sweden, France, the USSR, and Austria are philatelically generous to their scientists while other countries, including the USA, are misers in this respect.

The Nobel Prize is a popular topic, and Alfred Nobel himself appears on stamps from many countries. A 1976 Antigua stamp (stamp 16) is representative, although the $N_2 + 2H_2O$ shown among other symbols on the stamp is somewhat puzzling.

Nobel laureates are mainly presented here by using several of the corresponding Swedish issues. From 1961 to 1981 Sweden annually issued a series displaying the laureates of 60 years earlier. Of the 18 stamps, we show only 11 (stamps 17-27), as well as two from 1988 (stamps 28 and 29), which enable one to look at the development of a philatelic concept and the history of chemistry at the beginning of the century.

Stamp 17 displays the slightly shifted profiles of all four recipients in the various fields, but Van't Hoff's profile appears farthest left and back, and his name is the last in the accompanying list. In stamp 18 Emil Fischer's profile is still the farthest left and back, but his name now appears first. The number of laureates on a stamp in later years is reduced to two and then to one, and in 1909 and 1910 the laureates appear *en face* together with symbols associated with their chemistry, *e.g.* the camphor formula with Wallach (stamp 24). From 1974 the laureates appear mostly on the background of their institutes (stamps 26 and 27). The format was changed in 1982 to a strip of a few stamps devoted to a single discipline with symbolic pictorial representation, but regardless of consecutiveness. Examples are stamps 28 and 29, describing in a colourful and delightful way the work of laureates Libby (^{14}C dating, stamp 28) and Ziegler and Natta (a polymer, stamp 29).

The chemical and personal data, which can be extracted from stamps 17-27 and from those not shown from intervening years, are interesting. For example, the old and new chemistry sub-disciplines are nearly equally represented. The three founders of physical chemistry, Van't Hoff (stamp 17), Arrhenius, and Ostwald (stamp 23), are joined by Haber (stamp 27) and Nernst of the next generation. Four inorganic chemists - Ramsay, Moissan, Werner, and Richard, *e.g.* stamp 20, - are accompanied by the three representatives of the new branch of radiochemistry - Rutherford (stamp 22), Curie (stamp 25), and Soddy - while six organic chemists received five prizes: Fischer, Baeyer, Wallach (stamps 18, 19, and 24), Grignard, Sabatier, and Willstätter (stamp 26). Interestingly, the prize was given always to a single chemist, except in 1912, and only one biochemist (Buchner, stamp 21) and one American (Richard) are among the 1901-1921 recipients. The dominance of Germany, especially Berlin and Munich, is shown by the eight German laureates in addition to Van't Hoff, who worked in Berlin.

From the pictures taken when the prize was given, we learn that beards predominated in the first decade of the century and that moustaches dominated in the second decade. Was this change in fashion due partially to the need to wear gas masks in the First World War?

Each laureate left his name in our chemical vocabulary: Van't Hoff and Arrhenius equations, Fischer projection, Baeyer's strain theory, Buchner funnel, Ostwald dilution law, and Grignard reagent are just a few examples. Anecdotes connected with them enliven history of chemistry books: Baeyer's girl friend Barbara, who (so we were told) gave her name to barbituric acid; Rutherford's remark at the opening of this account, which reflects his relation to chemistry, for which, ironically, he received his prize; and Marie Curie, who received her Nobel Prize in 1903, but assistantship in the Sorbonne only a year later.

An inspiring teacher greatly helps. Fischer, Buchner, and Willstätter (stamps 18, 21, and 26) were Baeyer's (stamp 19) students, Moissan (stamp 20) was Marie Curie's (stamp 25) PhD thesis examiner, and Soddy collaborated with Rutherford. What Baeyer and Moissan thought when their students Fischer and Curie received the Prize before they themselves won it would be interesting to know. An insight into several of these complex personalities, including tributes to a teacher (Baeyer) and a friend (Haber), are given in Willstätter's beautiful autobiography.[6]

We note, however, that Moissan's prize given for preparation of fluorine should be immediately returned. The French stamp (stamp 30) commemorating the centenary of the preparation of fluorine depicts the highly exoergonic reaction $H_2 + F_2 \rightarrow 2HF$. A course for distinguishing forward and reverse reactions is recommended for the French philatelic service.

Chemists At Other Activities

Several chemists were honoured philatelically for non-chemical activities which brought them fame. Two of them were heads of states that met opposite fates. Ignaczi Moczicki, who improved the Haber ammonia process, was the last President of Poland before World War II, fled from his occupied country, and died in Switzerland. He appeared on several Polish stamps, *e.g.* stamp 31. Chaim Weizmann, the first President of Israel, was torn all his life between chemical research and political activity, lived most of his life abroad, but died in Israel. The importance of his fermentation process, which produced acetone for the British World War I effort, led to the unconfirmed legend that the Balfour Declaration, an important step on the way to the establishment of Israel, was granted in appreciation for it. He appears on several Israeli stamps, *e.g.* stamp 32.

The French chemist Claude-Louis Berthollet was commissioner of the national mint and of agriculture, a scientific advisor to Napoleon, and a senator (stamp 33). Another French chemist, Marcelin Berthelot (stamp 34), who first synthesized MeOH, EtOH, and benzene, had served in several cabinet posts, including the foreign ministry.

Political involvement may be dangerous. Antoine-Laurent Lavoisier, who appears on stamps from France, San Marino, Mali, and Grenada (stamp 35), was a tax collector, member of the "commission du budget", and deputy of the "Assemblée Constituante" and lost his head to the guillotine in the French revolution. Elena Ceausescu, who appears with her husband on a Roumanian stamp (not shown), ruled and brought destruction to Roumanian chemistry[7] before losing her life in the 1989 revolution.

Chemists were active in sport, literature, and music. Few know that Knute Rockne (stamp 36), the University of Notre Dame football coach with the highest winning percentage in football history, was also a chemistry instructor at Notre Dame. The poems and novels of Achim von Arnim, a German romantic author of the early 19th century (stamp 37), are known more than his works on chemical topics, including organic electrochemistry. The Russian professor Alexander Borodin, who published papers on aldol, benzidine, and the Br_2/RCOOH reaction, is much better known as a member of the "group of five" Russian composers with whom he appears on stamp 38. Composing when too ill to lecture, a musician friend greeted him, "I hope that you are ill". In contrast, Sir Edward Elgar, the British composer who wrote "Enigma Variations" (stamp 39), enigmatically had "stinks and bangs" chemistry as his hobby and even invented an apparatus for making H_2S.[8]

A Universal Chemist

One of the few scientists who were philatelically honoured by many countries is Louis Pasteur, and stamps 40-43 are samples from a larger number. On stamp 40, a surcharge of 0.25 F was added to the usual postal rate of 1.75 F for "the unemployed intellectuals". Could some government use a similar method for funding science in the future?

By a minor variation in his pose and hairdo, Pasteur was adopted into many local societies. The French intellectual on stamp 40 looks like a noble Pole on a Polish stamp (stamp 41), like a Russian general (without medals) on the Russian stamp (stamp 42), and like an African doctor on the Comoro stamp (stamp 43).

The Periodic Table And Its Father

Different periodic tables based on philatelic material can be constructed depending on the imagination of the constructor, by using the elements' names and their etymology, their minerals, and portraits of their discoverers.[9]

It is sad that philatelic services in the West do not find the originator of the periodic table, Dmitri Mendeleev, worthy of appearing on their stamps and that he appears only on stamps from formerly Eastern block countries, *e.g.* Russia (stamps 44 and 45) and Bulgaria (stamp 46). In stamps 44 and 46, a periodic table appears at the background (including elements A and X rather than Ar and Xe on stamp 44). An example of a deduction and prediction of a missing element appears on stamp 45.

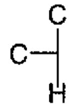
Space dictates only a few examples of stamps related to the periodic table. Most elements can be displayed in different ways, and an example for the presentation of uranium, dominated by the phenomenon of nuclear fission, is given in stamps 47-51. The uranium source, the pitchblende mineral, appears on a Zaire stamp (stamp 47) (as petchblende). Stamps 48 and 49 from the FRG and the DDR represent the nuclear fission reaction in two alternative forms, and the DDR stamp also displays Otto Hahn's (Nobel Prize, 1944) approving face. Hahn's two co-workers in this endeavour are also philatelically commemorated. Young Lise Meitner appears on a German stamp (stamp 50). Only the name of Fritz Strassman, who showed that the fission product is Ba rather than Ra, appears on stamp 51 showing the core of a nuclear reactor. However, he should be remembered also for his personal courage during the Second World War.[10]

Arbitrary examples of building blocks for the periodic table are stamp 52 (sulfur from New Zealand), stamp 53 from Portugal showing the mineral wolframite (for W), stamp 54 from Thailand displaying a zircon (for Zr), and stamp 55 from South Africa displaying chromium, which was chosen in order to recommend teaching the story bearing its name in Primo Levi's *The Periodic Table*[11] in analytical chemistry courses.

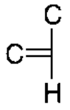
The Liberty Taken By Stamp Designers

Benzene, a symmetrical molecule with D_{6h} symmetry and C-C-H bond angles of 120° usually loses its symmetry on the drawing board of stamp designers. The 1964 FRG stamp (stamp 56) having white carbons and green hydrogens has a somewhat elongated benzene[2] and four sets of C-C-H angles of 90°, 120° and 150°. The DDR benzene is from 1979 (stamp 57) and is the Kekulé hybrid of stamp 56, including the wrong angles. The Belgians who celebrated in 1966 the benzene centennial tried to fit Kekulé's elongated face into a benzene ring and ended with a squeezed benzene having six parallel C-H bonds with some C-C-H angles of 180° (stamp 58). In the Argentinian 1971 version (stamp 59), the hexagon is perfect but carbon mitosis converted all C-H bonds to C-C-H bonds and the benzene to hexacarbenobenzene. Upper Volta honoured Linus Pauling in 1977 for his 1954 chemistry Nobel Prize (stamp 60). Pauling would probably prefer stamp 4 rather than a nuclear explosion at his back and will probably be surprised by the new bonding features:

The H3 and H4 hydrogens are differently located in the two resonance structures, and the C3-C4-H angles differ in both. Inspection also shows a double bond to hydrogen, *i.e.* C=HC, and bonds to the centre of the C-H σ bond which we call ϕ (for philatelic) bonds.[2] The Upper Volta benzene has two types of semi-ϕ-bonds, linking a carbon to the centre of a C-H bond by a single or a double bond, *i.e.*



and



Philatelofamilies

Both scientific families, *cf.* stamps 18, 19, 21, and 26, and related families [husband/wife, parent/child, and brothers-in-law like Guldberg and Waage on a Norwegian stamp (not shown)] appear on stamps.

The most famous philatelofamily are the physicists Pierre and Marie Curie. However, since isolation of Ra was an analytical chemistry task and Marie Curie received both the physics and chemistry (stamp 25) prizes, we regard her as one of us. The combination of a strong-willed woman, a science pioneer, a first woman in mostly a man's world, the fierce Polish nationalism, and her persistence in following her scientific goals resulted in her appearance on close to 100 stamps, either alone, *e.g.* stamps 62-67, or with her husband, *e.g.* stamp 61 from Monaco. In her mother country, Poland, after which she named the new element Polonium, she is a national symbol and is commemorated on many stamps, *e.g.* stamp 62, and numerous postal cancellations. She appears with her equipment (stamps 65 and 66), with the symbols of Ra and RaA (stamps 63 and 64), and on many stamps devoted to the fight against cancer, including stamp 67, where she personally stabs cancer with her own spear.

Children sometimes follow their parents, and stamp 6 commemorates the father and son team of the Braggs. Irène Joliot-Curie, Pierre and Marie's daughter, followed her parents' radiochemical research. She and her husband, Frédéric Joliot, who after marriage added the name Curie to his name, shared the 1935 chemistry Nobel Prize "for their synthesis of radioactive elements", thus increasing the number of the family prizes to five. They are shown on a French stamp (stamp 68). Frédéric Joliot-Curie also appears alone on several stamps from formerly Eastern block countries, as demonstrated by those from Albania (stamp 69) and the DDR (stamp 70). He is honoured there as the first President of the communist world peace movement and appropriately looks leftward in seven out of the eight stamps on which he is displayed.

Polymers

Complex molecules such as sugars, natural products, and DNA, which appear philatelically, are demonstrated by some polymer-related stamps. Leo Baekeland, the inventor of Bakelite, one of the first commercially used polymers, is displayed on Belgian stamp 71. Both the monomer isoprene and its polymer, *i.e.* rubber, are shown on Malaysian stamps 72 and 73, although the stereochemistry of the latter deserves attention. The related ethene-propene copolymer appears on stamp 29. Polyethylene glycol terephthalate (Dacron) appears on a German stamp (stamp 74), a polypeptide having S-S bonds appears on a Japanese stamp (stamp 75), and a mysterious polymer appears on a Russian stamp (stamp 76).

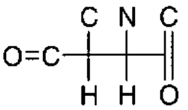
Great Chemists

Many of the pioneers of chemistry, including alchemists, *e.g.* Paracelsus, not shown, appear on stamps. An arbitrary sample includes Robert Boyle (Grenada, stamp 77), Joseph Priestley (USA, stamp 78), Joseph Louis Gay-Lussac (France, stamp 79), Justus von Liebig (FRG, stamp 80), and Carl Wilhelm Scheele (Sweden, stamp 81). Do we recognize in the solemn Gay-Lussac the scientist who ascended in a balloon to 7016 m without an oxygen mask and who asked his German supplier of glass tubing to seal the pieces and classify them under the custom-free item of "German air"? Did he realize that by training young Liebig (stamp 80) he transferred the French hegemony in chemistry to Germany? Who has priority in discovering oxygen, Priestly (stamp 78) as the British and probably the American post office think, or Scheele (stamp 81)?[12]

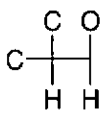
Some Organic Structures

Wohler's urea synthesis from ammonium isocyanate, which still opens introductory courses in organic chemistry, is shown on stamp 82. A very simple philatelo-organic species is CH_3, shown on Mexican stamp 83. Whether this "molecular symbol of carbon" is CH_4 with one hidden hydrogen or a methyl radical, its two H-C-H angles of >120° and yellow carbon and red hydrogens of equal sizes are of interest. We note that a recent stamp from China (not shown) uses methylene CH_2 (rather than CO_2) for synthesis of $NaHCO_3$. A fully saturated carbon species is adamantane, found in Czechoslovakian petroleum, whose structure was deduced in Prague. Appropriately, it is displayed on a Czech stamp (stamp 84) commemorating the centennial of the Czechoslovak Chemical Society.

Of the many medicinally important natural products that appear philatelically, we mention stamp 85, which shows Alexander Fleming near the Hungarian penicillin, which is isomeric with regular penicillin due to its three ϕ bonds, *i.e.*



Two ϕ bonds, *i.e.*



and N-H-H-C bonds appear in the structure of quinine, displayed near its discoverers Pelletier and Caventou on stamp 86.

The Author's Favorites

Stamps 87-90 and post card II (Figure 3) are a few of the author's favorites. Chinese stamp 87 was traded with a Hong Kong scientist for many reprints of our work. It displays the insulin molecule which was first synthesized in China, using a new, apparently efficient, type of catalysis

("Holding aloft the great banner of chairman Mao Tse-tung's thinking and manifesting the superiority of the socialist system, we have achieved under the correct leadership of our party, the total synthesis of bovine insuline").[13] Russian stamp 88 displays the structure of the $[Re_2Cl_8]^{2-}$ ion, whose structure was first determined by USSR chemists, who however missed the special meaning of the short Re-Re bond which was recognized as a quadruple bond by F. A. Cotton. Stamps 89 and 90 offer a philatelic rationale to recent behaviour in the Middle East. The amino acid displayed on 1975 Iranian stamp 89, which was issued on the occasion of an Iranian Chemical Society Symposium and mentions milk and protein, has the "abnormal" *R* rather than the natural *S* configuration. Israeli DNA stamp 90 also displays the "abnormal" helicity of DNA. Post card II (Figure 3) should console chemists who feel uneasy with the rapid progress of theoretical and computational chemistry. Even WATOC (World Association of Theoretical Organic Chemists) clearly recognizes that the Schrödinger equation is wrong, as shown by the inequality on the postcard issued for its 1987 conference in Hungary.

Philatelic Chemitowns

Many postal cancellations with chemical themes are known. I will end this account with a subgroup of these: cancellations from places carrying chemistry-related names, *i.e.* philatelic chemitowns.

