NZIC Chemistry IN NEW ZEALAND

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Articles and Features

Other Columns

Advertising

Cover

Front cover: Exploring plant-derived medicines in the 18th and 19th centuries. See article by Edmonds, page 123. Photo by Matt Walters, School of Biological Sciences, University of Canterbury.

Comment from the President

Time flies; welcome to the last issue of *CiNZ* for 2012. First of all a reminder of something I mentioned in the January issue: our membership; we had 905 members in 2011; the 2012 number of paid up members (to date) is only 798. Please remind your colleagues and students to support NZIC; we support chemistry in New Zealand at every level and the more members we have the more we can do. One of our major activities is providing national conferences; our national meeting will be in Wellington next year tentatively booked for 2-5 December, and the biennial ChemEd Teacher's Conference will be in Dunedin in 2013. The details of these meetings will be announced in future issues of *CiNZ* and *ChemEd NZ* so keep an eye out for updates in the next couple of issues of our publications.

Another key activity each year is the awarding of our prizes. In this issue you will find details of this year's winners. Congratulations go first to Rudi Jansen who was awarded the ABA Books Denis Hogan ChemED prize; the award was announced when Rudi was co-presenting the "Chemistry Extravaganza" in Christchurch – this is a series of practical demonstrations to a public audience. Congratulations also go to the recipients of our two research prizes. Our Industrial and Applied Chemistry award this year has been given to Professor Brian Robinson and Dr Stephen Moratti at Otago University; and the Maurice Wilkins Centre prize for Chemical Science this year has been awarded to Associate Professor Richard Tilley of Victoria University of Wellington. Each and every year the standard of applications for our prizes reinforces the high quality of chemistry research and teaching in New Zealand.

And, finally, back to my Comment from the July issue requesting entries for the "Top Ten List" of Chemistry's Greatest Challenges: Thanks to everyone for their emails – here is your list:

- Activation of nitrogen to reduce the energy (and cost) of the industrial production of ammonia (a process that currently sustains about a third of the world's population)
- The origins of chirality
- A stable and economic water-splitting catalyst to support biomimetic systems
- What is life? Why do some collections of molecules (i.e., living organisms) exhibit it and others not?
- C-H activation of alkanes
- The development of nanoscale cell-specific delivery systems to target drugs to diseased cells — an advance that would revolutionize many medical treatments
- Advances in battery technology to support pollution-free transportation
- An improved theory of chemical bonding
- Controlled nuclear fusion (we allow physicists in NZIC!)
- Development of photovoltaic systems using materials that are earth-abundant and cheap

If you have the answers, publish first in *CiNZ*!

Julian Eaton-Rye
NZIC President

New Zealand Institute of Chemistry

supporting chemical sciences

October News

NZIC NEWS

The 2013 NZIC Conference is to be held from 2-5 December in Wellington on the Pipitea campus of Victoria University. The venue is Rutherford House, a key down-town venue close to the Wellington railway station, public transport, accommodation and various hospitality options. The conference chairman is Richard Furneaux (IRL) and the organising committee is being led by Rob Keyzers (VUW). Planning is well advanced.

BRANCH NEWS

AUCKLAND

At a July NZIC branch seminar, Dr *Laurence* ***Eyres***, Chairman of the NZIC Oils and Fats Specialist Group, presented on *Industrial lipid chemistry: some experiences 1974-2012*. Laurence was able to provide a very interesting perspective on oils and fats, and various fatty acid derivatives, over his 35-year career in the New Zealand food industry. Topics included marine waxes, squalene, phospholipids and long chain polyunsaturated fatty acids, and their associated chemistry.

University of Auckland

The School of Chemical Sciences at the University of Auckland has been increasingly occupied with planning around a major building redevelopment project. An important step in the process came at the end of June when the University Council

approved the $200M upgrade to the '301' building on the corner of Symonds and Wellesley Streets that houses the School of Chemical Sciences. Future planning includes the demolition of an existing south podium, to be replaced by a 10 storey 23,500m^2 structure and refurbishment of the existing 301 tower building. Several departments within the Faculty of Science will be located in the new building, with completion planned for 2017. Over the next few years many of the current chemistry operations will need to be relocated as part of the building programme.

On the staffing front, Dr *Geoff* ***Waterhouse*** has been appointed as a senior lecturer in physical chemistry. Geoff has been involved in research and teaching within the School for some years, and he will have particular responsibilities for developing links with the Australian Synchrotron. Geoff was recently successful as a co-investigator on a Human Frontier Science Programme grant to investigate *the chemistry of visual trickery: mechanisms of egg colour mimicry in parasitic cuckoos*.

The annual Chemistry Research Showcase was held in June, and featured over 70 posters and 24 short oral presentations by first year PhD students, from which six students were chosen to give full oral presentations**.** A number of prizes were awarded within the student competitions. For the second-year poster competition, first place and the Baldwin Prize went to *Lian Hsien* ***Kho***, with second place to *Jiayi* ***Wang*** and third place to *Karl* ***Fraser***. In the general poster competition category, first place and the Fonterra Prize went to *Sarah* ***Thompson***, with second place to *Briar* ***Naysmith***, third place to *Marsilea* ***Booth***; and the visual design award was awarded to *Anna* ***Matuszek***. The MacDiarmid Prize for Best Materials Science Poster went to *James* ***Wu***, and the Maurice Wilkins Centre Prize for Best Biology Related Poster to *Anais* ***Noisier***. For the two-minute first-year PhD student talks, first place and the Aldrich Prize went to *Christopher* ***Wilcox***, with *Emily* ***Boyd*** and *Michael* ***Pullar*** being the runners up. In the research paper oral presentation by invited PhD students, the Fisher & Paykel Healthcare Prize went to *Meder* ***Kamalov***, with *Brendan* ***Harvey*** and *U Bin* ***Kim*** being second equal. PhD student Sarah Thompson was also one of eight students to make the final of the three-minute thesis talks in a University-wide competition.

Notable achievements by School staff include the appointment of Prof. *Margaret* ***Brimble*** as an Associate Editor for *Organic and Biomolecular Chemistry*, published by the Royal Society of Chemistry, following six years of service on the Journal's Editorial Board. Dr *Siew Young* ***Quek*** received a Fellowship Award from the New Zealand Institute of Food Science and Technology at their conference last week, to mark Siew Young's contribution and achievement in research and teaching in Food Science and Technology over the past 12 years. School manager *Cathy* ***Comber*** received a Faculty of Science Professional Staff Award in Professional Development. This will enable her to attend the 2012 Tertiary Education Management Conference in Adelaide in September.

The School of Chemical Sciences was pleased to welcome *Larraine* ***Barton***, Head of Science at Pakuranga College in Auckland, to spend time on an Endeavour Teacher Fellowship. Larraine is undertaking a project investigating soil geochemistry on the Goldie vineyard, Waiheke Island, hosted by A/Prof *Paul* ***Kilmartin*** and A/Prof *Jeff* ***Mauk*** from the School of Environment. In August the School farewelled *Vern* ***Rule*** on his retirement after 43 years of service as part of the Electronics team since 1968; many former colleagues were able to be present at the function.

On a sadder note, in August we learned of the passing of *Myrtle* ***Briggs*** who worked for many years as a Technical Assistant in the teaching labs. The same week a current PhD student, *Nikolay* ***Tonev***, supervised by *Neil* ***Edmonds*** and Prof. *Ralph* ***Cooney*** at the Tamaki campus suddenly passed away.