Warnings are in order. A letter sent to Bukit Timah (Tin Hill) in Singapore will return with a "Singapore" cancellation. If one obtains a postal cancellation of Ytterby, it is not from the place which gave its name to four elements (erbium, terbium, yttrium, and ytterbium) and has no post office, but it is from a chemically irrelevant Ytterby. Nevertheless, there is an appreciable number of chemitowns, and Figure 4 displays 15 cancellations from USA chemitowns, on the ACS stamp (stamp 2).

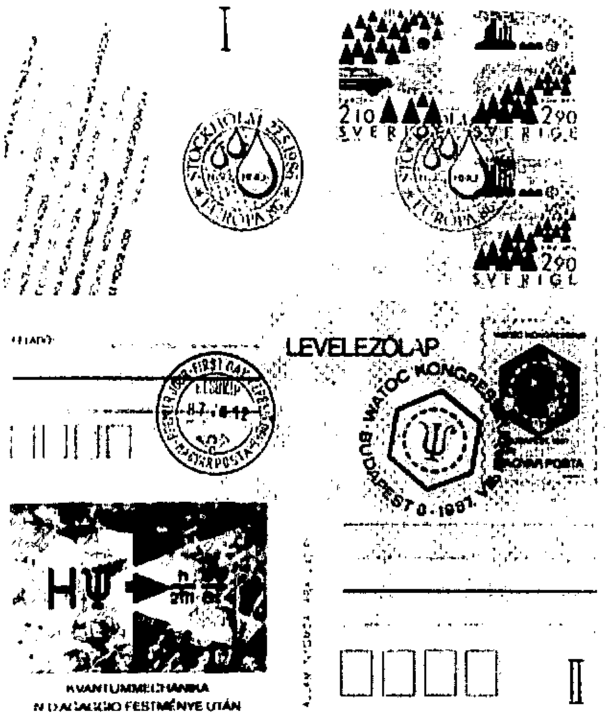


Figure 3.

Ancient metals such as lead (Lead, SD, No. 1), silver (Silver, TX, No. 2), and mercury (Mercury, NV, No. 3) are well represented, as are cancellations from Copper and Iron, which are not displayed. The names arise mostly from the presence of a nearby mine, which in most cases is already abandoned.

A popular chemitown name is Sulphur (No. 4-6), which is spread from Indiana to Louisiana either alone or in

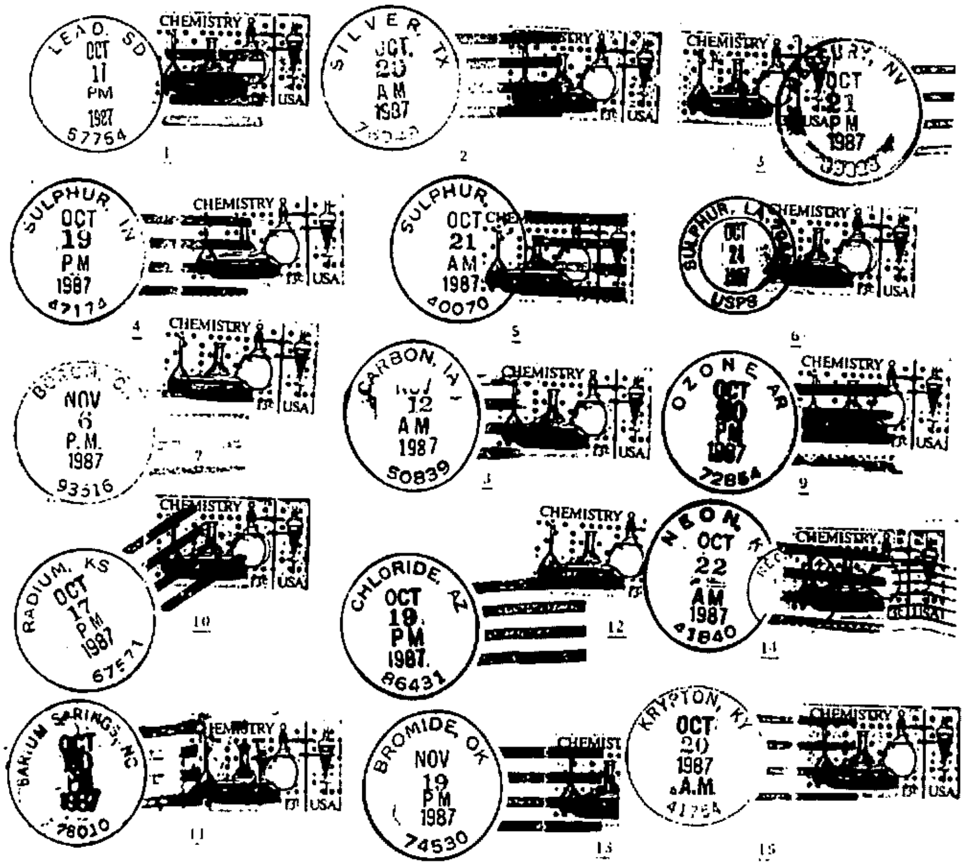


Figure 4.

combination, *e.g.* Sulphur Springs. For example, Sulphur in Louisiana supplied 75% of the sulfur produced in the USA at the beginning of the century, and the Frasch method of mining sulfur was invented there.

The second row in the periodic table is represented by Boron (CA, No. 7), Carbon (IA, No. 8), and Ozone (AR, No. 9). The size of Carbon does not correlate with the importance of the element since Carbon had a population of 45 in 1987, including a mayor and five council members.

Cancellations from Radium (KS, No. 10), Barium Springs (NC, No. 11), and Calcium (NY, not shown) represent the alkaline-earth metals. The name Barium Springs arises from a barium-containing local spring. The other uranium fission product, Krypton (KY, No. 15) is another philatelic chemitown. The origin of the name is unknown to me. The atmosphere above another noble gas chemitown, Neon (KY, No. 14), is not especially Ne-rich. According to its postmaster, it received the name "when the railway came to the area and passengers have to put their *knee on* a box in order to board".

Anionic chemitowns also exist. The name of Telluride (CO, not shown) derives from the presence of tellurium in nearby mines. Two anions, which appropriately end our Account, are Br^- and Cl^-. Bromide (OK, No. 13) is a town with 175 inhabitants, and according to its postmaster, the name arises from the "abundant supply of mineral water 'bromide of sulphur' in the area". Chloride (AZ, No. 12) is larger (population 12 000). The k_{Br^-}/k_{Cl^-} (population) ratio of ca. 0.03 is the lowest known, and it will make the "discoverer" of the "k_{Br}/k_{Cl} element effect"[4,14] and the first editor of *Accounts of Chemical Research,* to whom this paper is dedicated, frown about its mechanistic meaning.

Acknowledgements

Thanks are due to Professors Edgar Heilbronner and Foil A. Miller for comments, suggestions, and their articles on chemophilately, to Professor S. Patai for comments, and to many fellow chemists who supplied chemophilatelic material over the years. Thanks to Dr. David Darom for his help in photographing the stamps. I thank in advance readers who will share their chemophilatelic knowledge with me.

Supplementary Material Available

A list of countries, years of issue, and Scott catalogue numbers of the 90 stamps (2 pages) appeared following this article in the original journal. Photocopies of that supplementary material from the paper or microfiche (105 x 148 mm, 24x reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036, USA. Full bibliographic citation (journal, title of article, author's name, inclusive pagination, volume number, and issue number) and prepayment, check or money order for $US10.00 for photocopy ($US12.00 foreign) or $US10.00 for microfiche ($US11.00 foreign), are required. Canadian residents should add GST.

References And Notes

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About The Author

Zvi Rappoport is Professor of Organic Chemistry at the Hebrew University of Jerusalem. He was born in Jerusalem in 1936, started to collect stamps at a young age, and received both MSc and PhD degrees at the Hebrew University. This was followed by two years of postdoctoral work in UCLA with the late Saul Winstein. His research interests include nucleophilic vinylic substitution, vinyl cations, and simple stable enols, solvent effects, and reactivity and selectivity, and these have provided some 270 journal papers. He has been co-editor and is now principal editor of the Wiley Series *"Chemistry of the Functional Groups"* initiated by the late Professor Saul Patai.

He is a comparatively recent collector of chemistry-related stamps. In the latter part of 2001 he was a sabbatical visitor at the University of Auckland and gave his "Chemophilately" lecture there and in Wellington. After his New Zealand stay he wrote to the Editor saying "I also spent time at two stamp shops (in Dunedin and Christchurch) and got the Kauri and new Rutherford stamps, and even followed what one of your colleagues suggested - that "Reefton" is a "chemical name" - and I have the cancellation. Knowing Hebrew helped. I found a cancellation from a place called Ophir (Central Otago) and since King Solomon was dealing with Zehav Ophir (the gold of Ophir), I figured out that this was from a gold digger time. You probably know about the (New Zealand) stamps from the end of 19 century with advertisements on the back of the stamp (not a usual place where one will look). Anyway, there was one for nitrous oxide (I assume as anaesthetic) and for coal, and soap - all chemicals - so this was a useful philatelic experience.

Azamacrocycles

Neil F. Curtis
School of Chemical and Physical Sciences, Victoria University of Wellington

Azamacrocyles have been around for a long time. Old Mother Nature stumbled on their usefulness very early in the evolutionary process, though chemists recognized them only one hundred years ago, when a number of biologically significant compounds, *e.g.* the haeme of haemoglobin and the green of chlorophyll, were established as tetra-pyrrole porphyrin macrocycles. These 16-membered tetraaza macrocyles readily self-assemble from pyrrole and formaldehyde (Figure 1) and form complexes with many metal ions. This research field was largely the province of organic chemists, primarily interested in replicating the complex substitution patterns observed in nature, and not much concerned with the interactions with metal ions.[1,2]

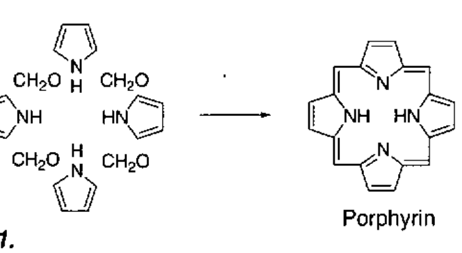


Figure 1.

The second burst of interest occurred in the 1930s when the intensely coloured phthalocyanin pigments/dyestuffs were serendipitously discovered and also shown to have 16-membered tetraaza macrocyclic structures. Again, these molecules readily self-assemble from a variety of components with *o*-benzo/amide/nitrile functions, this time about a metal ion (Figure 2). This field became the province of the dyestuffs industry, with primary concern in developing colour variations, solubility properties, etc, again with only marginal interest in the metal ions.[3]

The third wave of development occurred in the 1960s with discoveries of a variety of reactions in which suitably configured amines and carbonyl compounds assembled around metal ions, in what were termed "template reactions", to form macrocyclic imines.[4,5] Amines and imines primarily coordinate to the later *d*-transition metal ions, the traditional stamping ground of coordination chemists, so this time the focus was largely on the coordination environment of the metal ions.

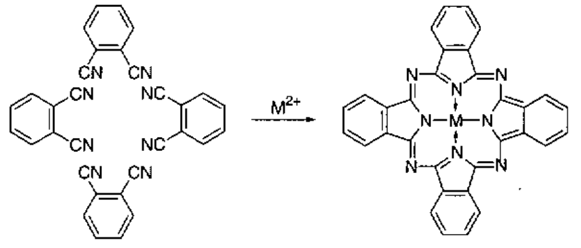
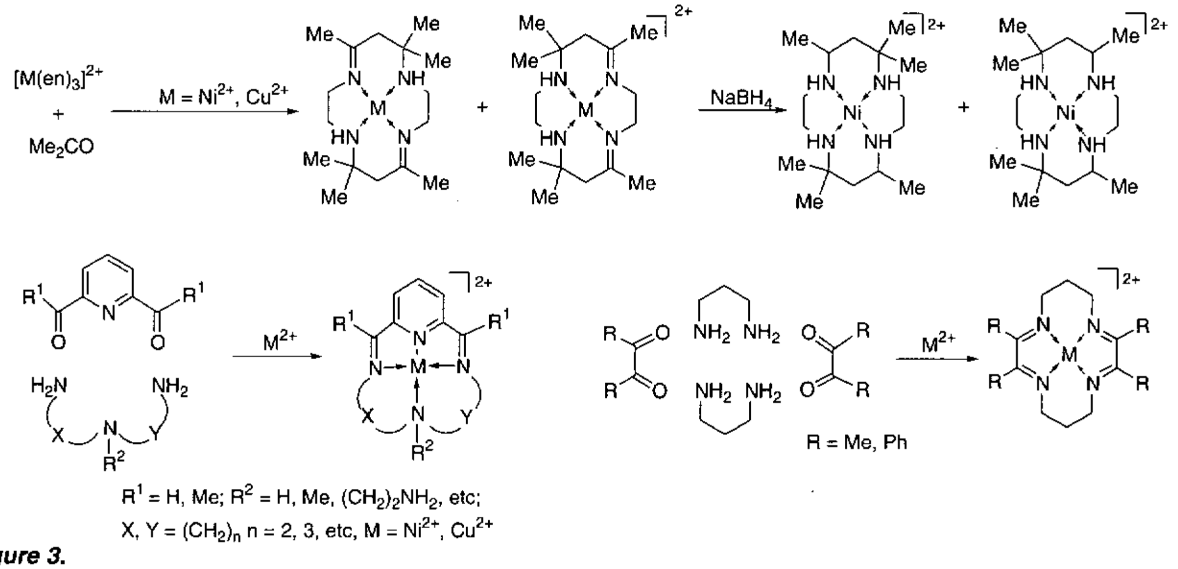


Figure 2.

A variety of these reactions has been described and some examples are shown in Fig. 3. The reactions tend to be idiosyncratic, forming compounds with particular metal-ions [usually nickel(II) or copper(II)], ring sizes (usually 14 or 16), numbers of nitrogen atoms (usually 4), substituent patterns, etc. The imine groups can often be reduced to form cyclic amines.

The new compounds fascinated inorganic chemists as they showed a number of novel properties, at first attributed to esoteric "macrocyclic effects". Amine compounds of nickel(II) and copper(II) are usually destroyed rapidly by acid, but the cyclic amine and imine compounds are extremely resistant to acid. The formation constants for these ligands were found to be orders of magnitude greater than those of non-cyclic analogues, which indicates high thermodynamic stability. The metal compounds had spectra indicating very high ligand field strengths, and often they had unusually short metal-nitrogen bond lengths. These effects showed that the cyclic ligands were more effective as ligands, forming stronger bonds than their non-cyclic analogues.

The development of a non-template conventional synthetic method, the Richman-Atkins synthesis shown in Figure



R^1 = H, Me; R^2 = H, Me, $(CH_2)_2NH_2$, etc;
X, Y = $(CH_2)_n$ n = 2, 3, etc, M = Ni^{2+}, Cu^{2+}

Figure 3.

4, enabled the preparation of cyclic amines in a systematic manner, with controlled ring size, numbers of nitrogen atoms and substituents (and also the inclusion of other heteroatoms and groups).[6]

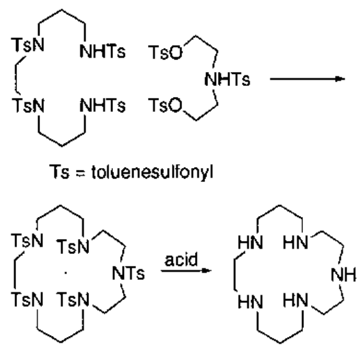


Figure 4.

Studies of series of macrocycles with varying ring sizes, numbers of nitrogen atoms, etc, demystified the various macrocyclic effects. The unusual resistance to acid arises because there is no terminal amine group that can protonate to initiate an "unzipping" reaction; cyclic diamines show the same effect. The higher ligand field strength and shorter, stronger bonds arise because the cyclic amines have all-secondary nitrogen donor groups (which are better donors than primary amine nitrogens), without the usual steric repulsion arising from the additional substituents present with non-cyclic secondary amines. The high thermodynamic stability arises from both an enthalpic component (from the stronger bonds) and an entropic component (from ligand pre-organisation), though there are large solvation components.[7,8] The thermodynamic stabilization arises from the presence of the macrocycle, it does not require a metal ion to be coordinated in the centre - watch the doughnut, not the hole, see *e.g.* compound **31**.

In 1967 Pederson reported the discovery and the coordinating abilities of the cyclic ethers.[9] These are poor ligands for transition metal cations, and so were of little interest to inorganic chemists, but their ability to coordinate the (boring) cations of groups I, II, etc, proved extremely useful. Organic chemists, who have prepared a wide range of compounds by conventional synthetic methods, have developed this field predominantly.