Seminars within the School of Chemical Sciences in recent months have included Prof *John* ***Protasiewicz*** from Case Western Reserve University of Cleveland, Ohio, on *Phosphorus as a carbon copy and as a photocopy for conjugated polymer and materials chemistry*, with a focus on new materials based on benzoxaphospholes, benzobisoxaphospholes, and higher analogues having high fluorescence quantum yields. A/Prof *Stephen* ***Moratti*** from the University of Otago spoke on the *synthesis and applications of gels for use in surgery*, including the synthesis and properties of a promising chitosan-dextran gel. Prof *Janine* ***Cossy***, from the Laboratoire de Chimie Organique ESPCI Paris Tech, presented on *Methods to access heterocyclic compounds applications*, with methods outlined for the synthesis of biologically active complex natural and non-natural heterocycles. Dr *Bill* ***Telford*** from the National Cancer Institute, Bethesda, Maryland, USA, presented on *Novel laser sources for flow cytometry – covering the entire visible spectrum*, including developments in laser technology and the ever-expanding palette of fluorescent probes available to life scientists. Dr *Nigel* ***Lucas*** from the University of Otago presented on *Well-defined, soluble synthetic graphenes and graphene-metal complexes*, covering the synthetic and supramolecular chemistry of graphenes, graphene-based ligands and complexes, along with their solution, solid-state and surface organisational properties. A/Prof *Shelli* ***McAlpine***, from the School of Chemistry at the University of New South Wales, talked about *Macrocyclic peptides – the perfect tools to explore protein function*, and a recent discovery that led to a new class of Hsp90 regulators. Prof *Sanghyo* ***Kim***, from Gachon University, South Korea, covered a number of topics under the heading of *Pervasive healthcare information laboratory: implications for bioimpedance, molecular diagnostics, and tissue engineering*.

CANTERBURY

Metallo-Supramolecular Chemistry

Leonard Francis ***Lindoy***, Emeritus Professor of Inorganic Chemistry at the University of Sydney and James Cook University, gave a presentation entitled *Metallo-supramolecular chemistry – architecture at the molecular level* on 25 July to a well-at-

tended NZIC gathering at the University of Canterbury. Supramolecular chemistry, defined as the chemistry of molecular assemblies, involves the use of molecules as the building blocks for the construction of larger aggregates. The most common way of building these structures is to use the interactions between metal ions and organic ligands (most commonly nitrogen-containing heterocyclic ligands) that have the added advantage of frequently being self-assembling. Using this technique it is possible to construct one-, two- and three-dimensional architectures. Prof Lindoy spoke about the synthesis of metallosupramolecular compounds, which looked for all the world like playing with LEGO on a molecular level. He also touched on the practical applications of being able to tune the hole-size of these molecules to accommodate very specifically different metal ions which could be used for their separation and/or detection.

A Chemistry Extravaganza!

An NZIC Canterbury Branch event featuring multiple displays of explosive high-energy chemical reactions was held August 23rd at the University of Canterbury. *Graham* ***Townsend***, Teacher and Head Start Co-ordinator at the University of Canterbury and *Rudi* ***Jansen***, from Middleton Grange School held an audience of young and old in a packed lecture theatre spell-bound with their brilliant presentation skills, accompanied by many examples of how chemical energy and catalysis can be harnessed to produce light, heat, sound and explosions to the delight of all present. At the conclusion of the presentation (which lasted approximately one and a half hours), the Denis Hogan Chemical Education Award, which is accompanied by prize money of $1000, was bestowed by Canterbury Branch Chair, Dr *Michael* ***Edmonds***, upon a very deserving Rudi.

Canterbury-Westland Schools Science and Technology Fair

Held on Sunday 26 and Monday 27 August at the Addington Events Centre in Christchurch, this year's event attracted around 400 entries from intermediate and secondary schools, as well as home-schooled students from throughout the region. The Fair has been held in Christchurch for over 30 years and throughout this time has grown considerably in size and reputation to become one of the premier Science and Technology events in New Zealand.

The senior prize (Years 11 – 13) was awarded to *Mayan* ***Baran*** from Cashmere High School for her project *How storage time effects vitamin C in lemons.* This was a well presented and researched project, looking at how vitamin C levels decrease in lemons as they age. The Year 8 Prize was awarded to *Hannah* ***Moreton*** from Ohoka School for her project *Secrets of red cabbage*. This project was a thorough examination of different naturally occurring pH indicators which, amongst other things, demonstrated that tamarillos produce a very effective pH indicator. The Year 7 prize went to *Jonn Micah* ***Arias*** and *Thanja* ***Llanza*** from Breens Intermediate School for their project *Homemade organic pesticide*, which explored pepper- and chilli-based solutions as possible pesticides, eventually (and correctly) concluding that they were not as effective against aphids.

Above: Graham Townsend reprises Harry Potter during "A Chemistry Extravaganza".

University of Canterbury

Comings and goings

Diane ***Martinez*** and *Prisca* ***Fricero***, both from France, arrived in June for two and a half month internships in the Chemistry Department, with Prof *Antony* ***Fairbanks*** and Dr *Vladimir* ***Golovko***'s groups, respectively.

Awards and appointments

At the faculty of Science Graduation on Friday 27th April, *Marlese* ***Fairgray*** graduated with a BSc while *Kim* ***Williamson*** and *Emma* ***Gin*** were both awarded MSc(Hons).

MANAWATU

The Manawatu branch of the NZIC, in co-operation with the Royal Society, hosted Susan Krumdieck from the University of Canterbury. Susan's public lecture on the issues facing New Zealand as the world approaches peak oil focused on transport problems that are likely to emerge in urban centres.

Massey University, Institute of Fundamental Sciences

Ajay Pannu has joined *Paul* ***Pleiger***'s group as a postdoctoral researcher to work on the synthesis of single molecule magnets.

In August *Mark* ***Waterland*** gave an invited talk at the 23rd International Conference on Raman Spectroscopy in Bangalore, India. Bangalore was home to Sir C V Raman in his later years, and the conference included an interesting exhibition on the discovery of the Raman effect and its subsequent development. Mark spent five weeks in the US where he gave talks at Kansas State University and the University of Kansas. He also visited the laboratory of Prof Vikas Berry (Kansas State University) where he learned how to make graphene

nanoribbons, and worked with Prof Viktor Chikan on electron-phonon coupling in CdSe Quantum Dots.

Recent talks at Massey University have included Professor *David* ***Penny*** (Massey University), who presented a well attended lecture entitled *Is life a natural property of matter?* David discussed research into the origin of life, and his thoughts on the state of the field. A/Prof *Martyn* ***Coles*** (Victoria University) presented his research on the coordination and catalytic properties of cyclic amidinate and guanidinate anions.

OTAGO

University of Otago, Department of Chemistry

Bill ***Hawkins*** was welcomed to the Department as a lecturer in organic chemistry from mid-July. Bill received his PhD from the University of Wollongong in 2007. He has held postdoctoral positions at the University of Melbourne, École Polytechnique (France) and the Walter and Eliza Hall Institute for Medical Research (Melbourne). His research interests focus on the synthesis of bioactive compounds and their use as tools to probe biological processes.

Sally ***Brooker*** is thrilled that *Jonathan* ***Kitchen***, after a top achiever PhD scholarship and a short MacDiarmid postdoctoral stay with her, followed by an IRCSET postdoctoral fellowship with Thorri Gunnlagsson (Trinity College Dublin) and Stephen Faulkner (Oxford), has accepted a lectureship at Southampton University, starting early 2013.

Following their recent success with the Prime Minister's Science Prize, the University of Otago Centre for Chemical & Physical Oceanography-NIWA collaborative research centre group has been awarded the inaugural University of Otago Research Group Award.