Since the 1980s the imine-forming template reactions have been joined by Mannich-type reactions. These involve template reactions of metal-amine compounds with an aldehyde (usually formaldehyde) and a protic acid, typically ammonia or an amine, or a compound with an active methylene group, such as present in nitromethane, nitroethane or diethyl malonate.[10] Clathrochelate cage compounds, **1** of Figure 5, formed by reaction of tris(ethane-1,2-diamine)cobalt(III), formaldehyde and ammonia were reported by Sargeson.[11] Extension of the reaction to bis(ethanediamine)nickel(II) and -copper(II), formaldehyde and primary amines gave a prolific source of new azamacrocycles, *e.g.* **2**, and a variety of aza-polycycles, such as **3**.[12] Reactions of the carbon acids nitroethane[13] or diethyl malonate[14] led to nitro **4** (and by reduction, amine **5**) or carboxylato **6** and **7** substituted macrocycles (Figure 6). Amine and carboxyl substituents are potential donor groups, and coordinate to the central (or another) metal-ion if a relatively strain-free chelate ring can be formed, opening up other possibilities.

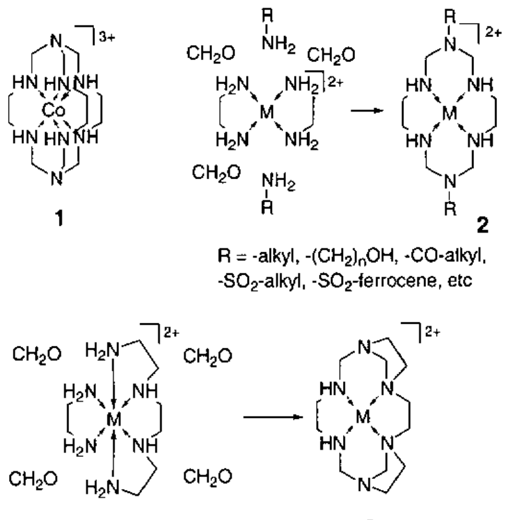


Figure 5.

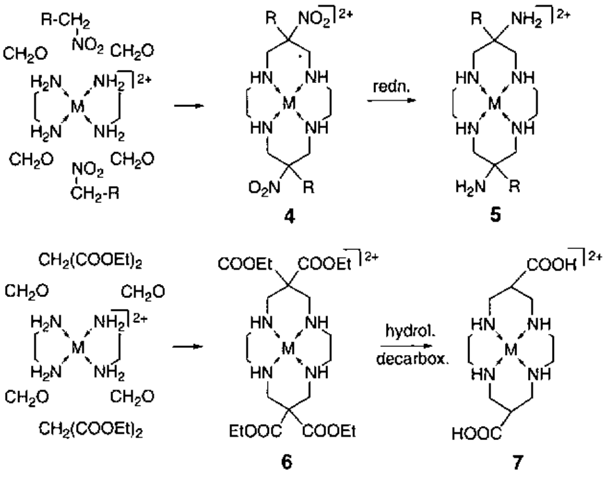


Figure 6.

Much of current research in macrocycle chemistry concerns macrocycles with amide functions, macrocycles with functional substituents, bi- and tricyclic amines and of linked macrocycles, all areas currently supported by funding bodies, with claims of potential bio-medical or catalytic applications almost mandatory.

Macrocycles with amide functions are prepared by conventional (non-template) synthetic methods. Unlike template syntheses, these preparations usually give the product in relatively low yields, and require extensive purification. Examples of the preparations are shown in Figure 7 and generally involve reaction of a polyamine with a bifunctional nucleophile, either an acrylic ester (Michael addition), *viz.* **8** → **9**, or chloroacetyl chloride, *viz.* **10** → **9**, to give a mono-amide. Use of malonate or oxalate diesters, as for **13** → **14** or **17** → **18**, give 1,3-dioxo- or 1,2-dioxodiamides. The *trans*-(5,14)-dioxocyclam is prepared by a double condensation as shown for the preparation **19** → **20** (Figure 7). The amide functions can be reduced (usually by diborane/tetrahydrofuran) providing another route to cyclic amines. Extensions of the amide formation reactions have also been used to prepare a variety of *C*-substituted amido macrocycles as illustrated by **21** and **23** (and after reduction, the *C*-substituted cyclic amines **22** and **24**) of Figure 8.

Cyclic peptides can be prepared by standard peptide syntheses. Cyclisation of four glycine units forms the 12-membered *cyclo*-(-NH-CH_2-CO-$)_4$ **25**, and four alanine units gives the 16-membered *cyclo*-(NH-$(CH_2)_2$-CO-$)_4$ **26**. *Cyclo*-(gly-ala-gly-ala) **27** is a 14-membered tetra-amido analogue of cyclam. Cyclization of other numbers of amino acid units produce rings with 5, 6, etc, amido nitrogen atoms. Chirality complicates the coordination properties of many cyclised naturally occurring amino acids, and the field is only just beginning to be explored. Non-cyclic peptides are extremely significant as biological coordinating groups, and cyclic peptide antibiotics such as valinomycin are known, so watch this space!

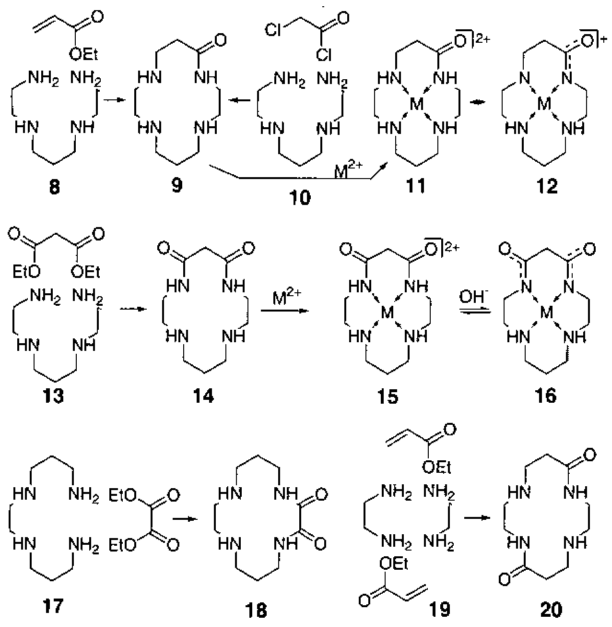


Figure 7.

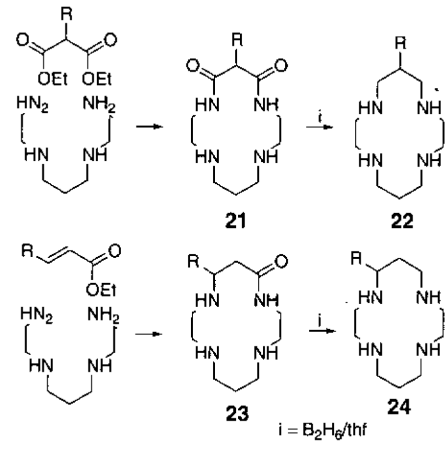


Figure 8.

Coordinated amido groups such as **11** and **15** readily deprotonate to form amidate groups **12** and **16**, respectively, which are strong donors and which stabilize higher oxidation states of metal ions, such as copper(III). This property has been utilized in the development of cyclic tetra-amides which form stable higher oxidation-state compounds of metal-ions [usually iron(III) or manganese(III)] which act as peroxidation catalysts, *e.g.* **28**. The hope is that they will enable hydrogen peroxide to replace chlorine in traditional bleaching processes, such as in paper production. The problem is making the macrocycle itself sufficiently resistant towards oxidation so that the number of catalytic cycles can be large enough to ensure the process is economic.[15]

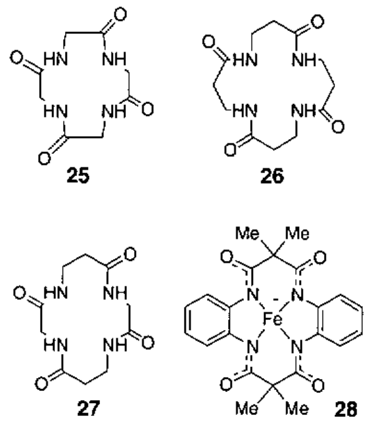


Figure 9.

The secondary amine groups of cyclic amines, free or coordinated, undergo facile nucleophilic substitution to form *N*-substituted cyclic amines. The substituents initially used were non-functional, *e.g.* methyl, though even alkyl substituents can introduce interesting properties; a recent report indicates that tetra-*N*-isopropyl and –isobutyl cyclam inhibit tumour growth. A great variety of *N*-substituents with some functionality have been developed, such as with coordinating, redox, or biologically significant abilities, *e.g.* coupling to antibodies.[16]

The most studied compounds are of tetra-*N*-carboxymethyl substituted (commonly called acetic acid substituted) macrocycles (Figure 10).[17] While cyclic amines coordinate predominantly with the later *d*-transition metal-ions, the presence of oxygen donor substituents such as carboxyl or carbamoyl (amide) increases the coordinating range to include most cations. The compounds resemble the non-cyclic carboxymethyl amines, such as "ethylenediamine tetraacetic acid", EDTA, or "iminodiacetic acid". They combine the thermodynamic stability associated with a macrocycle with that associated with the formation of many chelate rings. The tetra-*N*-carboxymethyl-substituted cyclen, "dota" **29**, and –cyclam "teta" **30**, form thermodynamically very stable compounds with most metal-ions. In particular they form very stable compounds with the lanthanide ions, and especially with gadolinium(III). These compounds have the cation coordinated by the four ring nitrogen atoms and four carboxylato functions in a basket arrangement, together with water molecules. The gadolinium(III) ion has seven unpaired electrons and is used as a nuclear magnetic resonance contrast enhancing agent in medical scanning. The requirement is for a compound which strongly binds the Gd(III) ion (thermodynamic stability), releases the toxic ion only slowly (kinetic stability) yet permits rapid exchange of coordinated water molecules (the mechanism of spin-relaxation). The currently favoured (and widely used) compound is "dota", though there is intensive research to find better ligands, and some carbamoylmethyl (acetamide) compounds such as tetra-*N*-carbamoylmethyl-cyclen, "dotam", are showing promise. The high stability (both thermodynamic and kinetic) of these carboxymethyl and carbamoylmethyl *N*-substituted azamacrocyles also permits their use as carriers and targeting agents for other radio-pharmaceuticals, such as ^{64}Cu, ^{105}Rh or ^{99}Tc.

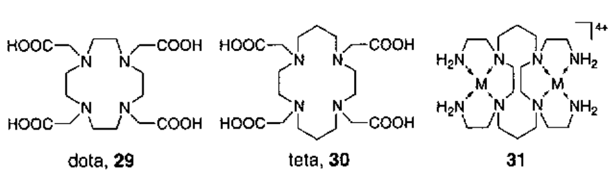

dota, **29** teta, **30** **31**

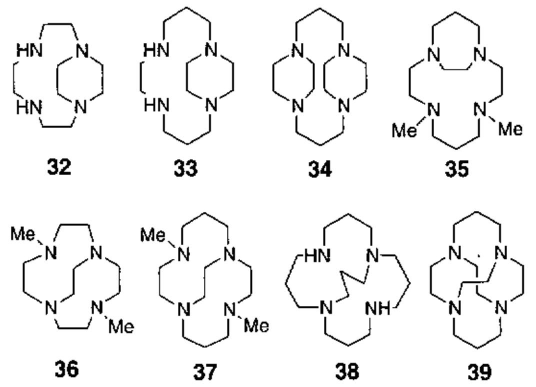
Figure 10.

Macrocycles with *N*-donor substituents have also been prepared, such as tetra-*N*-(2-aminoethyl) and tetra-*N*-(2-pyridylmethyl)-substituted cyclic tetraamines. These have eight potential nitrogen donor groups, and form a variety of compounds, many of which have the metal-ion coordinated exocyclically, by two ring and two pendant nitrogen atoms, as for **31**. The MN_4 planes are parallel, with an anion firmly bound between the two metal-ions. It is not clear yet whether adoption of this arrangement is determined by kinetic or thermodynamic considerations.

As well as the fully *N*-substituted macrocycles, procedures for introducing one, two, or more, substituents, or combinations of substituents, have been devised. These permit development of an enormous variety of ligands, with properties that can readily be fine-tuned by adjusting the substituent pattern. Again, watch this space for developments!

A variety of "bridged", **32-35**, and "cross-bridged", **36-39**, bi-and tri-cyclic azamacrocycles have been prepared (Figure 11), usually by reaction of a cyclic amine with a bifunctional nucleophile. The molecules often form extremely stable coordination compounds, which show great resistance to demetallation. The doubly cross-bridged tricyclic amines, *e.g.* **39**, are very strong bases (proton sponges), and strongly coordinate metal-ions, while leaving other coordination sites on the ions labile. There is again strong interest in their potential use as catalysts, particularly for peroxidation reactions.

A report in the early 1990s that compounds which had two azamacrocyles linked by an alkyl chain (and their zinc coordination compounds) inhibited the replication of HIV, at least *in vitro*, has led to the preparation of many compounds in which two (or sometimes more) azamacrocycles are linked by chains of varying lengths and varying types.[18] The linkages can be *via* *C*-substituents or *via* *N*-substituents (synthetically much easier). Compounds with *N*-links, *e.g.* **42**, can be formed from a cyclic amine, *e.g.* **39**, by reaction with a suitable bifunctional nucleophile, *e.g.* **40** → **41**, usually after protecting all but one nitrogen with some suitable protecting group as for **39** → **40** shown in Figure 12. Alternatively, many of the synthetic methods used to prepare azamacrocyles can be adapted by using bifunctional reagents, for example the amide synthesis **43** → **44**, extended to linked amines by reduction, *viz.* **44** → **45**, also shown in Figure 12. Many of the compounds have interesting physiological properties, though no major "breaks-through" have as yet been reported!

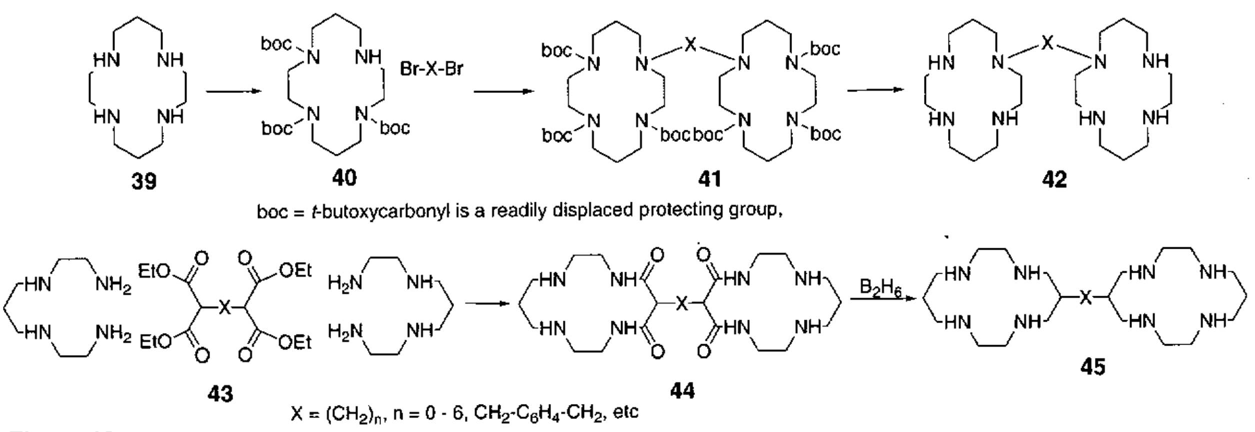

32 **33** **34** **35**

36 **37** **38** **39**

Figure 11.

Azamacrocycle chemistry is now a mature field, with a very large number prepared, and with a variety of nitrogen types: secondary and tertiary amine, imine, amide (and amidate), pyridine, hydrazine (and hydrazone), etc., as well as variants with other hetero atoms. Rings with 3-12 nitrogen atoms and with ring sizes up to 66 are known. Rings incorporating pyridine, di- and tri-pyridyl, *o*-benzo (and larger aromatics) are known, as well as rings which coordinate more than one metal-ion. Azamacrocycles bound to organic and inorganic polymers have been used for metal-ion recovery. Azamacrocycles linked by sharing bonds (fused rings), sharing atoms (spirocycles), or *C*- or *N*-bonded chains are known. A great diversity of *C*- and *N*-substituted rings have been prepared, and the range of substituents is rapidly being expanded. Compounds with all cations are known. A great variety of biomedical effects have been reported, with selectivity for peptide and DNA base sequences established, and interactions with bacteria, viruses and tumour cells known.[19] Dota, **29**, is a widely used contrast enhancing agent in medical magnetic imaging, and a variety of other applications appear probable.

I published a paper describing the first azamacrocycle compound (other than porphyrin and phthalocyanin) in


39 **40** **41** **42**

boc = *t*-butoxycarbonyl is a readily displaced protecting group,

43 **44** **45**

$X = (CH_2)_n$, n = 0 - 6, CH_2-C_6H_4-CH_2, etc

Figure 12.

1961.[5] I had stumbled on the compound by chance, while trying to make something quite different, and was so intrigued by its novel properties that I persevered with it until the structure was resolved. It would be interesting to know how a proposal to fund this research could have been written, and what the response of the current New Zealand funding bodies would have been (though I guess I know the answer to the latter question). The phthalocyanin and cyclic ether discoveries were similar, unexpected riches resulting from perseverance by an individual scientist trying to understand a chance observation. Our present research models are designed to develop and commercialize known phenomena (innovation as defined by political rhetoric), but leave no space for innovation (as defined in the dictionary). Sigh!

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Chemistry Enrolments In New Zealand Secondary Schools - 25 Years Of Change

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Introduction

I have previously presented analyses of trends in enrolment in chemistry[1,2] and physics[3] in New Zealand secondary schools. The previous report[2] was soon after a rapid rise had occurred in the retention rate of students from Form 6 (Year 12) to Form 7 (Year 13+). The rate of change of this retention rate has now slowed down, so it is worth discovering what is the new equilibrium situation. In response to a decline in secondary school participation in science in Australia, a combined campaign[4] "Rebuilding the Enabling Sciences" was launched in 2001. Linear projections of current trends suggest no chemistry academic staff left in Australia after about 2015 and no students studying chemistry in secondary schools after about 2020! Is the situation the same in New Zealand?

Enrolment Trends

The number of males and females at Form 7 (Year 13+) level are shown in Figure 1. About 1986 the enrolments in Form 7 began to climb significantly. In 1975 only 15.4% of the males in the parent Form 3 (Year 9) classes had remained to Form 7 and 10.3% of females. In 1985 this had risen to 17.9% of males and 16.6% of females. Since 1989 the retention rate for females has exceeded that for males and is now about ten percentage points greater than that for males. In 2000 it was 60.9% for males and 71.1% for females. The blip around 1995-6 in this and all other graphs is due to a change in the way the Ministry of Education reported data,[5] moving from level of study to year of study. For most students this is the same. The main exception involves students previously classified as second year Form 6 who are now classed as Year 13. The number of students in the parent Year 9 classes has been increasing since 1995, and so the numbers in Year 13+ should continue to increase.

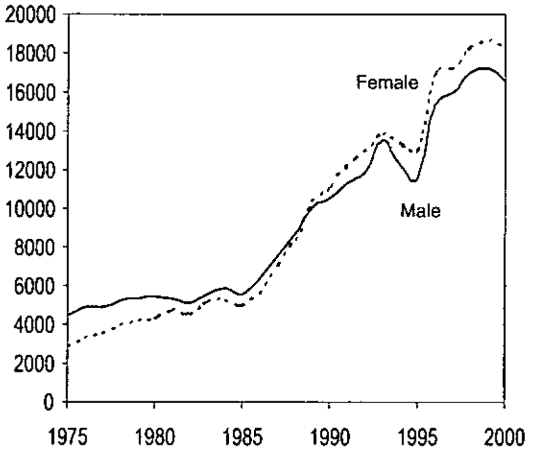

Figure 1. Enrolments of Males and Females in Form 7 (Year 13+) 1975-2000.

The numbers of students studying various science subjects in Year 13+ are shown in Figure 2. The trend apparent in 1994 that physics was overtaking chemistry has continued and about one percentage point more students study physics than chemistry, whereas in 1975 it was three percentage points the other way. The introduction, and increasing popularity of science in Year 13 is a new factor. Whereas chemistry and physics continued at the same growth rate after 1986, there was an rapid increase in the number of students studying biology, the science subject of choice for those staying on at school for Year 13, rather than leaving school. Biology numbers seem to have peaked and are now actually declining.

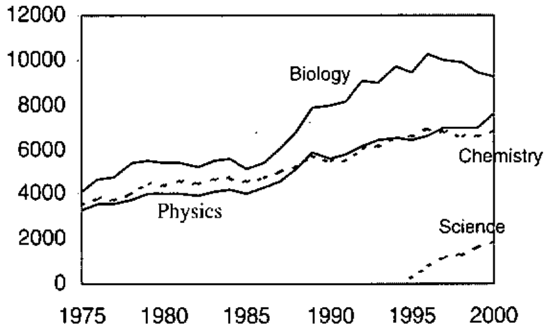

Figure 2. Enrolments in Form 7 (Year 13+) science subjects - 1975-2000.

In Table 1 are shown the order of popularity of the nine most popular subjects in Form 7/Year 13+ from 1975 to 2000. In 1975 chemistry was the fourth most popular subject. With the rapid rise in numbers of students staying on to Year 13, starting in 1985, and with the appearance of newer Bursary subjects such as classical studies, chemistry has dropped in the popularity stakes, being ninth in 2000. The rise and fall in popularity of chemistry in the period 1990-2000 is due mainly to fluctuations in the popularity of physics amongst females. In Table 2 the order of popularity is shown separately for males and females. The drop in popularity of chemistry has been greater for males than females. The social sciences have continued to be more popular than the physical sciences for females. In fact, the trend towards a greater proportion of females studying chemistry, apparent in the 1980s, may be reversing itself. Some newer Bursary subjects, like physical education for males and classical studies for females, have led to a lower ranking for chemistry. The students who now remain at school, who in earlier times would have left school, are studying a different mix of subjects. In 1975 the "average" student studied 1.5 science subjects. In 1985 it had dropped slightly to 1.3 subjects. In 2000 it was only 0.73. This compares with 0.70 for mathematics, 0.62 for english and 0.58 for social studies (history, geography, classical studies). The students who now stay on for a fifth year at secondary school, who twenty years ago would have left school, tend not to study science subjects. For university teachers, the problem now is the increasing number of students in stage 1 classes who have not studied chemistry at Year 13 level. A more satisfactory statistic is that in 1975 the percentage of the parent Form 3 class who studied chemistry in the seventh form was 6.2% (8.6% for males and 3.7% for females). In 2000 it had risen to 12.8% (13.3% for males and 12.4% of females). In 2000, 3620 males and 3202 females studied chemistry in Year 13+. A significant proportion of these students continue studying chemistry at university level.

Gender Balance

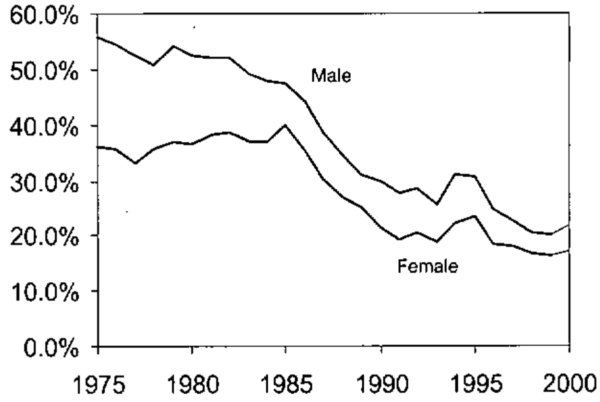

Figure 3. Percentage of Males and Females in Year 13+ studying chemistry - 1975-2000.

Figure 3 shows the percentage of males and females in Year 13+ studying chemistry. Twenty-five years ago males greatly outnumbered females, but in the next ten years females narrowed the gap, and since then have kept pace with males as the percentage of Year 13 students studying chemistry has declined. In 2000 the ratio of males to females in Form 7 was 1.13 compared with 2.37 in 1975 and 1.33 in 1985. In biology, the ratio of males to females was 1.15 in 1975, but it has since fallen, dropping to a low value of 0.64 in 1990, and was 0.66 in 2000. Physics remains a male subject, but the ratio of males to females has dropped from 3.27 in 1975 to 2.15 in 2000. In mathematics the ratio dropped from 2.12 in 1975 to 1.49 in 1985. The ratio of males to females in mathematics has not changed significantly in the last ten years, fluctuating from 1.32 to 1.50.

Table 1. **Changes in the popularity of various subjects in Form 7/Year 13+ 1975-2000.**

Rank	1975	1980	1985	1990	1995	20001
1.	English	English	English	English	English	English
2	Mathematics	Mathematics	Mathematics	Math w. Stats.	Math w. Stats.	Math w. Stats.
3	Biology	Biology	App. Maths	Math w. Calc.	Biology	Biology
4	**Chemistry**	**Chemistry**	Biology	Biology	Math w. Calc.	Geography
5	Physics	Physics	**Chemistry**	Geography	Geography	Math w. Calc.
6	Geography	App. Maths	Physics	History	**Chemistry**	Physics
7	History	Geography	Geography	Physics	Physics	History
8	Physical Ed.	Economics	History	**Chemistry**	Economics	Physical Ed.
9	Economics	History	Physical Ed.	Classical Stud.	Physical Ed.	**Chemistry**

Table 2. **Changes in the popularity of various subjects in Form 7/Yr 13+ 1975-2000 by gender.**

Rank	**1975**		**1985**		**1995**		**2000**	
	Male	**Female**	**Male**	**Female**	**Male**	**Female**	**Male**	**Female**
1	English	English	Mathematics	English	English	English	English	English
2	Mathematics	Biology	English	Biology	Maths w. Stats.	Maths w. Stats.	Maths w. Stats.	Biology
3	Physics	Mathematics	App. Maths	Mathematics	Maths w. Calc.	Biology	Physics	Maths w. Stats.
4	**Chemistry**	Geography	Physics	**Chemistry**	Physics	Geography	Maths w. Calc.	Geography
5	Biology	History	**Chemistry**	App. Maths	Biology	Maths w. Calc.	Physical Ed.	History
6	Economics	**Chemistry.**	Biology	Geography	Geography	History	Geography	Classical Stud.
7	Geography	Physical Ed.	Geography	History	**Chemistry**	**Chemistry**	Biology	Maths w. Calc.
8	Liberal Studies	Physics	History	Physics	Economics	Economics	**Chemistry**	**Chemistry**
9	Addtl. Maths.	French	Physical Ed.	Art History	Physical Ed.	Classical Stud.	Economics	Economics

Retention Rates

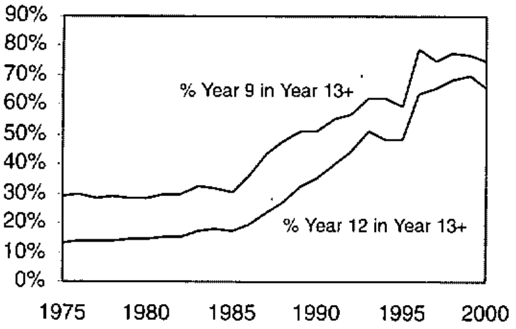

Figure 4. Retention Rates from Form 3 (Year 9) and Form 6 (Year 12) to Form 7 (Year 13) - 1975-2000.

The percentage of students carrying on from Year 9 and from Year 12 to Year 13 is shown in Figure 4. Both retention rates have increased greatly since 1986, but now seem to be levelling off. The percentage of students carrying on from Year 12 to Year 13 in chemistry and physics are shown in Figure 5. In the 1970s about 45% of students studying chemistry in Form 6 (Year 12) continued studying chemistry in Form 7 (Year 13). The retention rate for physics was poorer – less than 40%, although this is probably due to the larger number of students studying physics in Form 6. The retention rate for chemistry is now about 70%, but it appears that physics may be retaining a greater percentage than chemistry, particularly amongst males. For both subjects the retention rate is poorer for females. The retention rate for biology is 74%. Of the students studying Form 5 science in 1974, 27.8% went on to study chemistry in Form 6 in 1975. The retention rate from Form 5 science was 26.3% from 1984 to 1985. For 1999 to 2000 it was 23.6%. In 1975 the total Form 6 class was 52.9% of the previous year's Form 5. In 2000 the corresponding figure was 84.8%. Retention rates moving from Year 11 to Year 12 appear to be less than desirable. Because students choose to study science subjects, particularly chemistry, for the rest of their time at high school at the end of Year 11 is one reason why the focus of the University of Canterbury Science Outreach program is Year 11 students.

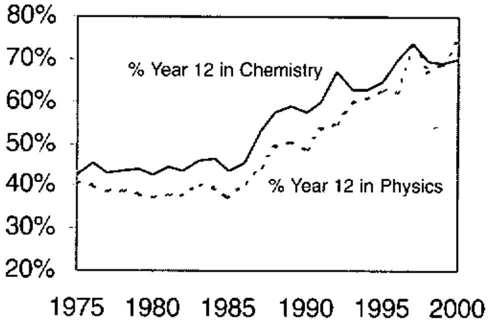

Figure 5. Retention Rates from Form 6 (Year 12) to Form 7 (Year 13+) for chemistry and physics - 1975-2000.

Conclusions

The statistics detailed above show some encouraging trends, such as the increase in the percentage of students entering high school, who eventually study chemistry in Year 13, and the gender balance in chemistry classes. However there are other matters of concern. Chemistry is dropping in the popularity stakes. The proportion of students who studied science in Year 11 who study chemistry in Year 12 is not increasing. At the University of Canterbury we are finding many students drop chemistry in Year 13 but then find they are required to study it at university. New Zealand is not alone in seeing a decline in secondary school participation in science. In Australia a combined campaign[5] "Rebuilding the Enabling Sciences" was launched in 2001. The same naive linear extrapolation as that made in Australia, has no students studying chemistry in Year 13+ in 2010 in New Zealand! The solution to these problems will not be easy but anything that chemistry professionals can do to help chemistry teachers will be useful.

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Nanotubes In A Nutshell

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Until recently it was believed that carbon science was a mature field, but the discovery of C_{60}, a new molecular form of carbon, by Smalley, Curl and Kroto in the early 1980s acted as a spur to further exploration. Theoretical predictions that carbon could form not only C_{60} but also elongated, tubular shapes were confirmed in 1991 by Sumio Iijima's observations of perfect carbon tubules.[1] Computer simulations had predicted that these molecules would have a variety of interesting and unusual mechanical and electronic properties, and confirmation of their existence sparked a wide interest within the scientific community.

Carbon nanotubes consist of one or more seamless cylindrical shells made of hexagonal graphitic sheets, closed by the inclusion of twelve pentagonal rings, six at each end. The tubes can be termed helical, as the hexagonal planar network that makes up their body can exhibit a spiral conformation; three examples[2] are illustrated in Figure 1. Nanotubes can be categorised according to their helicity, and also according to the number of concentric shells of which they consist. Single-walled nanotubes are made up of only one cylindrical graphitic shell and they are frequently formed as ropes, that is tightly packed bundles of aligned tubes, during their synthesis. By comparison, multi-walled nanotubes consist of two or more layers arranged like a Russian doll. The spacing between each of the concentric shells is 0.34 nm, a value very close to that for the interlayer spacing of graphite. However, the layers of a nanotube may be rotationally disordered with respect to each other compared to the repetitive ABAB ordering found within graphite. This variation in the helicity is believed to be necessary to obtain the best possible fit between successive shells.[3,4]

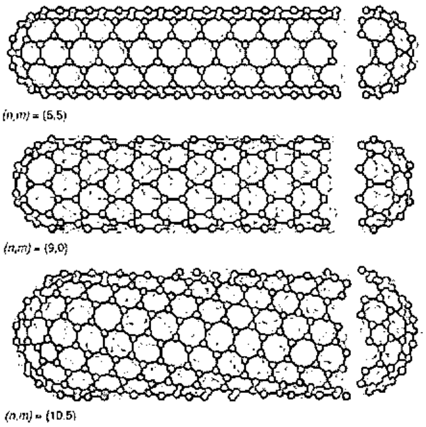


Figure 1. Single-walled nanotubes of varying helicities – see ref. 2.

Carbon nanotubes can be synthesised in a manner very similar to that of C_{60}, that is, through use of an electric arc discharge apparatus. The use of a plain graphite electrode results in the generation of C_{60} spheres, but if the graphite electrode is doped with a small weight percentage of a metal such as iron, nickel or cobalt, nanotubes are grown preferentially. Current research at Victoria University is concentrating on an alternative synthetic route known as chemical vapour deposition. Here, carbon moieties are generated at high temperatures from simple hydrocarbons such as acetylene. These undergo catalytic assembly to form either single- or multi-walled nanotubes upon vapour deposition.