PhD student *Katie* ***Baer-Jones*** was awarded the Best Student Oral Presentation prize at the joint NZ Marine Sciences Society and Australian Marine Sciences Association conference in Hobart. Katie has also accepted a postdoc at the Institute of Marine and Antarctic Studies at the University of Tasmania in Hobart, which commences in September.

The Department's Outreach Team, led by *Dave* ***Warren***, and the Otago Centre for Science Communication combined to present the very successful BANG! stage production as part of the International Science Festival in Dunedin. The live action and interactive show based around chemistry (including thermite reaction and liquid oxygen demonstrations) played to full houses every night.

University of Otago, School of Pharmacy

Another new face around the University is *Allan* ***Gamble***, who joined the School of Pharmacy as a lecturer in biopharmaceutical sciences in May. Following a PhD in organic chemistry at the University of Wollongong (2007), Allan spent three and half years as a postdoctoral fellow at ANU with Chris Easton, before a Sir Keith Murdoch Fellowship (American Australian Association) allowed him to spend time in Paul Wender's group at Stanford University last year. Allan's main research interests are in the synthesis of biologically active molecules, developing new bio-orthogonal reactions, and drug delivery using targeted molecular transporters.

WAIKATO

The Branch recently held its annual recruitment evening to promote the NZIC. Guest speakers *Dylan* ***Harrison*** (Nalco) and Dr *Jacob* ***Babu*** (Milktest NZ) told the attendees about their experiences through higher study at the University of Waikato, and then moving out into the workforce. Their enthusiastic talks reinforced how essential a knowledge of chemistry is to diverse industries and inspired those who attended, prompting some interesting questions and discussion. During the evening the 2011 undergraduate (chemistry major) student prizes were presented.

Above: Waikato Universtity Analytical Chemistry Competition first prize winners: Aaron Boot, Tejal Acharya, Jack Dyche, Zaak Wijdeven, from Pukekohe High School.

Congratulations to the winners who were: Orica Chemnet prize for First Year Chemistry, Hayley Fox; NZIC JE Allan prize for Second Year Chemistry, Lily Lian; Dow AgroSciences prize for Third Year Chemistry, Jess King. The evening concluded with pizzas and refreshments.

Analytical Chemistry Competition 2012

This annual event was held at the University of Waikato in June. A total of 24 teams, each comprising four students, from the wider Waikato/Bay of Plenty region competed in the event. The task was to analyse a sample of $NiCl_2.nH_2O$ using a gravimetric procedure for Ni^{2+} and a spectrophotometric method for Cl^-. This allowed the value of 'n' to be calculated in the empirical formula by difference. This was a demanding task in the time available but some excellent results were achieved, with very little to differentiate the first six teams.

The competition allowed enthusiastic Year 13 chemists to spend a day in the University laboratories working on an experiment that would be beyond the resources of their schools. Rivalry was fierce, but the main emphasis was on enjoying the experience and meeting students from other schools. Results were:

1st Prize, Pukekohe High School (Aaron Boot, Jack Dyche, Tejal Acharya, Zaak Wijdeven); 2nd Prize, Forest View High School (Zane Farrow, Josh Pennefather, Ryan Goodhue, Catherine Dean); 3rd Prize, Katikati College (Toby Hendy, Melanie Knoltenbelt, Leighton Hu, Lucy Newlands); 4th Prize, Te Awamutu College (Matt Harker, Liam Mackintosh, Hayden Berkers, Rochelle White); 5th Prize, Tauranga Boys College (James Gilbert, Liam Kampshof Matthew Helem, Daniel De Mel). The day involved many of the Chemistry Department staff in setting up the competition and supervising the labs. Bryant Hall provided excellent excellent lunches (sponsored by the NZIC) and Hill Laboratories generously donated the prizes.

University of Waikato

Yuan ***Wang*** and *Christina* ***Strawbridge***, both supervised by *Michael* ***Mucalo***, successfully completed their MSc degrees and both found employment in chemically relevant industries immediately after completion of their degrees. Both were also recipients of MSI Capability Fund stipends and did their research in collaboration with industries based in Taranaki or the Bay of Plenty.

Both Michael Mucalo and *Kethsiri* ***Alwis*** have recently returned from Melbourne, where they have done some EXAFS work at the Australian Synchrotron on corrosion product solutions from IR spectroelectrochemical studies of transition metal electrodes in non-aqueous solvents. They were impressed with the instrumentation there and the quality of the accommodation offered to researchers.

Retirement of Professor Brian Nicholson

Brian ***Nicholson*** retired from the Chemistry department at the end of June after 37 years of service. His retirement was marked with a farewell function at which some unusual gifts were presented. He was given a plaque acknowledging his pioneering research on the structure of salvarsan, an arsenic compound formerly used in treatment of syphilis. The plaque reads *Saving the world from syphilis, 1975-2012*. He was also presented with a scrapbook of photographs and anecdotes of his time in the Department.

Brian's research career was outstanding. He had an extensive publication output which was a key component of the Department's international recognition as one of the centres of excellence in inorganic and radiochemistry. Brian enjoyed a number of longstanding and successful collaborations such as with *Mike* ***Bruce*** (University of Adelaide); *Ken* ***MacKay*** (University of Waikato), on metal carbonyls incorporating Group 14 elements; *Lyndsay* ***Main*** (University of Waikato), on orthomanganation; and *Bill* ***Henderson*** (University of Waikato), on noble metal chemistry. He also played a major role in the X-ray crystallographic community.

In addition, Brian made a major contribution to chemistry at Waikato with the joint research that he undertook with other university chemistry departments, CRIs and private industry, initiating many of these collaborations. Through supervision of students on industrial placements, Brian played a significant part in making industry recognise the value of joint research with the University. There were many occasions on which a student research seminar led to suggestions for industry research from Brian. One memorable example of how fundamental knowledge solves problems and of the value of industry-university liaisons was at a seminar by a Forest Research student about the problems with borate as a wood preservative leaching in a wet (exterior) environment. Brian immediately suggested the use of hydrolytically stabilised tricyclic trialkanolamine borates, which led to research and process development at Forest Research.

Brian was very committed to all of his teaching, but especially so to teaching first-year chemistry. He coordinated level one chemistry classes for many years and taught half of the general chemistry course. Unlike most academic chemists who avoid first-year labs, Brian revelled in them and insisted on taking the direct entry stream. He also had an important role in teaching liaison, with Tauranga Boys' High School, Hillcrest High School and Tairāwhiti Polytechnic.

Brian's contribution to senior labs was outstanding. In the second year inorganic laboratory, he made available the Cambridge crystallographic files online for student access. He devised very challenging, but rewarding projects, for third year inorganic laboratory classes, which often led to publications. Brian's contributions to undergraduate laboratory classes helped to recruit graduate students, and his graduate students could be assured of gaining expertise in a variety of techniques and of unstinting care in supervision. His publication output from not only PhD but also MSc theses was quite exceptional.

Brian served two stints as Chairperson of the Chemistry Department and was also on many University committees. He was well known for his outreach activities, and was the organiser of the secondary schools analytical chemistry competition for

Above: Chemistry Research at Otago (early 1970s), and an enlargement from the right-hand corner of that photo. Three Otago graduates joined the staff at Waikato within a relatively short period: from left, Alistair Wilkins, Brian Nicholson, and Tony Cartner.

many years. Along with *Bill* ***Henderson***, he was responsible for many demonstrations at University Open Days and was always a willing Chief Judge at Chemistry quiz nights.

Brian was a dedicated conference person. Of special note was his role as secretary of the NZIC/RACI IC 91 conference held at Waikato in 1991 and acknowledged by some of the Aussies as the 'best ever'. A former collegaue recalled that at this conference, it was Brian's idea to have a television set in the lecture block foyer as there was a cricket test match on at the time between New Zealand and Australia. Apparently, some of the non-Commonwealth delegates were a bit baffled by it all! Another memorable conference for Brian was an NZIC one held at Massey. Returning to his hostel room after the conference dinner he found that his bed had been stolen! The students had found that the master key for Waikato chemistry was the same as for the Massey hostel. Some of the delegates were heard asking in a puzzled way at breakfast the next morning "Did that bloke come knocking on your door at midnight to see if you had taken his bed?"

Brian was the ultimate academic for the largely now defunct late twentieth century era of co-operation, communication and non-territorial ambition, which was a hallmark of Waikato research and undoubtedly a major factor leading to the Department's success in topping successive PBRF chemistry research rankings nationwide.

Brian was also an open-door communicator, generous with his time in problem-solving in research. He was always prepared to take up a new research idea someone came along with, and was excellent in application of instrument techniques, initially ESR, then X-ray crystallography, and later ESMS. He will be sorely missed from the Chemistry Department, but has promised to haunt our corridors for a while yet.

WELLINGTON

The July Branch meeting featured the 2012 Presidential address entitled *Photosynthesis: How plants power the planet* and given by A/Prof *Julian* ***Eaton-Rye*** (Biochemistry, Otago). He gave an historical perspective of the basic discoveries that led to the contemporary picture of photosynthesis and in particular to those that have led to Nobel Prizes in Chemistry. In contrast, the August meeting saw the return of Dr *Neil* ***Milestone*** (Industrial Research Ltd.) who, in 2009, returned from Sheffield where he was Director of the Immobilisation Science Laboratory. He spoke on novel uses of Portland cement, the grey powder we know. In excess of 3000 million tonnes is produced annually, most of which is used in developing countries such as China and India. The original production dates from 1824 and is usually credited to Joseph Aspdin. Nonetheless, today's production chemistry differs little from that developed then. Key to its success is formation of the main ingredient, tricalcium silicate ($3CaO.SiO_2$) through burning finely pulverized lime and clay at high temperatures (clinkering) for the formation reactions to occur. The tricalcium silicate will then react with water to harden into a solid mass akin to Portland stone, a good building material in the UK. Apart from use in the construction industry, it is used in electricity production from geothermal wells, distribution in high voltage lines and in ways in which we can clean up the environment with waste stabilisation feature. It can even be used as an art form. It was these more alternative uses that Neil addressed in his fascinating lecture.

Environmental Science & Research Ltd.

Dr Hilary ***Hamnett*** has joined the team at ESR as a forensic toxicologist. She gained a Master of Chemistry and DPhil from the University of Oxford, and then an MSc in Forensic Science from the University of Strathclyde. Prior to her move to New Zealand, Hilary worked at the UK's Forensic Science Service before taking up a postdoctoral position

at the University of Queensland.

Dr Paul ***Fitzmaurice*** (Manager, Bioanalytical Programmes) represented ESR in July as a Ministry of Science and Innovation delegate on a visit to the Research Triangle Institute (RTI) in North Carolina. There is significant alignment between the ESR and RTI Forensic groups and discussions with Peter Stout, RTI's Senior Research Forensic Toxicologist, identified several areas where ESR and RTI can collaborate. Ideally this will lead to co-applications for National Institute of Justice (http://www.nij.gov/funding/current.htm) funding to provide forensic training and forensic technology evaluations. A return visit is scheduled before the end of the year to advance these discussions.

Matthew ***Hosking*** (Forensic Toxicologist) attended the 17th Annual Meeting of the Society of Hair Testing (SOHT 2012) in Toronto in June. He then travelled to the US for the Society of Forensic Toxicologists Meeting (SOFT 2012) in Boston. Also in July, analytical chemist and former VUW mass spectroscopist, *Oleg* ***Zubkov***, visited IMB A*STAR in Singapore, where he gave a talk on the mass spectrometry capabilities at ESR, and methods of characterising sulfated multiply-charged compounds. Oleg then accompanied his wife Dr *Olga* ***Zubkova*** (Industrial Research Ltd) to the 26th International Carbohydrate Symposium in Madrid. Oleg used this opportunity to present ESR's capabilities in the relevant service areas to potential collaborators and clients there.

Victoria University – SCPS

Prof *Leiv* ***Sydnes*** (University of Bergen, Norway) made a return revisit to the School on July 11. Leiv first visited us in about 1988 and he has been a regular visitor every four years since then, his last visit being for two months in 2008. Continuously active in IUPAC (a former President and now Chairman of CHEMRAWN), his visit followed the ICOS-19 meeting in Melbourne the previous week. He met with staff and delivered his lecture *The synthesis of compounds from some conjugated acetylenic ketones* that has its origin in his earlier cyclopropane ring-opening studies.

Dr *Jane* ***Allison***, a former colleague of *Matthias* ***Lein*** at Massey, Auckland, visited on Friday 13 July to meet staff and deliver her lecture *Shake, rattle and roll: using simulations to explore how proteins move*. She explained how changes in protein structure are integral to their function and malfunction, and the techniques she had evolved to explore and describe conformational motions, including how they are influenced by other molecules. Biomolecular simulations are especially valuable in probing structural and thermodynamic characteristics of protein conformational changes, and allow direct visualization. She described the various simulation techniques that have been developed and focused on different levels of the multiple scales on which protein motion takes place.

Interviews for the Physical Chemistry position in the School started on 16 July. Dr *David* ***Cheung*** (Centre for Scientific Computing, Warwick, UK) gave a research seminar entitled *Molecular simulation of complex molecules at interface*, in which he described interfaces involving soft matter systems and polymers that play a key role in a number of applications in materials science, nanotechnology, and biomedicine. Complex molecules, e.g., nanoparticles, polymers, and biomolecules (such as proteins) can adhere to liquid interfaces, and have generated much interest in the use of fluid interfaces as potentially convenient and elegant templates for the creation of nanostructured materials. The adsorption of biomolecules on to liquid interfaces plays a key role in many biological processes, including digestion and immune response, while a number of their materials applications (in areas such as food technology and drug delivery) also rely on their interfacial behaviour. Exploiting soft interfaces for these (and other) applications requires an understanding of the underlying physics and chemistry of these systems, which molecular simulation is ideally placed to provide. David also gave an overview of his recent work studying the adsorption of complex molecules on liquid interfaces.

On 25 July Dr *Nicola* ***Gaston*** **(**Principal Research Scientist, IRL) gave her presentation entitled *The trouble with metals*. She outlined why and how metallic systems are a challenge for *ab initio* theoretical chemistry. The most frequently used computational methods have been developed for the description of covalently bonded molecules, leaving 80% of the periodic table relatively unexplored. However, analysis of the electronic structure of metals produces interesting surprises, as a function of changing size (number of atoms), structure (lattice or local geometry) and composition. Thus, she explored questions such as 'Why is gallium the only metal in the periodic table to exist in a dimeric, orthorhombic structure?' and 'Why does it melt at such a low temperature, relative to its neighbours such as aluminium?' and 'What happens to a piece of metal when you shrink it down to nanoparticle size, and how does the changing electronic structure affect its properties?' Answers to such questions are important in the development of better catalysts, and in understanding how electronic properties depend on structure, thereby enabling the design of specific functions into materials. Recent results involving superheating, superatoms, and the description of gallium as a molecular metal were presented, elaborating on the complexity of even the simplest metallic system.