The mechanism by which the nanotubes are grown has been a matter of debate for some years and complicated further by different experimental observations for different methods of growth. Proposed mechanisms have included the "scooter" mechanism which suggests that a small catalytic particle moves around the open edge of a growing tube, absorbing carbon and adding it to the growing structure.[5] By comparison. the "yarmulke" mechanism argues that a small metallic particle, anchored to the reaction vessel surface, will be covered by a graphitic cap in the first stages of the process. Further absorption of carbon by the catalytic particle will force this initial hemisphere upwards as the additional carbon is extruded as a cylindrical tube underneath and adjoining to it.[6] Recent experimental work has suggested that it is this second mechanism that is a more correct representation of the process. Isotopic labelling of carbon nanotubes, in which alternating flows of ^{12}C and ^{13}C were introduced during the growth process, has shown that after initiation additional carbon is added to the bottom of the tubes while the previously grown segment moves upwards and away from the catalytic particle.[7]

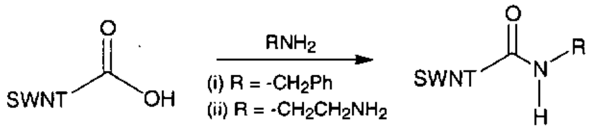
The physical properties of carbon nanotubes are such that the tubes have high strength and extraordinary flexibility and resilience. Experimental measurements of the elastic modulus have returned values greater than 10 TPa for single-walled nanotubes,[8] a value some 50 times greater than that of 1040 carbon steel alloy. Simulations have predicted that nanotubes will be able to sustain extreme strains of up to 40% in tension, and that also they will be able to distort hugely without fracture under bending, torsion or axial compression.[9] The reason these tubes can withstand such great stresses is that the hexagonal network that makes up their body can distort reversibly.

Nanotubes also display unusual electronic properties. Theoretical predictions of the electronic conduction process concluded that the conductance of a tube depended on the diameter and helicity of the tube concerned, where some nanotubes are predicted to have a conductivity on a par with a metal as opposed to all others which are semiconducting.[2,9] The majority of experimental work carried out to date has supported these predictions, but recent work has shown that the electronic properties of carbon nanotubes are extremely sensitive to their chemical environment.[10] Exposure to different environments such as oxygen or ammonia atmospheres, dramatically influences the properties of the nanotube, such as the electrical resistance.

Despite this apparent variability in electronic behaviour, it is believed that carbon nanotubes will have wide-ranging future applications based upon their unusual combination of electronic and mechanical properties. These applications range from quantum wires and heterojunction electronic devices to composite materials, nanoprobes, energy production and storage devices, chemical sensors, and flat panel displays. It is in the field of flat panel displays that carbon nanotubes are closest to mass commercialisation. Prototype models have been made using the nanotubes as an intermediary, focussing electrons onto a surface where they react with a fluorescent material to produce light for picture displays.[11] Due to the very small size of the nanotubes it is hoped that the finished product will be smaller than previous flat screen displays.

While some of the applications outlined above can use the nanotubes as prepared, several of them, in particular sensor applications, require functionalisation of either the sidewalls or the tip of the nanotube. Modified nanotubes can be used as robust atomic force microscopy probes, providing chemically sensitive imaging with nanometer scale resolution. One approach to chemical modification is to selectively oxidise the nanotubes at the more reactive sites on the caps at each end, resulting in an open tube terminated with carboxylic acid ($-CO_2H$) groups. These carboxyl groups are then coupled to amines, as in Scheme 1, to create probes with basic or hydrophobic functionality. By measuring the adhesion force between these modified nanotube probe tips and the surface being studied it is possible to undertake chemically sensitive imaging which could be used to study binding in biological and chemical systems.[12,13]

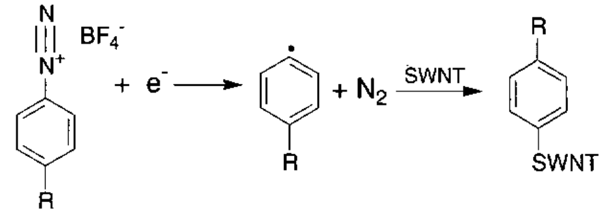
Scheme 1



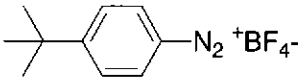
SWNT = single-walled nanotube

A route has also been developed for the non-covalent functionalisation of the sidewalls of single-walled carbon nanotubes. It involves the use of a bifunctional molecule, the succinimidyl ester of pyrene-1-butanoic acid of Scheme 2, where the pyrenyl group interacts strongly with the sidewalls of a nanotube via π stacking as shown in the Scheme. Both proteins and smaller biomolecules can be immobilised on the functionalised nanotubes through the nucleophilic substitution of *N*-hydroxysuccinimide by an amine group on the biological molecule, resulting in the formation of an amide bond. This has potential application in the field of biosensing, as immobilisation of various biological molecules onto these nanotubes can be achieved with a high degree of control and specificity.[14]

Scheme 3



Another important driving force behind current research into the functionalisation of nanotubes is the desire to enhance their solubility, thereby facilitating the manipulation and processing of these materials. For example, this could allow for easier composite preparation. One such method for functionalisation involves the electrochemical reduction of aryldiazonium salts to give a radical as is illustrated in Scheme 3. This method had previously proved successful for the covalent attachment of an aryl radical to both highly ordered pyrolytic graphite and glassy carbon electrodes; it proved applicable to carbon nanotubes as well. Solubility tests performed on carbon nanotubes derivitised with such diazonium salts showed that those tubes functionalised with the *t*-butylphenyl moiety **1** had considerably improved solubilities in organic solvents compared with the pure nanotube. It is claimed that the bulky *t*-butyl group could inhibit the close contact necessary for aggregation or "roping" of the nanotubes.[15]



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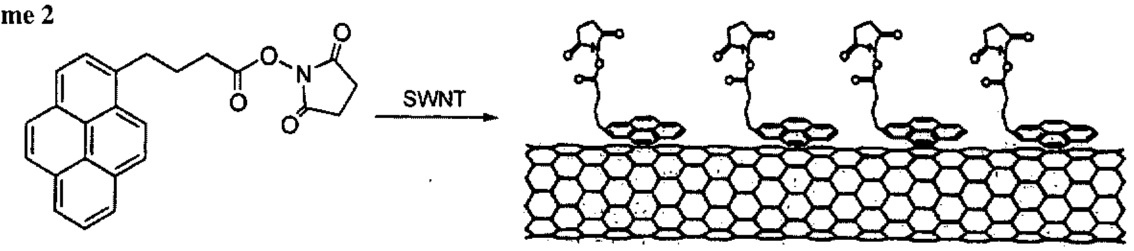
Research in the field of carbon nanotube functionalisation is currently under way in New Zealand, as are other projects concerning the synthesis, properties and applications of these unusual molecules. Interest is spread throughout the country, with groups at Massey University, Industrial Research Ltd., Victoria University and the University of Canterbury all developing programmes of research. The work of John Abrahamson (Professor of Chemical Engineering at the University of Canterbury) is in fact very long standing, to the extent that, almost certainly, he made and characterised the first carbon nanotubes in 1979.[16] However, this groundbreaking work preceded the discovery and acceptance of C_{60}, which made the scientific community receptive to new possibilities in carbon chemistry, and paved the way for Iijima's work in 1991.

Current research at Victoria University of Wellington (in collaboration with IRL and other research groups overseas) is concentrated on both improving methods of synthesis, and the fundamental physics of the materials. Work is in

Scheme 2



progress on developing methods to generate aligned fields of multi-walled nanotubes for sensor applications, and on the design of catalysts for the growth of single-walled nanotubes. Electron micrograph images of both of these types of nanotubes are shown in Figures 2 and 3, respectively.

Since 1991 interest in both the pure and applied science of carbon nanotubes has increased dramatically. The current work of physicists and chemists worldwide in understanding the physical and electronic properties of these materials will have a profound impact on developing technologies, with predictions ranging as high as the replacement of all silicon by carbon nanotubes in the future, and the construction of a nanotube-based space elevator! Such ideas make the field of nanotube research a very interesting one to watch.

Figure 2. A field of 10 μm high multi-walled carbon nanotubes synthesised at Victoria University.

Figure 3. A 4 nm diameter single-walled nanotube synthesised at Victoria University.

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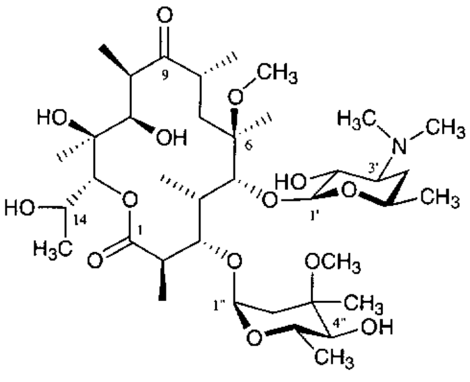
How To Make Money Out Of Fine Chemistry

Barry Dent
B Dent Global Limited, Lower Hutt, Email: info@bdg.co.nz

It is a bit strange that the owner of a four-person chemical firm with turnover only in 7 figures gets asked to dispense wisdom on "how to make money out of fine chemistry".

The fact that I am doing so implies disrespect for the activities of our larger chemical, petrochemical, biotechnology and research enterprises, but none is intended. This article is an attempt to identify the factors which enabled my firm to achieve relative success in a short time, whilst the events are still clear enough in my mind to be of some use to others contemplating start-up. The purpose in putting them on paper is so that *you* may analyse your own situation, particularly if you have aspirations to start your own business. My challenge to you is to think about the success factors I talk about, and apply them to your situation, or indeed to think of some other advantage that you may have. This approach worked when I spoke to the Wellington Branch recently on the same subject, and the invitation to write this article arose from that talk.

These statements appeared[1] recently on the history of the fine chemical industry in Canada: "Reid [a Vice President at PEI biotech BioVectra] notes that the early 1970s were bleak times for chemistry graduate students in Canada. 'Raylo [founded in 1963 by the late R.U. Lemiuex] and Dalton Chemical Laboratories [founded in 1970 by J. R. Duffy] were both started by entrepreneurial professors who were able to employ their Canadian students,' he says. 'They showed that you can make a living by being a chemist without leaving the country.' Kubela [first President of the fine chemicals firm Torcan] tells a similar story. When he finished his PhD in 1971...'all of my friends were jobless. ..... No one dreamed of going into industry because, with the exception of Delmar [formed in 1941 in Quebec], it didn't exist.' " Does any of this sound familiar to you? How about this - "'People in Canada don't see science as sexy. They want to get into computers or business,' [P Pekos, President of Dalton Chemical Laboratories] says."



Made by us - a metabolite of clarithromycin prepared by biotransformation. A known literature compound.

The article[1] goes on to say that Canada now has a pretty vibrant fine chemicals industry. By any standards, we don't. I reckon we are about where Canada was 25 or 30 years ago. Guess what- it's not the Government's fault. It's yours and mine. ***There is no parallel universe of smart people in New Zealand***. We are the ones who have to make it happen.

The firm I'm going to use to analyse some critical success factors is my own, and it goes under the modest and self-effacing name of B Dent Global Ltd. We are at the Gracefield Research Centre in Lower Hutt, and have four PhD scientists and 200 square metres of labs. We make stable isotope-labelled compounds and drug metabolites on the milligram to gram scale for the bio-analytical industry, and also buy and sell chemicals, particularly the Cerilliant range of forensic reference standards. Some 94% of sales are overseas, mainly the United States. We've been in business six years. The following critical success factors are those, which I think have applied to my own business, but they are definitely not the only things to worry about getting right.

Working at an interface between two disciplines

After I returned to New Zealand in 1986 with some organic chemistry skills, the first person prepared to give me a job was Dr Stuart Dickson, Toxicology Section, Chemistry Division, DSIR. Stuart had already recognised that a combination of analytical and synthetic organic chemistry was required to take full advantage of the relatively new mass spectrometric technique called isotope dilution.[2] In this technique, a stable isotope labelled version of an analyte is used as its internal standard. The close physicochemical similarity of analyte and internal standard means that the internal standard is almost ideal, and the wizardry of the mass spectrometer makes it possible to distinguish between the two. Few labs could utilise the technique, because the analysts couldn't make the standards, and the organic chemists were off doing something else. Stuart employed me as an analyst, where I was able to learn about the problem, and as a synthetic chemist where I could implement his solution.

This was all before formalised funding mechanisms beyond head office bulk distribution existed in government science. It took Dr Terry Manning to redirect some of the forensic chemistry money, derived at least in part from the Police, to the project. I was to try to do enough in the analytical lab not to let the side down, and to spend time on synthesis with the hope of a payoff later in improved accuracy, precision, and productivity for the toxicology lab. From 1987-1992, we got together labelled standards for nearly all of the analytes that were being encountered in numbers in casework, and we think that the hoped-for benefits did accrue enough to justify the time spent. Today, Stuart Dickson and his team at ESR are still using the compounds, we are still making new ones for them, and the ESR lab remains at the forefront of uptake of the isotope dilution technique, which has gone on to become the compulsory confirmatory method of analysis for many analytes in some jurisdictions. Terry Manning is now an owner of successful Seaview-based analytical firm ELS.

Take-home message: intrapreneurs - latch onto a visionary in a field which has not been exploited, get the project supported by your managers, and try not to stick too rigidly to the job you think you were educated for.

Useful first step: make a friend in a different part of your company.

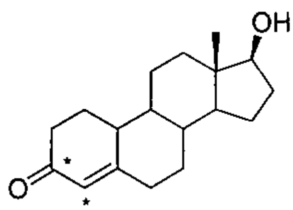
Recognising gaps in your knowledge and doing something about it

My parents are from the first generation to have grown up after the Depression, and rightly they value the benefit of a stable long-term job. The universities taught that if you were smart you stayed at the university, and if you were not quite so smart you worked for the Government (what else were they to do?). Chemical industry, self-employment and business ownership were therefore foreign to me.

Dr David Bibby at DSIR Chemistry Division sent me on a course about business planning, with the idea to apply my chemistry project to the coursework. Geoff Todd was involved with the course, and he asked me at the end of the course if I wished to take the project private. I thought this was an extraordinary thing to suggest given that Geoff worked for Head Office, and I was uncharacteristically stuck for a smart answer. The course told me about Marketing (finding out what your customers want and finding a way of getting it for them profitably), how to do budgets, and how to extract money from banks. Today, David and Geoff work for IRL, where one of the things they do routinely is spin off new high-tech companies.

Take home message: new businesses fail not because of the lack of technical skills, but because many technicians don't have a clue about marketing or money. People are queued up three deep to help you, maybe even your own managers.

Useful first steps: go to a free seminar by one of the entrepreneurs who run those "business oriented self-improvement courses", and do not resist too strongly their pitch for the weekend version; buy a book[3] on how to run small businesses.



Made by us - Nandrolone-$^{13}C_2$. A known literature compound prepared to help a client shed light on the "endogenous nandrolone" controversy.

Doing it the hard and expensive way

How many intrapreneurs have you heard say "I could just walk out of here and set up on my own. They couldn't stop me!" If you are working for a company, using their resources and drawing a salary from them, then the intellectual property you develop in work time belongs to them. If you want to take it private, then they have to agree.

I first discussed a buyout with Dr Gordon Leary, DSIR Chemistry Division Director, in 1992. Gordon was interested, but did not really have the mandate. After the science restructuring that saw CRIs created, my little project became a joint venture between IRL and ESR, whilst I worked for IRL. The CRIs were freer to pursue opportunities like this one, and because the project had become less research-oriented and more a production line, they were willing to sell. Dr Doug Crump at IRL was the person I dealt with most, and he was able to negotiate a sale that gave adequate recompense to the government, but which did not cripple me from the 1996 start. Because I'd acted in an open way, IRL was willing to help with renting me premises, access to instruments, library membership, and even a part-time job for a few months.

Take home message: New Zealand is a small place, and it is better to make friends than enemies. The people who give you a job deserve credit for the intellectual property you generate.

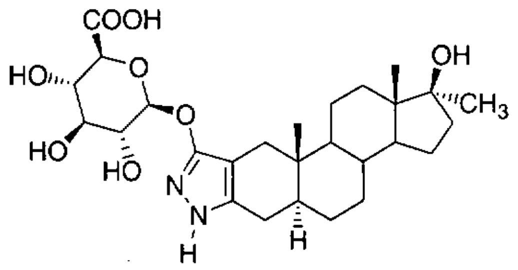
Useful first step: if you are interested in a buyout, tell the boss.

Keeping the financiers on-side

The prevailing "wisdom" at the time was that high street banks were nasty places that did not lend money to start-ups. What I could do with the banks was demonstrate some previous self-discipline with personal finances, and go to them ahead of time with a comprehensive business plan. I asked two banks for the money and both offered.

Take home message: banks, rich uncles, private equity investors will all be interested in your proposition if you can show a record of prudence, and a map for the future.

Useful first step: send your bank a personal balance sheet and go and meet the manager.



Made by us- 3′-hydroxystanozolol glucuronide. A human metabolite of stanozolol prepared for the Sydney Olympics by chemical and enzymatic means. Unpublished.

Starting with some kind of "guaranteed" income

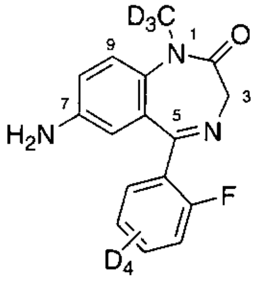
Stuart Dickson and I started selling our leftover compounds whilst I still worked for the government. We targeted other forensic toxicology labs through an initially fortuitous relationship with a respected foreign distributor. Many start-ups fail whilst still waiting for the first order, or through having such uneven cash flow that they cannot pay the bills. The relatively modest, but regular, income from our distributor was the certainty that I needed to start up, and it was worth paying for. Today, we still have that first client on board.

Take home message: to get some initial cash flow, it's a good idea to buy into something that's already running, or to dip your toe into a new venture by keeping the day job to begin with.

Considering government assistance

After I'd hung out the shingle, there were lots new things to cope with - debt, no salary, and no one else to blame. It was quite a step to hire my first employee, since I wanted to offer long-term prospects rather than "we've had a bad month, goodbye". FRST, through Technology New Zealand, offered a postdoc to our first employee, which paid his wages for a significant portion of the initial term. I found I could spend time on marketing, quote for new work (including a large contract to supply standards to the drug testing programme at the Sydney Olympics), and develop a bit of confidence. The subsequent hires, all on our own money, were a much less traumatic prospect, and we are now able to grow steadily. Today, the government subsidy has been paid back many times over in company tax, and we have four Kiwi chemists in work, in chemistry. ***Take home message:*** even if it does not fit with your worldview, be pragmatic and take a subsidy if they want to give you one. When you don't need it any more, let someone else have his or her turn.

There were some other critical success factors for us, but they are tied up in our ***marketing plan***, and that is the final part of this story. Have a look at how we have taken the fine chemicals universe and a myriad of possible competitors, segmented the market, and identified our unique selling propositions. Think about what type of marketing plan you are going to develop around your own good technical idea, and go for it.



Made by us - 7-aminoflunitrazepam-d_7. An 8-step synthesis of an internal standard for analysing a drug used by date rapists. Unpublished.

The Marketing Plan

Depending on whom you listen to, custom synthesis of fine chemicals is worth $US20 billion a year, with 300-1000 firms in the game. Let me pick a few things to show you how we get a piece of that market:

Custom firms elsewhere can have a lot of problems hiring top chemists in competition with, say, the big pharmaceutical companies. Because we have a relatively undeveloped chemical industry, a small player like us has a chance of getting the best people. Look at our line-up: Drs Dennis Page, Neil Beare and Susan Maddock all have top New Zealand degrees behind them, and they joined us after further education in the labs of Beckwith at ANU, Hartwig at Yale, and Sharpless at Scripps, respectively. So, that should let us undercut our competitors and knock out some simple molecules quickly, right? I don't think so! We decided to reduce our competition by going for the very difficult targets, where there is little or no literature, where other firms will not quote because they may not have staff qualified to the level of our people.

I also had experience in a particular area of chemistry, so we looked for customers who were interested in reference standards - namely the bio-analytical departments of contract research organisations. These people are contributors to the drug development pipeline and they require lots of different chemicals on a small scale, and this does not suit vendors who have large capacity. It suits us, because chemistry on a sub-gram scale lowers capital requirements, and removes any logistical difficulties associated with being where we are. Our clients are used to dealing with small firms, and it's not too much of a leap to get them to look at New Zealand. We reward them by passing on some of the advantages of a low Kiwi dollar, but one of my aims is to construct a firm that is competitive because of its abilities rather than some transient exchange rate advantage. We price, therefore, on value to the customer, rather than by reference to the historical costs of doing science in New Zealand. This enables us to drive up wages for our people, which of course feed back into our ability to hire the best. If we were to operate by being a cheap place for people to buy chemicals, it would last precisely until the next cheapest place came along. By specialising in the top end, we can be different from all that.

The Internet as part of the Marketing Plan

The Internet has been important for us, not so we can have a trendy website and feel good about it, but as a considered component of the marketing mix. The Internet allows small firms to punch above their weight as you know, but to get noticed in the clutter, you need a good offer. On our site, we offer free searching for the type of chemicals we know about. In response to an enquiry, we'll look everywhere we know to identify an existing supplier, and we'll tell the enquirer where to find the chemical without trying to take a cut. If we can't find the chemical, then we will offer to give them, within a day, a quote for its synthesis. The free search would appear not to have a benefit to us most of the time, but the search is precisely what we need to do behind the scenes before quoting any job. After all, there would be nothing worse than quoting an expensive custom synthesis, only to discover later that the client could have got it for $200 from a catalogue. So, we take a necessary behind-the-scenes chore, present it as the benefit that it is, and attract a certain portion of the site visitors into a well-considered custom purchase. We require minimal site traffic to convert enough prospects to customers. Seem too simple to bother with something like that? One client, who started out with a series of free enquiries, is now working with us very closely and is worth over $1 million to us.

Conversely, the Internet is also an essential supply line for us. Clients often have very tight deadlines - if we can save them time it means we are more likely to get the work. Through our searching strategies we can buy advanced intermediates for our syntheses online (meaning shorter syntheses than may be quoted by those solely reliant on catalogue chemicals), and also obtain useful chemical information. This, combined with our membership of the most responsive library in the country, shortens lead-time and helps us reach our target of overnight quotations.

Conclusion

In conclusion, we have been able to take a relatively simple chemistry idea, and turn it into a nice little business, giving gainful employment to our scientists, here. There was nothing complicated about the implementation. Marketing principles are transferable from the corner dairy to, well, our corner dairy, to your next idea. Good luck!

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Email: am.brimble@auckland.ac.nz
Website: www.conference.canterbury.ac.nz/icos14

15-16 July 2002
First Symposium On New Zealand-France Collaborative Research In Geosciences
Website: http://www.gsnz.org.nz/gsfr.htm

21-25 July 2002
INTERACT 2000 Conference
Venue: Sydney, Australia
Contact: Jane Yeaman
Tulips Meeting Management
P O Box 116 Salamander Bay
NSW 2317, Australia
Tel: (+61-2-)-49842554
Fax: (+61-2-)-49842755
Email: interact@pco.com.au
Website: www.pco.com.au/interact2002

23-24 July 2002
Water: The Life Blood Of New Zealand - MAF/MFE Conference On The Allocation Of Fresh Water
Venue: National Library Auditorium
Molesworth Street, Wellington
New Zealand
Contact: Catherine Ibell
Royal Society of New Zealand
Tel: (04)-470770
Email: catherine.ibell@rsnz.org
Website: http://www.rsnz.org/secure/events/water.php

CONFERENCES & SEMINARS

11-15 August 2002
Fourth World Congress On Alternatives And Animal Use In The Life Sciences
Venue: New Orleans, United States of America
Contact: dpease@hsus.org
Website: http://www.worldcongress.net

12-15 August 2002
New Zealand Plant Protection Society 55th Annual Conference And Biosecurity Symposium
Venue: Centra Hotel, Rotorua, New Zealand
Contact: lois.mckay@agresearch.org.nz

24-28 August 2002
The 20th International Australasian Winter Conference On Brain Research (AWCBR)
Venue: Queenstown, New Zealand
Website: http://www.awcbr.org

25-30 August 2002
Gondwana 11, Correlations And Connections
Venue: University of Canterbury, Christchurch, New Zealand
Contact: Professor Bryan Storey, Gateway Antartica
Website: http://www.anta.canterbury.as.nz/gondwana

1-4 September 2002
QMB2002. The 12th Annual Queenstown Molecular Biology Meeting
Venue: Queenstown, New Zealand
Website: http://www.qmb.org.nz

2-3 September 2002
Nutrition Society of New Zealand Conference - Food For Thought
Venue: Massey University, Albany Campus, Auckland, New Zealand
Contact: Elizabeth Stewart
Email: e.stewart@massey.ac.nz

4-6 September 2002
The New Zealand Dietetic Association National Conference: "From “Pasture to Plate"
Venue: Palmerston North, New Zealand
Contact: Mandy Wynne
New Zealand Dietetic Association
Tel: (04)-4790419
Email: nzda@paradise.net.nz

8-12 September 2002
52nd RACI Cereal Chemistry Conference “From Grain To Grain”
Venue: Hotel Grand Chancellor
Christchurch, New Zealand
Contact: Belinda Jeursen
Crop & Food Research
Private Bag 4704
Christchurch, New Zealand
Phone: +64-3-3256401 ext 3597
Fax: +64-3-3252074
Email: jeursen@crop.cri.nz
Website: www.crop.cri.nz/conferences/raci/

15-20 September 2002
12th Australasian Plant Breeding Conference
Venue: Perth, Australia
Website: http://www.congresswest.com.au/PB/

24-27 September 2002
3rd World Congress On Emulsions
Venue: Lyon, France
Contact: CME
50 Place Marcel Pagnol
92100 Boulogne-Billancourt, France
Tel: (+33-1-)-47617689
Fax: (+33-1-)-47617465
Email: alain.lecoroller@wanadoo.fr
Website: www.cme-emulsion.com

29 September - 3 October 2002
ComBio2002
Venue: Darling Harbour Convention Centre
Sydney, New South Wales, Australia
Contact: Scientific Program: Philip Kuchel
Email: p.kuchel@biochem.usyd.edu.au
Registration/Exhibition: Sally Jay
Email: asbmb@bigpond.net.au
Phone: (+61-8-)-8362 0009
Fax: (+61-8-)-8362 0038
Website: http://www.asbmb.org.au/combio2002

2-3 October 2002
ICOLA'02 The First International Conference On “Opto-electrotechniques And Laser Applications
Venue: Jakatra, Indonesia
Contact: Suganda Jutamulia
Email: suganda@blueskyresearch.com
Website: http://www.geocities.com/icola2002

7-8 October 2002
New Zealand Energy Conference - The Way Forward
Venue: Duxton Hotel, Wellington
Contact: energyconference@crl.co.nz

20-25 October 2002
28th Meeting Of The Federation Of European Biochemical Societies
Venue: Jerusalem, Israel
Contact: Conference Secretariat
28th International Conference
P O Box 50006, Tel Aviv 61500, Israel
Website: www.kenes.com/febs

26-28 November 2002
“Microbes And Molecules 2002”
The annual combined meeting of the New Zealand Microbiology Society, The New Zealand Society for Plant Physiology, and the New Zealand Society for

Biochemistry and Molecular Biology.
Venue: University of Canterbury, Christchurch New Zealand
Website: www.conference.canterbury.as.nz/microbes2002/

29-30 November 2002
The 37th Annual Conference Of The Operational Research Society Of New Zealand
Venue: The University of Auckland Auckland, New Zealand
Contact: Matthias Ehrgott
Email: m.ehrgott@auckland.ac.nz
Website: http://www.orsnz.org.nz

2-6 December 2002
Geological Society Of New Zealand's Annual Conference "Northland 2002"
Venue: Forum North, Whangarei
Website: http://www.gsnz.org.nz/gsco.htm

3-6 December 2002
NZ Hydrological Society Symposium "The Easy Water Is Gone: Making The Most Of A Scarce Resource"
Venue: Blenheim, New Zealand
Contact: cmi@marlborough.govt.nz
Website: http://www.hydrologynz.org.nz/society-conferences.html

5-8 December 2002
The NZ Association For Research In Education Annual Conference
Venue: Massey University, Palmerston North New Zealand
Contact: nzare-conf02@massey.ac.nz

8-11 December 2002
19th International ASCILITE (Australian Society for Computers in Learning in Tertiary Education)
Website: http://www.unitec.ac.nz/ascilite

6-10 January 2003
10th International Symposium On Deep Seismic Profiling Of The Continents And Their Margins
Venue: Taupo, New Zealand
Website: http://www.gns.cri.nz/news/conferences/seismix2003

24-26 March 2003
Fifth International Conference On Electromagnetical Wave Interaction With Water And Moisture Substances
Venue: Novotel Hotel, Rotorua, New Zealand
Contact: k.thankur@irl.cri.nz

24-28 March 2003
7th International Conference On Southern Hemisphere Meteorology And Oceanography
Venue: Wellington, New Zealand
Contact: Meteorological and Marine Sciences Societies

7-11 July 2003
Fifth International Conference on Industrial and Applied Mathematics
Venue: Sydney, New South Wales, Australia
Website: http://www.iciam.org

1-5 December 2003
3rd International Wildlife Management Congress
Venue: Christchurch, New Zealand
Website: www.conference.canterbury.nz/wildlife2003

Waters Automated Methods Development System

Introducing the Waters Automated Methods Development System, the premier HPLC system for scientists who need to quickly develop high quality, robust methods. The Waters Automated Methods Development System combines the precision, accuracy and reliability of an Alliances System with the ease and flexibility of the new Empower data management software, plus the enhanced capability of automated methods development. Just load your samples, input your method criteria and let the system's LC decision algorithms do the work in developing your methods.

Contact: Alphatech Systems & Co. Ltd
P O Box 37583 Parnell, Auckland
Phone: (09) 3770392, Fax: (09) 3098514
Email: sales@alphatech.co.nz
circle number 21 on the reader reply card

Waters Empower™ Software

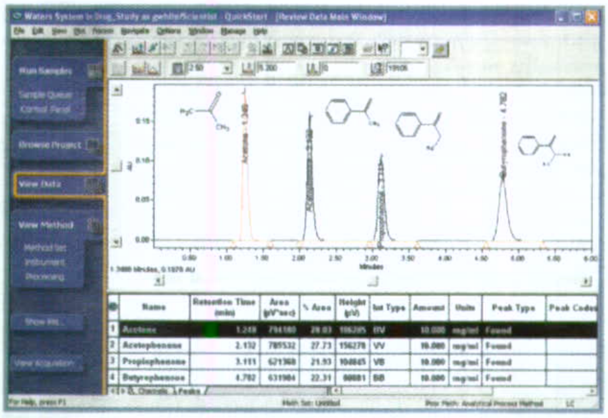
For laboratories that need to maximize productivity, minimize downtime and maintain regulatory compliance, Waters introduces Empower software. Built upon the powerful Millennium software, Empower software allows you to focus on running samples, generating results and creating meaningful reports that are easy to share. Enhanced 21 CFR Part 11 compliance capabilities take data integrity, security, audit trails and reporting to new levels. The embedded Oracle relational database stores and retrieves your chromatography data quickly and easily. Instrument control includes Waters Alliance Systems, Waters detectors, including the ZQT11 Mass Detector and other third-party instruments. Empower Software is scalable from workstations up through enterprise-wide networks. Empower Software makes everyone in your lab more productive. Now chemists can work with the interface most appropriate for their laboratory.

QuickStart is a new user interface based upon a single window construct. QuickStart highlights where the user is within the application at all times, presenting required functionality to allow chemists to run the assays they need without confusion.

Pro user interface is perfect for system administrators or anyone who needs total control and access to all software functions.

Web user interface makes accessing information for remote users easy via the World Wide Web or an intranet.

Open Access interface is for walk-up users. It lets them select the method and the number of samples they need to run and then start them with the click of a mouse.



Contact: Alphatech Systems & Co. Ltd
P O Box 37583 Parnell, Auckland
Phone: (09) 3770392, Fax: (09) 3098514
Email: sales@alphatech.co.nz
circle number 22 on the reader reply card

Versatile Connectors For Laboratory Tubing

Omnifit's inert colour-coded connectors provide a simple, versatile system for connecting different types of laboratory tubing instantly, including PTFE, glass, silicone and stainless steel. Applications include sampling, stream splitting, mixing and fluid line interconnection.

Manufactured from inert PTFE, the connectors have zero dead volume and are available in bore sizes of 0.8, 1.5 and 4.7mm. Tubing sizes between 1 and 11 mm can be connected using either O-rings or PTFE cones, and adaptors are available to allow connection directly to luer fittings and flexible tubing. No tools or 'plumbing skills' are required to use the connectors and colour coding helps to simplify the process. Starter kits are available for people setting up or expanding their existing laboratories or for laboratory workers wanting to familiarise themselves with the connectors.