Liza ***Rassaei*** (MESA/Institute for Nanotechnology, University of Twente, Netherlands) was the third applicant interviewed for the School's physical chemistry position and, on 25 July, she presented *Bionanofluidics: toward electrochemical single enzyme kinetics*. She described how large biomolecules may act as machines that generate motoric motions or, in the case of enzymes, catalyze individual reaction events. To understand the functions of enzymes at a molecular level, experiments with single molecules are of high importance. Nanoscale devices can be utilized in this regard because they approach the size of individual molecules and offer the opportunity for investigating biological systems from new physical perspectives. Her work is directed towards a new method to study single-enzyme kinetics by coupling electrochemical nanofluidic de-

vices with biological components.

Three new students, *Joanne* ***Rogers***, *Mahroo Falah* ***Poorschiani*** and *Mohammad* ***Alzeer***, have begun their PhD research with Prof *Ken* ***MacKenzie***, working on functionalizing of inorganic polymers for new applications in catalysis and luminescence. *Michael* ***Welter***, another PhD student with the group, will shortly submit his thesis on fibre-reinforced inorganic polymers. Joanne and Michael were recently guests at the Vice-Chancellor's reception for Victoria University's Top Scholars. *Bryan* ***O'Leary***, a Master's student working with this group on the development of advanced engineering ceramics from inorganic polymers, has successfully completed his degree. A new Master's student, *Siti Noor Md* ***Hairi***, has started her research on the use of waste materials from the aluminium industry to produce construction materials. The group was joined in August by Dr *Amirabbas* ***Nourbakhsh***, a visiting scientist on sabbatical research for six months from Islamic Azad University, Iran. In August, Ken delivered an invited lecture on inorganic polymers to the International Conference on Traditional and Advanced Ceramics in Bangkok. Subsequently, he conferred with colleagues at the Universities of Lancaster and Warwick in the UK.

Kate McGrath (Director of the MacDiarmid Institute) delivered her inaugural lecture as Professor of Chemistry to the University on 14 August. It was entitled *From soap to bones: understanding nature's underlying patterns*, in which she gave an over-view of her work on the self-assembly of complex naturally occurring soft and hard materials in what was a tour de force of clearly defined concepts, applications and outcomes that was entirely appropriate for the general audience of an inaugural lecture – one of the best this correspondent has had the privilege of attending. *Jacqui* ***Kane-Barber***, a former student representative on the Branch Committee, has completed her PhD under *Peter* ***Northcote***'s direction, working on Tongan marine natural products. She is working now on the IRL campus. *John* ***Spencer***'s student, *Brad* ***Anderson***, has submitted his PhD thesis on a study that examines the synthesis and co-ordination chemistry of pincer ligands with electron-withdrawing substituents; the vagaries of Victoria's Faculty of Graduate Studies means Brad is unlikely to have an oral until November.

SCPS hosted the Wellington Science Fair on 30 November. The senior NZIC Prize was awarded to Sarah Novak, Queen Margaret College, for her project *Oil Spill! What happens to dissolved oxygen in seawater?*, while the Finn Connell from Muritai School received the Junior NZIC Prize for a project *How does Vitamin C deteriorate in milk?*

Chemistry in the news

Anthea Lees

A chemistry extravaganza

On the evening of 23rd August my family and I attended The New Zealand Institute of Chemistry 'A Chemistry Extravaganza' lecture at The University of Canterbury. The aim of the lecture was to present 'an explosive display of high-energy chemical demonstrations, illustrating the impact of chemistry on our lives.' On line booking of seats resulted in all the tickets being sold out and a lecture theatre filled with an audience of both young and old attending a highly entertaining demonstration. There were loud explosions, brilliantly coloured lights, liquid nitrogen demonstrations, glow sticks and barley sugar sweets. Rudi Jansen (Middleton Grange School) and Graham Townsend (University of Canterbury) showed us a variety of experiments which included: using liquid nitrogen to change the properties of rubber to make nails which they hammered into wood; how to detect forged bank notes using UV light; making electrons dance; turning night into day with extremely bright flames; making test tubes sing and making green flames by burning boron. My nine-year-old daughter was one of the many children who attended and she was very impressed and really enjoyed the lecture. It has renewed her interest in science and she came out saying that she wanted to add Chemist to the long list of 'things she wants to be when she grows up'. Two of the younger members of the audience won Chemistry prizes and there were a large number of both junior and high-school children in attendance.

Photos of the event can be seen at: *sciblogs.co.nz/molecular-matters/2012/08/27/chemistry-is-magic/*

Chemistry and conservation at Te Papa

Te Papa textile conservator Rangi te Kanawa and Gerald Smith an associate Professor of Chemistry at Victoria University have been working together on the conservation of cultural treasures Maori taonga.

They have been looking for chemical processes to stabilise the acids responsible for the breakdown of the fibres in traditionally dyed cloaks and skirts. The flax fibres of these garments are dyed by soaking them in tannin and then immersing them in mud known as paru, which is acidic. This acid causes the fibres to break down and the weave to collapse resulting in very dry and brittle garments.

A zinc-alginate consolidation treatment process has been employed which appears to bind the fibres together and shows signs of soaking up these acids. However, it is a last resort option as the process is irreversible.

Ms Te Kanawa states, "All the treatments we do, we try to make reversible because such is science that in the future some bright spark might come up with a better method. In theory they've all got to be reversible but this one is not." The process should conserve and extend the lifetime of the clothing by about ten years.

Chemistry in the news continues on p. 144

Article

Ionic liquids: Some of their remarkable properties and some of their applications

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Keywords: *ionic liquids, materials, solvents, catalysis*

Introduction

Ionic liquids are a fascinating class of materials which, although they have been known about since 1914,[1] have only come to prominence over the last decade or so. Commercially, electrochemical applications (e.g., non-volatile electrolytes for batteries) represent just one area in which there is significant interest. Publications and patents have grown dramatically since 2000[2] (there have been over 15,000 papers and well over 1,000 patents on ionic liquids!) and there are now many books on the topic.[3,4] The somewhat arbitrary definition of an ionic liquid (IL) is that it is a salt [R]X with a melting point below 100 °C. It would be tempting to define them as those that are liquids at room temperature (these are called room temperature ionic liquids (RTILs)); however, in practice even salts with melting points above 100 °C are potentially useful. Most commonly, an IL consists of an organic cation $[R]^+$ and an inorganic anion X^-. Figure 1 illustrates the most commonly used cations.

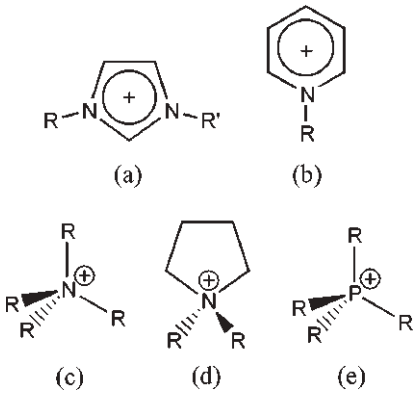


Fig. 1. Common classes of cations used in ILs: (a) imidazolium, (b) pyridinium, (c) ammonium, (d) pyrrolidinium and (e) phosphonium.

There are several factors that make ILs particularly interesting and potentially useful. As salts, they have almost no vapour pressure. Not only does this inhibit their release into the environment, but it also provides for interesting new applications. An example is fine control for jet propulsion in space (having essentially no vapour pressure, the ejection of liquid can be easily controlled), as well as applications more relevant on earth (discussed below). ILs also conduct electricity and this, coupled with their low volatility and high electrochemical stabilities (especially the imidazolium salts), makes them of interest for battery applications, dye-sensitised solar cells and a host of other related applications. Additionally, it is relatively easy to tune the properties of an IL by either changing the substituents on the cation or exchanging the anion; there are many thousands of readily prepared ILs. Interestingly, ILs are usually very good solvents – some can even dissolve up to 20% by weight of cellulose, normally a difficult-to-dissolve structural polymer. Generally, they are very similar in terms of their solvation properties to common polar organic solvents such as dichloromethane, ethanol and acetonitrile. However, while you can make ILs that are soluble in water but immiscible with non-polar solvents such as hexane, you can also make ILs that are immiscible with water but soluble in, or even miscible with, hexane!

Historical background

Despite the relatively long time since the first publications about ILs, two very early reports on ionic liquids and their properties have been key to the progress made in the last decade or so. The first IL was, in fact, reported in 1914 by Paul Walden using the reaction of ethylamine with nitric acid to give ethylammonium nitrate ,which has a melting point of just 14 °C.[1] This IL is now recognised as belonging to a class of ILs termed protic ionic liquids (PILs) owing to the presence of a hydrogen-bonding NH group.

$$EtNH_2 + HNO_3 \longrightarrow [EtNH_3]^+ + NO_3^-$$

Non-protic ammonium salts $[NR_3R']X$ are readily prepared by alkylation of tertiary amines NR_3 with alkyl halides R′X:

$$NR_3 + R'X \longrightarrow [NR_3R']^+ + X^-$$

In 1934, a US patent described the use of halide salts of nitrogen-containing bases as solvents for the dissolution of cellulose and uses of these solutions.[5] Examples included 1-ethylpyridinium chloride (prepared from pyridine and chloroethane). Today, significant resources are being put into the dissolution and regeneration of cellulose using ILs, as cellulose-derived materials are structurally strong, biodegradable and environmentally friendly.[6,7] This is potentially of great benefit to the New Zealand economy because of our significant cellulose resources. The anion is important in the dissolution process: chloride and acetate anions, for example, are able to break up the cellulose interactions due to their hydrogen-bonding ability.

It was quite some time before more advances were made in IL technology. In the 1970s and 80s, chloroaluminate anion mixtures $Cl^-/[AlCl_4]^-/[Al_2Cl_7]^-$ were described for use as battery electrolytes;[8] firstly using pyridinium cations, but then using the more electrochemically stable imidazolium cations. Unfortunately, these are very water-sensitive materials and the area remained quiet for a few more years after these electrolytes were developed.

Wilkes and Zaworotko presented a landmark paper in 1992 on air- and water-stable imidazolium-based ionic liquids.[9] The significant change was the use of water- and air-stable anions such as acetate, nitrate and $[BF_4]^-$. Consequently, we now had stable salts that are liquid at room temperature, as well as having a wide electrochemical window (this defines how easily they are oxidised and reduced). Since then, a wide variety of anions have been developed. Interestingly, although the focus in the IL literature is often on the cation, it is usually the anion that is most influential in determining the properties of the ionic liquid. Varying the alkyl chain lengths on the organic cation, for example, is usually used to fine tune the properties, whereas changing from a hydrophilic anion (such as nitrate) to a hydrophobic anion (such as $[PF_6]^-$) leads to a large change in solubility and other properties. Figure 2 shows a selection of anions with which many chemists would be unfamiliar, but which are now commonly used for producing ILs.

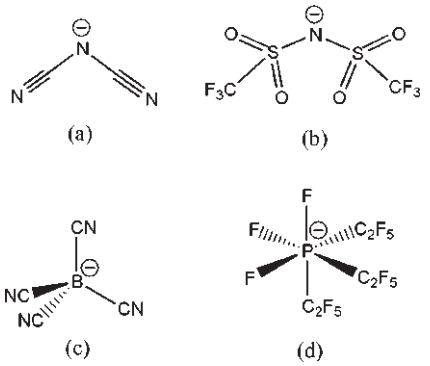


Fig. 2. Common anions used for ILs: (a) dicyanamide (DCA), (b) bis(trifluoromethanesufonyl)amide (TSFA, TFSI or NTf_2^-), (c) tetracyanoborate and (d) tris(pentafluoroethyl)trifluorophosphate (FAP).

Melting points and viscosities

The reason for using such exotic anions is a desire for low melting and low viscosity materials, since these are ILs that are easy to handle (transfer, stir, etc.) and have high conductivities (making them useful for electrochemical applications). The factors affecting melting point and viscosity are complex and, quantitatively speaking, poorly understood. The most common technique to lower the viscosity is to reduce the molecular weights of the ions; however, this generally raises the melting point owing to the increased ionic attractions. Consequently, there is a balancing act required to obtain the lowest viscosity ILs without the melting points being too high. As the ions get smaller and ionic attractions increase; this can be counteracted by using ions with delocalised charges to spread out the charge and reduce the electrostatic attractions. The imidazolium and pyridinium cations, as well as the anions like those shown in Fig. 2, are, therefore, well-suited for preparing RTILs. Additionally, decreasing the symmetry (imidazolium cations) reduces crystallinity, and so also lowers the melting points, as does increasing the conformational flexibility of the ions (compare FAP and TFSA to DCA and $[B(CN)_4]^-$, or *n*-propyl to isopropyl). Symmetry and shape also play a role in determining the viscosity of a liquid; remarkably, these factors are especially poorly understood.

So what are the viscosities of typical ILs? This is certainly one aspect that often concerns scientists when considering whether or not to use an IL. Compared to water with a viscosity of 0.83cP at 25 °C, a viscosity of 32cP for 1-ethyl-3-methylimidazolium TFSA ([EMIM]TFSA) seems high.[10] However, you should compare it to olive oil at about 80 cP, 10W40 motor oil at about 250 cP, and tomato sauce at about 75,000 cP! Also, viscosities decrease significantly as the temperature increases (Fig. 3[11,12]) and even a small increase above room temperature is greatly beneficial.

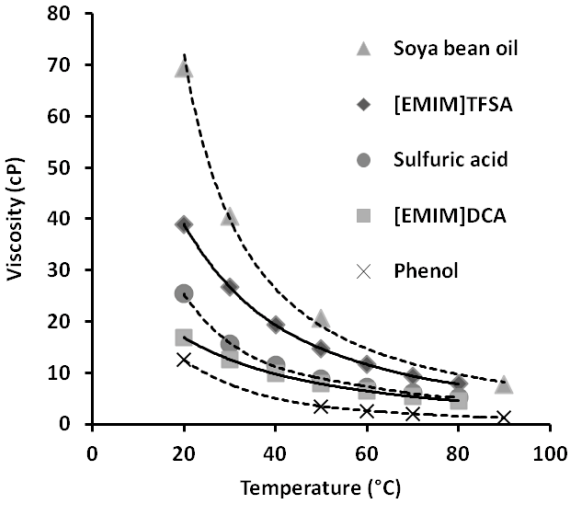


Fig. 3. Plot of viscosity versus temperature for [EMIM]TFSA, [EMIM]DCA and some common liquids.

Another interesting aspect to consider when optimising the melting point is that while lower molecular weights raise melting points, so do higher molecular weights. This is, of course, attributed to the increasing van der Waal's interactions. Thus, there is frequently an optimum alkyl chain length for low melting points.