Contact: Sue Barton, Omnifit Ltd
2 College Park, Coldhams Lane, Cambridge CB1 3HD, UK
Phone: (+44-1223)-416642, Fax: (+44-1223)-416787
Email: sue.barton@omnifit.com
Internet: www.omnifit.com
circle number 23 on the reader reply card

Thermo Finnigan Announces The New Focus Gas Chromatograph

Specifically targeted for routine quality control and high productivity laboratories, the Focus GC is a single-channel gas chromatograph, available in a unique SSL/FID configuration. Conceived and built around the "core" of the Trace GC's high quality hardware and unique features, and incorporating new, best of breed electronics, this instrument is considered the reference for precision and accuracy of results as well as a standard for ruggedness in QA/QC and high throughput environments.

Standard Features:

Compact size
Small footprint for bench space optimization.

Wide oven
The accessibility of a wide oven with front opening, permits easy installation of capillary columns mounted on standard diameter cages.

Optimized user interface
Permits easy control of the main functions of the GC but preventing access to the more critical parameters of the method from unauthorized personnel. In line with the requirements of QA/QC environments.

Automatic column characterization
Automatic measurement of the effective column's resistance for exceptional column-to-column and instrument-to-instrument Retention Time reproducibility at no additional cost.

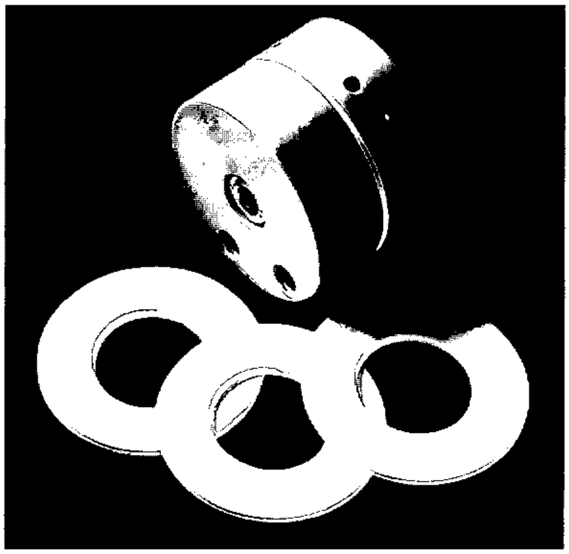
Leak check
Automatic leak check function for routine system control.

Additional instrument control
Real-time clock programming (with auto-start), instrument start-up diagnosis, real-time system diagnosis, on-line help on each parameter, logbook with deviation records for temperature, local keyboard lock.

Contact: Alphatech Systems & Co. Ltd
P O Box 37583 Parnell, Auckland
Phone: (09) 3770392, Fax: (09) 3098514
Email: sales@alphatech.co.nz
circle number 24 on the reader reply card

Bubble Trap Prevents Disruption To Liquid Flow

A unique device for removing in-line gas and air bubbles from laboratory tubing is now available from Omnifit. Manufactured from inert PEEK and PTFE material, this timesaving device prevents the errors that can be caused by gas bubbles in the flow system and stops columns from running dry. It also eliminates the need for a degassing carrier buffer or eluent.



The bubble trap can be used in flow analysis systems, as a guard in liquid chromatography, for enzyme reactors and flow-through biosensors. It is pressure rated to 5 bar and has zero dead volume. One- or two-channel versions are available and membrane replacement is quick and easy.

Contact: Sue Barton, Omnifit Ltd
2 College Park, Coldhams Lane, Cambridge CB1 3HD, UK
Phone: (+44-1223)-416642, Fax: (+44-1223)-416787
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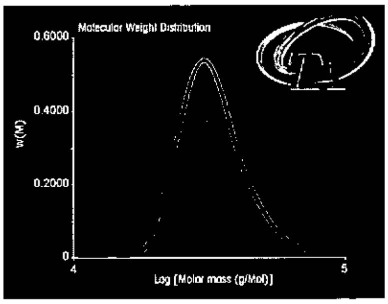
Internet: www.omnifit.com
circle number 25 on the reader reply card

TA Instruments Introduces Enhanced Polymer Library With New Molecular Weight Distribution (MWD) Software For Rheological Applications



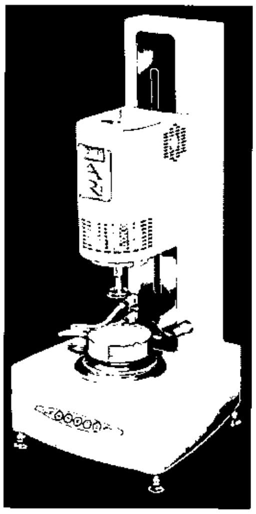
TA Instruments, Inc. has introduced the Enhanced Polymer Library, an advanced software package that provides TA Instruments AR Series Rheometers with the ability to generate polymer MWD data from readily-performed rheological measurements in a more comprehensive fashion than ever before. Available as an option for the latest TA Instruments Rheology Advantage software, the Enhanced Polymer Library was developed in collaboration with Professor J. Honerkamp and Dr. C. Friedrich, eminent researchers at the University of Freiburg, Germany. An important advance in this software is that no prior assumption is made as to the shape of the MWD curve.

The software has two parts. The first generates a linear relaxation spectrum from measured viscoelastic functions, such as storage and loss modulus. The spectrum is an intrinsic property of the polymer and cannot be measured directly. The second part generates polymer MWD data from the relaxation spectrum after removal of other relaxation modes (*e.g.*, Rouse) that do not directly affect MWD. The software contains a comprehensive library of parameters for many polymers needed to calculate MWD. These include parameters for the scaling and exponent in the zero shear viscosity/Mw relationship, plateau modulus, and entanglement Mw. Users can add parameters to the library.

Contact: TA Instruments Ltd
109 Lukens Drive, New Castle, DE 19720, USA
Phone: (+1-302)-4274000, Fax: (+1-302)-4274001
Email: info@tainst.com
Internet: www.tainst.com
circle number 26 on the reader reply card

The New AR 2000 Advanced Rheometer From TA Instruments Offers Controlled Stress And Controlled Rate Measurement, For Optimum Measuring Flexibility

Incorporating state-of-the-art technology, the new AR 2000 Rheometer features superior torque range, very low inertia, superior strain detection and excellent dynamic range.



TA Instruments, Inc. has introduced the AR 2000 Advanced Rheometer, whose Mobius Drive™ system permits state-of-the-art controlled rate and stress relaxation measurements and unparalleled control stress performance. The AR 2000 offers a wide torque range (0.1mN.m to 200 mM.m), very low inertia (50 mN.m.s^2), superior strain detection (0.04 mrad), and excellent dynamic range in frequency (1.2 x 10^{-7} up to 100 Hz) and normal force (0.01 to 50 N). It has the industry's widest range of operational modes, and its unique Smart Swap™ technology provides rapid, error-free connection of available temperature systems to the AR 2000.

Powerful, industry-leading TA Instruments Rheology Advantage software now offers even greater flexibility for modeling, and is enhanced with polymer MWD analysis capability developed in collaboration with leading scientists in the field.

Contact: TA Instruments Ltd
109 Lukens Drive, New Castle, DE 19720, USA
Phone: (+1-302)-4274000, Fax: (+1-302)-4274001
Email: info@tainst.com
Internet: www.tainst.com
circle number 27 on the reader reply card

Titration Analysis Of Metals In The ppm Range

Multitrator announces a breakthrough in the analysis of a wide range of metals in solution in the ppm (parts per million) range. Using Multitrator's exclusive thermometric titration technology, the analyst can now dispense with using expensive, delicate, short-lived and maintenance-intensive ion-selective electrodes, replacing them with a robust zero-maintenance thermometric probe. Get accurate, precise results in a few minutes. Ideal for analyzing holding tanks and ponds, tailings, dams and mine site and plant runoff.

Contact: GBC Scientific (NZ)
P O Box 68-330, Newton, Auckland
Free Phone/Fax: 0800 428 428
Email: dpayne@xtra.co.nz
circle number 28 on the reader reply card

The New Spectrolaser

The Spectrolaser™ incorporates state-of-the-art technology where a high-power laser is used to induce a bright spark (or plasma) at the surface of a material being analysed. Light emitted by this plasma is then resolved by a unique spectrometer and detection system consisting of multiple spectrographs and CCD sensors. This enables the concentrations of all detectable elements to be determined simultaneously in a matter of seconds.

The analysis method used by the Spectrolaser™ possesses several superior features when compared to other technologies capable of elemental analysis. For instance, it is sensitive to a wide range of elements, including light elements (hydrogen to carbon) that are not easily detected by alternative methods. The small amount of preparation required for analysis also enables a high throughput of samples to be maintained.

An easy to use Windows® control program enables materials analysis, comparison of data to calibration standards, file saving and the printing of reports. Advanced features include storage of multiple sets of calibration data, automatic peak assignment and deconvolution of spectra from complex materials. Once configured normal operation of the instrument simply involves presenting the sample for analysis - no further data manipulations are required.

Contact: GBC Scientific (NZ)
P O Box 68-330, Newton, Auckland
Free Phone/Fax: 0800 428 428
Email: dpayne@xtra.co.nz
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New Sterile NALGENE® Disposable Flasks For Bench Top Or Shaker Table Use

Crystal-clear, sterile, single-use PETG flasks reduce chances of cross-contamination in suspension cell culture, media preparation or storage applications.

New NALGENE Sterile Disposable Flasks, manufactured of crystal-clear PETG plastic, are offered with either plain or baffled base, making them ideal for bench top or shaker table use. A high-quality manufacturing process allows Nalge Nunc International to offer these lightweight disposable flasks at very competitive prices. All NALGENE Disposable Flasks have graduations to allow for quick volume assessment, and all are provided with a polyethylene screw closure that is leakproof when closed, but is easily opened for venting with just a quarter turn. Sterile and disposable flasks reduce the chances of cross-contamination whether used for suspension cell culture, media preparation or storage.

NALGENE Sterile Disposable Flasks are the Erlenmeyer design. Both plain and baffled base configurations are available in 250 mL, 500 mL or 2000 mL capacities. Each flask is individually packaged for ease of storage and handling.

Contact: Biolab Scientific
Private Bag 102922, North Shore Mail Centre, Auckland
Free Phone: 0800 933966
Fax: (09) 9806788
Internet: www.nalgenunc.com/flasks
circle number 30 on the reader reply card

The New Titrando From Metrohm

Metrohm Ltd proudly presents the fourth generation in automatic titrators. The titrando system is based on completely new instrumentation and utilizes state-of-the-art microelectronics and new software tools.

The titrando is the central building block of a flexible titration system, which includes the titrator, dosing systems, sample changers and components for communication and automation. What is new?

- Touch screen control with large colour display – "touch button chemistry"
- PC control for operation via a computer
- Intelligent dosing elements
- Interactive data base
- Lab link for intranet and internet
- Unique Dosino for space saving titrant delivery
- Fulfills FDA regulation 21 CFR Part 11
- USB interface for printer, PC keyboard, barcode reader.

Contact: MEP Instruments Ltd, P O Box 113125, Newmarket, Auckland
Phone: (09) 3661236, Fax: (09) 366 1235, Email: info@mep-instruments.co.nz
Internet: www.titrando.com
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KnowItAll Product Line Expands Into Analytical, Forensic, General Chemistry, And Academic Markets

Bio-Rad Laboratories, Inc., Informatics Division has announced four additions to its KnowItAll product line. These products, targeting specific market segments are the new Analytical, Forensic, ChemWindow, and Academic Editions of the KnowItAll Informatics System. "Since its inception, KnowItAll has provided powerful and fully integrated software, databases and database creation tools for users who acquire and manage multiple analytical techniques," remarked Gregory M. Banik, PhD, General Manager of the Informatics Division."The new KnowItAll editions are logical product line extensions that have been precisely tailored to the needs of analytical, forensic, general chemistry, and academic scientists." Main features in each edition:

Analytical Edition:
— Database search and retrieval tools for those who manage analytical data from one or more techniques including NMR, MS, IR, UV/Vis, Raman, and GC.
— Sophisticated reporting and drawing tools that allow the combination of analytical information from multiple techniques, tables, and more in one easy-to-generate report.
— Access to exclusive on-line community for KnowItAll users.

Forensic Edition:
— Database search and retrieval tools for those who work with forensic data, including searching tools for NMR, MS, IR, UV/Vis, Raman, and GC.
— A subscription to spectral databases, including IR databases for Paint Chips, Dyes, Pigments, Fibre and Textile Chemicals, Fibres by Microscope, Enhanced Georgia State Crime Lab, Pharmaceuticals, Steroids, Prepared and Prescription Drugs, Solvents and MS databases from NIST, NIOSH, and AAFS Toxicology Section: Mass Spectra of Drugs.
— AnalyzeIt software plug-ins to perform IR and Raman Functional Group Analysis. Simply load a spectrum and click on a peak of interest to generate a list of all functional groups possible at that position.
— Reporting and drawing tools with specially designed templates.
— Access to exclusive on-line community for KnowItAll users.

ChemWindow Edition:
— Tools for drawing chemical structures and publishing professional reports, complete with structures, spectra and chromatograms, chemical reactions, lab experiment setups, chemical engineering diagrams, data tables, and more!
— In-place editing from within MS Office programs.

The Student Edition:
— Powerful chemical structure drawing tools.
— Ability to create high-quality lab reports.
— IR and Raman functional group analysis; complete with tools designed so the student can learn how to interpret IR and Raman spectra.
— A multi-technique sample database to provide examples of cross-references spectra.
— Tutorial movies to train students on the use of the software; saving valuable classroom time.
— Complements a required academic subscription to HaveItAll IR, HaveItAll Raman, HaveItAllNMR, or HaveItAll MS.
— Affordably priced for students.

Contact: Bio-Rad Laboratories, Informatics Division
Phone: (+1-215)-3827800
Internet: http://www.informatics.bio-rad.com
circle number 32 on the reader reply card

Biotest Introduces The P3610 APC Portable Airborne Particle Counter

With the introduction of the new Model P3610 APC Portable Airborne Particle Counter, Biotest becomes the only company to offer a full line of products for air and environmental monitoring in cleanrooms. The new Model P3610 completes the Biotest product range, which includes a number of handheld particle counters, market-leading RCS Microbial Air Samplers and Contact Slides for environmental monitoring of clean manufacturing facilities.

Cordless operation and long battery life - up to four hours - make the new Biotest APC Portable Airborne Particle Counter convenient for sampling multiple locations. The P3610 stores data for up to 1,000 sample locations, and a unique name for each location - up to 22 alphanumeric characters - may be created and stored, to help make data analysis easier and more accurate. Its unique back-lit LCD touch-screen provides exceptional ease of use. The Biotest APC Portable Airborne Particle Counter measures up to six size ranges down to 0.3 µ, at a high 1 cu ft/min flow rate, and measures total particles in three concentration modes - particles/m^3, particles /L and particles/ft^3. It performs ISO 14644 and Federal Standard 209E calculations, and is easily computer-programmable. Optional sensors are available for monitoring temperature, relative humidity, differential pressure, and air velocity.

Contact: Carol Julich, Biotest Diagnostics Corporation
66 Ford Road, Suite 131, Denville, NJ 08934, USA
Internet: www.APCportable.com.
circle number 33 on the reader reply card

Bio-Rad's KnowItAll Product Line Now Offers Enhanced NMR Assignment For Both ^{1}H And ^{13}C NMR

Bio-Rad Laboratories, Inc.,Informatics Division announces AssignIt HNMR, a new software option for theKnowItAll Informatics product line, as well as a major upgrade to AssignIt CNMR. AssignIt allows chemists to add assignments to NMR databases built using KnowItAll's database building option, greatly enhancing the accuracy of their NMR spectra predictions. "AssignIt's easy-to-use interface allows you to quickly enter information into your databases such as chemical shift assignments, intensities, coupling constants, and multiplicities," remarked Victoria Rafalovsky, Bio-Rad Informatics Division Software Product Manager, "This is yet another testament to our continued commitment to providing complete and efficient solutions for NMR spectroscopists."

Key features include:
— Import a wide variety of NMR formats
— Ability to assign atoms to peaks in the experimental spectrum
— Interactive coupling calculation tool
— Automated calculation of J value within a multiplet signal
— "Find similar J" feature to find similar splitting in a spectrum
— Intuitive interface with summary view and data-entry forms to add/edit assignments
— Automated and manual peak picking tools
— Full integration with DrawIt (structure drawing) and MineIt Database Building applications
— Publication-ready reports with spectra, structure, and coupling data.