The liquidus range – the temperature range at which a compound is liquid

Given that ILs are essentially non-volatile (none have measureable boiling points at atmospheric pressure), the upper level of their liquidus range is determined by their thermal decomposition temperature (this is often reported as the onset decomposition temperature as the temperature is raised by 10 °C/min); the weight loss is measured by Thermal Gravimetric Analysis (TGA). It can often be more than 400 °C in an inert atmosphere. However, generally of more relevance to practical applications is ILs' isothermal decomposition behaviour, i.e., how quickly an IL decomposes at a fixed temperature. Unfortunately, these measurements are relatively time-consuming and so are not usually reported. Practical upper limits for the liquidus range of ILs are more typically about 250 °C. Nonetheless, that still gives ILs a very large useful liquidus range compared to common molecular liquids. Whereas the alkyl chain length affects the melting point, the upper limit of the liquidus range is most affected by the anion, as decomposition temperatures decrease with increasing nucleophilicity of the anion.

A brief and incomplete discussion of applications

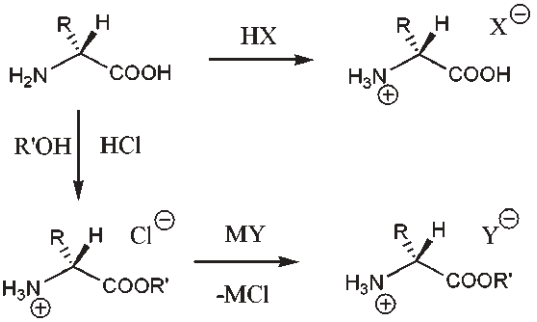
The variety of potential applications for ILs is quite incredible.[2,4] It seems that almost any process involving a liquid or solvent can use ILs. Here, I briefly summarise only a few that I think are interesting and/or important. A partial list of applications already in use, but not discussed further here, includes: the gas company Linde has liquid pistons in which ILs act as functional fluids for the compression of gases; the Swiss company Novasina uses ILs as sensor electrolytes; BASF uses the BASIL process to prepare the photoinitiator precursor alkoxyphenylphosphines on the multi-tonne scale; ionikylation is a process for the alkylation of four-carbon olefins with isobutane – Petrochina operate a 65,000 tonne per year plant; the Difasol process is an add-on to the Dimersol process to dimerize short chain alkenes into branched alkenes; and the company Air Products uses ILs instead of pressurised cylinders as a transport medium for reactive gases such as trifluoroborane, phosphine and arsine.

Electrochemical applications

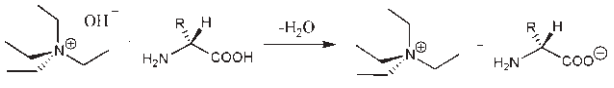
These are generally considered the most commercially important. This is because of the inherent conductivity of the ILs, as well as their non-volatility. Typical electrochemical applications are in dye-sensitised solar cells, fuel cells, electro-optics, lithium-ion batteries and electrolytes for metal plating. An important requirement here is that the liquid is stable to a wide range of redox potentials, i.e., it has a wide electrochemical window. Electrochemical windows vary significantly: they can be as large as 6 V but are typically 3–5 V. This compares to 2.4 V for water and 5.0V for acetonitrile.

Applications in chiral syntheses

There have been few applications in chiral syntheses, though research in the area is very active.[13] It is relatively easy to make a chiral ionic liquid (CIL) in which either or both the cation and anion are chiral. Alkylation of amino acids, for example, generates ammonium CILs when combined with appropriate anions (Scheme 1[14]) while deprotonation of an amino acid and combination with an appropriate cation generates ILs in which the anion is chiral (Scheme 2[15]). There are many other inexpensive sources of chirality for ILs.[19]



Scheme 1. Generation of ILs with chiral cations.



Scheme 2. Generation of ILs with chiral anions.

Depending on the mechanism of the process, it may be advantageous to use a CIL to enhance enantioselectivities. This area is clearly of much significance to the pharmaceutical industry. I should note that chiral molecular solvents, on the other hand, are rare and very expensive. Surprisingly, there has been very little work on combining CILs with chiral organometallic catalysts which are often used in the pharmaceutical industry to introduce chirality.

Potential lubricants

As potential lubricants, ILs usually have much greater thermal stability than petroleum-based oils. However, owing to their greater expense, they are most likely to be used as additives or in specialty high temperature applications. The ionic nature of ILs has an interesting and useful impact on their properties as lubricants. For example, the use of phosphate or sulphate anions with hydrophobic cations generates a system in which the anion interacts with the two metal surfaces that are trying to come into contact while the cations are sandwiched in between (Fig. 4).[16] This results in less friction and less wear and tear on the two surfaces.

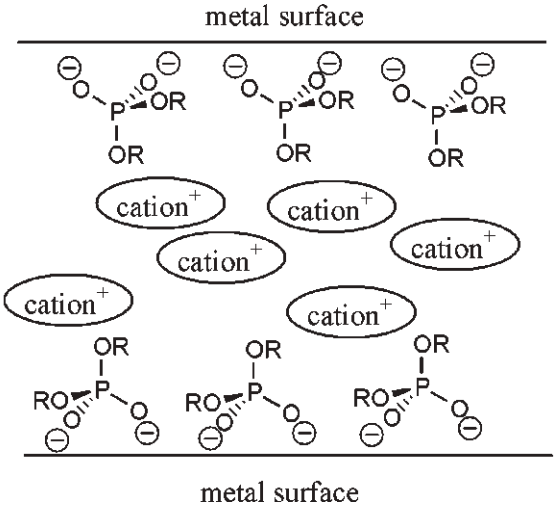


Fig. 4. A phosphate IL between two metal surfaces.

Chromatography

ILs can be used as the stationary phase for GC and HPLC columns. Their non-volatility as well as the ability to tune the properties of the IL, most notably to introduce chirality, give them ideal properties for these applications.

Microwave chemistry

It is well known that water and other small polar molecules readily absorb microwaves. Remarkably, ILs absorb microwaves to a much greater extent than water.[17] Whereas water may take a minute or so to boil in a conventional microwave, an IL will reach the same temperatures in a matter of seconds. The high liquidus range of ILs means that very high temperatures can be reached very quickly. I suspect that many applications that take advantage of this property are still to be realised.

Catalysis

As well as providing a new class of solvents, ILs also provide a new method called supported ionic liquid phase catalysis (SILPC).[18] In this method, a thin layer of IL is

adsorbed on small particles of alumina, for example, and this is then placed in an organic medium in which the IL is insoluble. An organometallic catalyst is dissolved in the thin layer of IL. The large interfacial area between the IL and the organic solvent means that organic substrates are able to readily access the catalyst and the products can quickly return to the organic phase for subsequent separation (see Fig. 5). It can be viewed as a homogeneous version of heterogeneous catalysis!

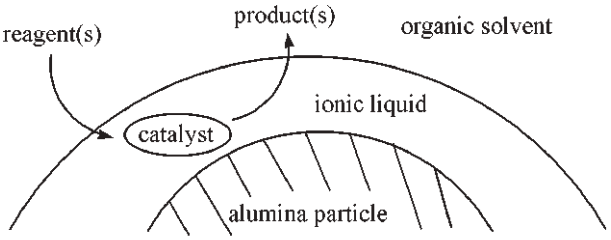


Fig. 5. Schematic of supported ionic liquid phase catalysis (SILPC).