Contact: Bio-Rad Laboratories, Informatics Division
Phone: (+1-215)-3827800
Internet: http://www.informatics.bio-rad.com
circle number 34 on the reader reply card

New NALGENE® Capsule Filter Provides Sterile Filtration Of Up To 50 Litres Of Fluid

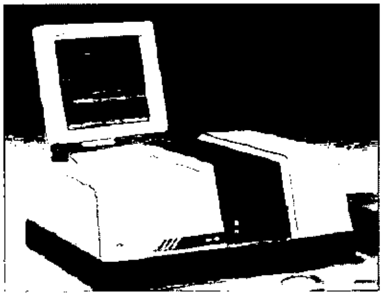
Asymmetric PES membrane, with larger pores on upstream side, allows faster flow than symmetric membranes and saves processing time.

Nalge Nunc International announces the introduction of the new NALGENE Capsule Filter with an asymmetric, low-binding 0.2 μm PES membrane. With larger pores on the upstream side and a 500 cm^2 surface area, it provides sterile filtration of 5 to 50 litres of fluid. The membrane's asymmetric design provides faster throughput than symmetric designs. Ideally suited for sterile cell culture media, the new filter is easy to use and reduces processing time, making it especially valuable in scaling up from benchtop to production or pre-production volumes in biotechnology, pharmaceutical, university research or manufacturing applications. The filter includes an attached 67 mm diameter clear filling bell on the outlet to reduce splatter and help in maintaining sterile technique. A built-in vent requires just 1/4 turn to help in maximizing recovery and minimising air locking. The filter's stepped hose barb inlet and outlet configurations fit standard 6 to 12 mm diameter tubing.

The new NALGENE Capsule Filter extends the line of NALGENE Filtration Products that includes syringe filters for smaller fluid volumes, MF75 Vacuum Filters for processing up to 1 litre of fluid, and the FastCap™ filter for processing up to 5 litres.

Contact: Biolab Scientific
244 Bush Road, Private Bag 102922, North Shore Mail Centre, Albany, Auckland, New Zealand
Free Phone: 0800 933966, Fax: (09) 9806788
Internet: www.nalgenunc.com
circle number 35 on the reader reply card

New Spectrophotometer For Accurate Measurement Of Microvolume Samples



Beckman Coulter, Inc. introduces the DU 800 Spectrophotometer, with new Windows-based PC software control. The DU's exclusive micro-focused beam technology is the benchmark for accurate measurement of microvolume samples, important for DNA, protein and enzyme mechanism applications.

"Beckman Coulter has long been the leader in micro-focused beam technology for accurate measurement of microvolume samples," explains Ron Steiner, Strategic Market Manager for Beckman Coulter. "The new software and PC control take our exclusive technology one step further with a new, highly intuitive user interface."

The DU 800 can integrate easily into a network environment. Each system comes configured with a standard set of general and life science applications; a variety of expanded software options are available separately. The DU 800 software supports compliance with 21 CFR Part 11 guidelines.

Contact: Beckman Coulter
Free Phone: 0800 442346, Fax: 0800 442347
Email: lifesciencenz@beckman.com
Internet: http://www.beckmancoulter.com
circle number 36 on the reader reply card

Radiometer Analytical Titralab Series Of Titrators Now Offer The Best Solution For Potentiometric And Karl Fischer Titrations

Accuracy, reliability and easy of use are key features. Whether you are working within the petrochemical, pharmaceutical or chemical industries, you often perform potentiometric titrations using endpoint (EP) / inflection point (IP). A dedicated Karl Fischer volumetric titrator for your water content determinations (KF analysis) is also available. By choosing Radiometer your new titrator with automated burettes adapted for various titrants, sample changer and dedicated software is a dream to use! With an 18,000 step burette motor and built-in user selectable traceability options, the Titralab series is the most accurate on the market.

TitraLab is a complete solution. When you order a TitraLab workstation, it arrives with all you need to get started immediately.

Choose from one of our range of high-performance titration managers together with a dedicated application package.

Contact: Radiometer Pacific
Phone: (09) 5741400, Email: aubreyd@radiometer.co.nz
circle number 37 on the reader reply card

Patent Proze

by Jane Calvert and Greg Lynch

Increasing Your Slice Of The Pie By Building A Patent Portfolio

There are many reasons why it is worthwhile trying to build up a patent portfolio. A single patent application/patent, while a good step in securing exclusive rights in a particular invention, might not provide a slice of pie that is large enough to carry significant commercial weight.

Each patent provides exclusive rights in a particular invention. However, often after filing an initial patent application for an invention, further improvements or developments surrounding the invention might be developed. It is for these improvements that one ought to consider filing further patent applications. For example, if a newly developed synthetic method provides significant improvements in the yield of a product and/or overcomes a synthetic difficulty, such as a difficult reaction step or use of more cost effective reagents, the commercial significance of the synthetic method increases. An effective intellectual property strategy would include pursuing a further patent application to the improved method because this might provide some exclusive rights in the market place even after the main compound patent has expired.

Many companies regularly employ such a strategy. The following example illustrates how this strategy can work very successfully. Smith Kline Beecham* [SKB] (now GlaxoSmithKline) developed the selective serotonin reuptake inhibitor or anti-depressant compound Paroxetine. When Paroxetine was first manufactured by SKB it was an amorphous solid that was hygroscopic and slightly unstable. Nevertheless, it was very successful as an anti-depressant. Some 5-6 years after filing patent applications for the Paroxetine compound, and pharmaceutical compositions containing it, SKB developed a reasonably straightforward synthesis for crystalline Paroxetine as the hydrochloride salt. The crystalline Paroxetine hydrochloride was very stable and completely revolutionised the commercial process for manufacturing Paroxetine. SKB obtained patent protection for the method of making the Paroxetine salt. Over the past few years the original SKB Paroxetine compound and composition patents have expired around the world. However, no one else can currently make the desired crystalline Paroxetine hydrochloride because of the later filed process patent and also because it is not commercially viable for anyone to make the amorphous Paroxetine. The SKB process patent has effectively added another 5-6 years exclusivity in the market place for Paroxetine placing SKB in a commercially powerful position.

Of course, when developing further improvements or modifications surrounding an initial invention there are a number of assessments that should be made. Questions that should be considered include:

- will the development enhance or add to the commercial objectives?
- are the benefits likely to outweigh the cost of securing patent protection?
- will filing a patent application for the improvement make it more difficult for competitors?
- will filing a patent application for the improvement enhance the likelihood of securing a research partnership or provide commercial leverage, for example by providing licensing opportunities?
- will a subsequent patent application in this area provide some back-up should the originally filed patent/application be challenged by a third party?

While the answers to these questions will differ on a case-by-case basis, generally it is worthwhile filing for patent protection if there is a likelihood of increasing the slice of pie. By building up a portfolio of patents and patent applications in this manner, one can essentially carve out chunks of intellectual property around an initial invention. As the strength of a portfolio increases the commercial leverage should increase accordingly, provided the portfolio is managed correctly and regularly reviewed against the commercial objectives.

Because of the importance of a strong patent portfolio many research organisations are choosing to establish an intellectual property committee to actively manage and review innovations as they are developed. The committee is often also tasked with promoting the importance of intellectual property to its scientists and researchers to ensure that all possible innovations are assessed as to whether or not they would add value to a patent portfolio and increase the slice of pie.

*SKB is not a client of Baldwin Shelston Waters and the details provided about the Paroxetine example are publicly available.


Jane Calvert

Jane Calvert and Greg Lynch are both patent attorneys and solicitors at Baldwin Shelston Waters, where they specialise in chemistry and biotechnology patents. Jane joined BSW after completing a PhD in chemistry at the University of Canterbury in 1994. Greg also joined BSW in 1994 after three years research at Industrial Research Limited in Wellington. Following completion of a PhD in chemistry at the University of Otago in 1989, he spent two years as a post-doctoral researcher at Oxford University.

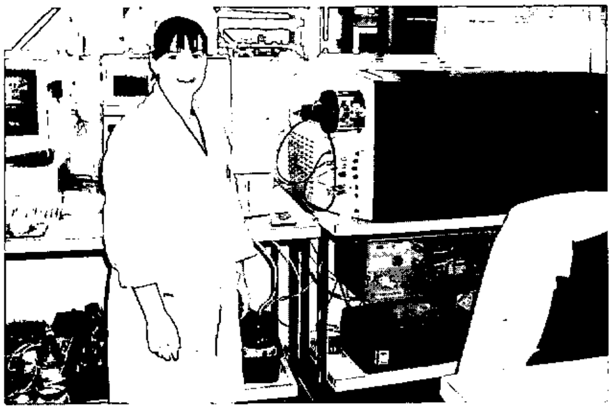

Greg Lynch

LC-MS Seafood Testing

Cawthron Institute is a science and research centre based in Nelson. It is a not for profit organisation that offers commercial science and research across New Zealand. A recent development at Cawthron is now seeing Liquid Chromatography Mass Spectrometry (LC-MS) used to develop better ways of ensuring the safety of New Zealand's seafood export industry. Use of LC-MS to screen for shellfish toxins is totally unique and Cawthron is leading the world in this technology.

Toxins accumulate in shellfish flesh when there is a dominance of certain types of algae in their diet. Commonly occurring when there is an algal bloom, toxin build up can have serious implications for the industry and consumers. The shellfish themselves are unaffected, but a high level of toxins can cause poisoning when the flesh is consumed. The toxins are grouped, according to their symptoms, as Amnesic Shellfish Poisoning (ASP), Diarretic Shellfish Poisoning (DSP), Paralytic Shellfish Poisoning (PSP) and Neurological Shellfish Poisoning (NSP). Poisoning is rarely fatal, but the conditions can range from unpleasant to serious.

Cawthron's commitment to developing a biotoxin testing facility for the New Zealand shellfish industry arose out of the industry's need to develop an alternative to the current bioassay. Cawthron has a long history of involvement with the seafood industry, and was a natural choice when considering the integration of commercial testing and research and development of LC-MS technology. This new programme will eventually replace the bioassay test with chemical based methods. The main advantages are the greater degree of accuracy using LC-MS, and the removal, or prevention, of non-tariff barriers once product can be tested using LC-MS.



Above: *Senior Analyst Tracey Neil with Cawthron's Micromass Ultima LC-MS system.*

The new tests also provide quicker turn-round times and an overall more cost effective service.

Cawthron's Micromass Ultima LCMS was purchased in December 2000 for the analysis of marine biotoxins as part of the extensive research and development project into shellfish testing. The project includes method validation and certification that will ultimately see all tests approved by MAF and accepted by Europe and the US FDA. In December 2001 the first LC-MS test was fully approved by MAF for use in the New Zealand Biotoxin Monitoring Programme. This test is for both ASP and DSP toxins and expresses the result for each toxin in mg/kg. The toxins detected by this test are detailed below (see table).

A New Testing Programme

By using tests such as the one above it is no longer necessary to wait up to a week for DSP toxin test results. The new LC-MS tests provide fast, accurate and highly specific results usually the following day after a sample arrives at the laboratory. In some cases results have been available the same day. New Zealand's seafood industry have been quick to adopt the new technology and over eighty per cent of commercial testing is now carried out through Cawthron's laboratory.

The LC-MS commissioned in 2001 represented a huge investment for Cawthron, and was a demonstration of the confidence in the what the new test would mean for the seafood industry. So far the results have been extremely encouraging and, in the eyes of the international seafood industry, LC-MS is now recognised as a progressive tool for toxin testing.

Toxin Name	Definition	Comment
Total Domoic Acid	The sum of domoic acid and its isomers	ASP toxins
Gymnodimine		Not of regulatory significance
PTX-2	Pectenotoxin 2	A group of related toxins associated with *Dinophysis spp.* blooms
PTX-2 seco acid	The sum of the isomers of pectenotoxin 2 seco acid	
PTX-1	Pectenotoxin-1 a toxin closely related to PTX-2	
PTX-1 seco acid	The sum of the isomers of pectenotoxin 1 seco acid	
AZA-1	Azaspiracid	This toxin has not been found in New Zealand
YTX	Yessotoxin	Toxins associated with *Protoceratium* blooms
45-OH-YTX	Forty five hydroxy Yessotoxin, similar to Yessotoxin	
Okadaic acid		DSP toxins, known to cause toxic symptoms when consumed. A toxin produced by *Dinophysis spp.*
DTX-1	Dinophysis toxin, similar to Okadaic acid	

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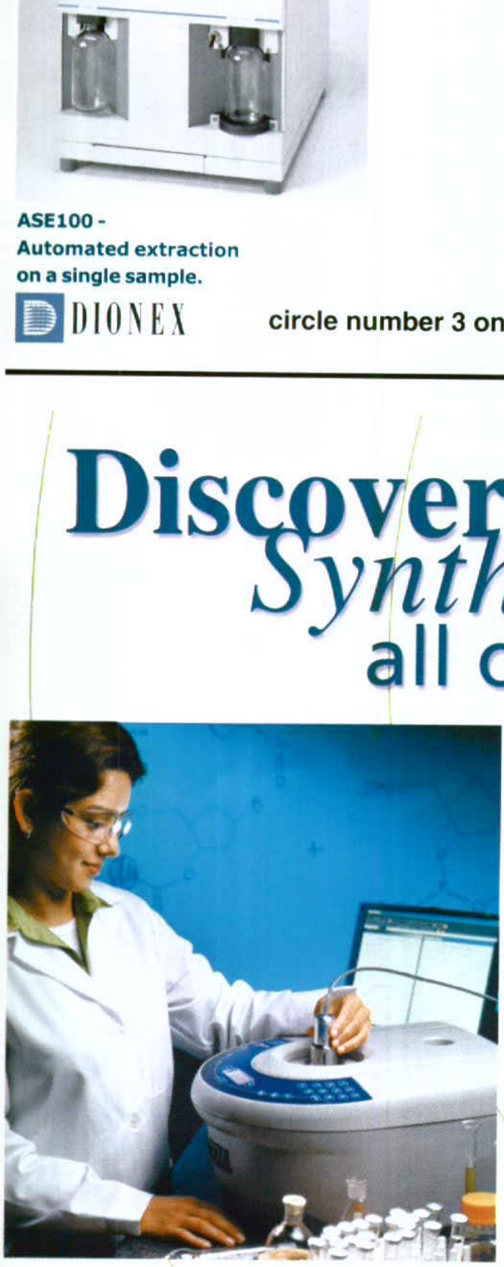

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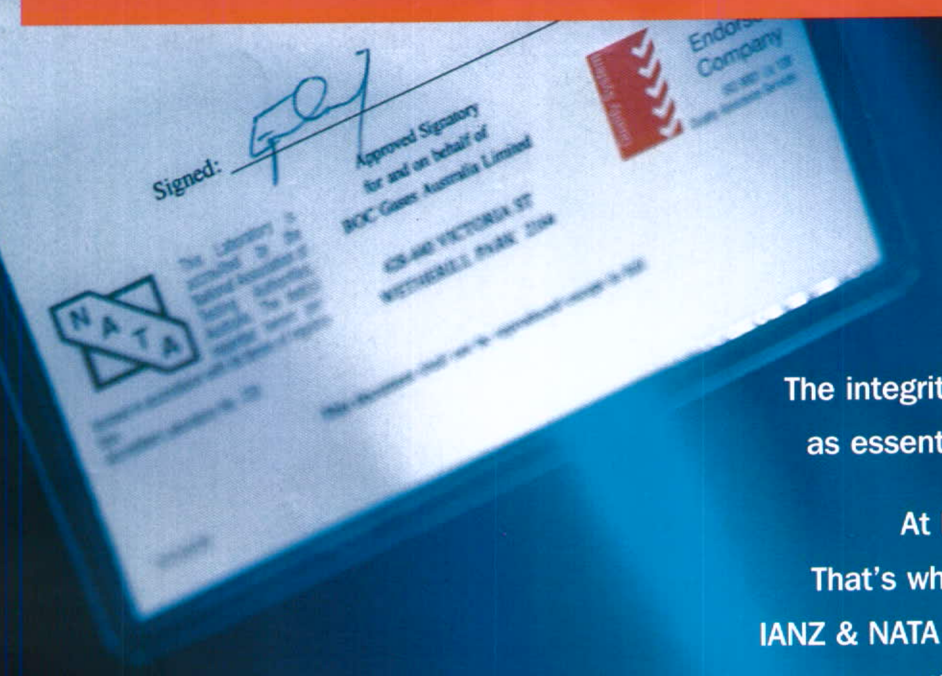
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