Biochemical applications

Early investigations suggested that ILs are poor solvents for enzymes, as the enzymes were rapidly denatured. However, subsequently it was found that many enzymes are, in fact, stable in ILs when the IL is carefully chosen, and there is now a lot of highly-competitive research in this rapidly growing field.[19]

The cost

Another factor affecting the take-up of IL technology is, of course, their cost. Fortunately, costs have decreased significantly in recent years as demand has led to larger multi-ton production runs. For the research chemist, there is now a large variety of affordable ILs in fine chemical catalogues.

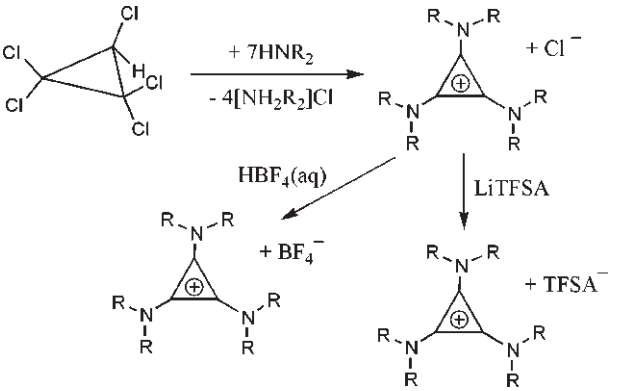
How green is green?

One of the attributes commonly applied to ILs is that they are "green solvents". Regrettably, this is somewhat of an over-statement. Like many materials, they certainly have aspects to them that can be taken advantage of to enhance the 'greenness' of a process. For example, they are essentially non-volatile, and this hinders their release into the environment; also, they can be easy to recycle and reuse. However, they are not intrinsically green. Not only is it relatively trivial to design highly toxic ILs, but toxicity studies on ILs in general are still at an early stage. Perhaps more of an issue is that, should an IL be released into the environment, their non-volatility and high stabilities can make them difficult to remove.

Our research at Canterbury

At Canterbury, we have developed a new class of ILs based on the triaminocyclopropenium (tac) cation, $[C_3(NR_2)_3]^+$.[20] These simple cations are readily prepared from pentachlorocyclopropane (or tetrachlorocyclopropene) and a secondary amine (Scheme 3).

The ammonium by-product can be removed by a number of methods, depending on the amine. Ammonium salts of volatile amines can be removed *in vacuo* after neutralisation with base, whereas other ammonium salts require crystallisation or solvent extraction procedures for their removal. Conversion of the chloride salts to other anions is generally quite easy, although removing the last of the chloride can be problematic in some instances. Anions of strong aqueous acids (HBr, HBF_4, HNO_3, etc.) can be introduced by addition of the aqueous acid followed by extraction of the IL with an organic solvent. When the acid is not readily available, addition of the corresponding group 1 or silver metal salt followed by organic extraction is usually the favoured procedure.



Scheme 3. Synthesis of tac ILs.

Despite the ring strain of the three-membered ring, these cations are incredibly stable: they can be heated to reflux in water; some salts have thermal decomposition onset temperatures (T_d) as high as 400 °C; and they have good electrochemical windows with low reduction potentials. The reason for this stability is the charge delocalisation on the three carbon and three nitrogen atoms, as well as the aromaticity of the 2π-electron cyclopropenium system.

The ILs presented in Table 1[20] have very good T_d values and acceptable melting points. The viscosities are typical of many ILs; unfortunately, they do not approach those of the least viscous ILs (Fig. 3). Our ability to manipulate specific properties of these ILs gives us enormous potential to target specific applications.

Table 1. Data for selected tac ILs.

Compound	T_m (°C)	T_d (°C)	Viscosity at 20 °C (cP)	Viscosity at 60 °C (cP)
$[C_3(NEt_2)_3]BF_4$	27	377	210	29
$[C_3(NEt_2)_3]$TFSA	23	393	95	20
$[C_3(NPr_2)_3]BF_4$	81	397	–	–
$[C_3(NPr_2)_3]$TFSA	34	409	220	32
$[C_3(NBu_2)_3]BF_4$	34	373	–	90
$[C_3(NBu_2)_3]$TFSA	7	400	230	38
$[C_3(NBuMe)_3]BF_4$	n.o.	374	360	40
$[C_3(NBuMe)_3]$TFSA	n.o.	386	105	20

Summary

My last four or five years as a researcher in ionic liquids have been quite fascinating. As a synthetic organometallic chemist who was used to purification by distillation or crystallisation, dealing with ILs that will neither distil nor crystallise (rarely, anyway) has frequently proven to be a challenge! Fortunately, of the one hundred or so ILs

that we've now produced, only a handful have not (yet) been successfully purified. The future of ionic liquids is very bright and getting brighter. Increasingly, ILs find themselves in significant commercial applications and the costs of ILs continue to decrease. And I haven't even mentioned the chiral-magnetic-luminescent or hypergolic ILs!

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NZIC Annual General Meeting

The NZIC AGM will take place in the Chemistry Department, University of Otago, Thursday 22 November 2012 at 4 pm

Agenda

- Apologies
- Minutes of the 2011 AGM held at the NZIC Conference University, Waikato, 1 December 2011
- Matters arising
- Financial Report including audited accounts
- Election of Officers:
  - President
  - 1st Vice-President
  - 2nd Vice-President
  - Treasurer
  - Honorary General Secretary
- Appointment of auditor
- Other Business

Moved that the rules of NZIC be amended to include the following clause:

No addition to or alteration of the aims/objects, payments to clause or the winding-up clause shall be approved without the approval of Inland Revenue. The provisions and effect of this clause shall not be removed from this document and shall be included and implied into any document replacing this document.

Note: This clause is to be included on instruction from IRD to allow NZIC to retain its tax exemption status.

Nominations for officer positions close with Hon. Gen. Sec. (rendle@xtra.co.nz) on 30 October 2012.

Article

The evolution of chemistry and medicine in the 18th and 19th centuries

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Keywords: *chemistry, medicine, history, 18th Century, 19th Century*

Introduction

Throughout history there have always been close ties between chemistry and medicine. For millennia, healers, shamans and physicians have applied many essentially chemical techniques including distillation, smelting and soap-making in their search for new ways to treat disease. Much of this chemical experimentation was associated with various mystical, astrological and other pseudoscientific beliefs, and is, therefore, best described using the term 'alchemy' rather than 'chemistry'.

By the 18th century, the mysticism of alchemy was being replaced by rigorous quantitative experimentation and the new science of chemistry was emerging, although it was still often considered a subset of medicine. Consequently, most chemistry teaching and research was carried out in medical schools and apothecaries, and this would not change until the latter part of the 18th century when the applications of chemistry outside of medicine, for example in manufacturing and mining, became obvious.

However, researchers remained limited by their inability to accurately conceptualise the microscopic and atomic worlds. Physicians had not yet discovered the role microorganisms play in many diseases, while chemists were still debating flawed ideas such as phlogiston, and whether an element was a physical or philosophical concept.

As chemistry advanced into the 19th century a framework of core chemical concepts such as chemical affinity, valency and bonding began to emerge. At the same time medicine was freeing itself from the thrall of the "four humour" model of disease, a model which had been embraced since the time of the ancient Greeks. According to the four humour model, disease was caused by an imbalance of the four humours in the body: blood, phlegm, black or yellow bile. Attempts to rebalance a patient's humours included some potentially lethal practices, including the bleeding of patients and the use of toxins such as mercury (results in excessive salivation), antimony and arsenic as medicines. An unfortunate by product of these drastic treatments has been that they enabled non-effective, but essentially harmless pseudoscientific treatments, such as homeopathy, to establish themselves as viable medical therapies (at least in the eyes of the general public).

Airs and gases

At the turn of the 18th century, it was understood that air played a role in combustion and respiration and that it exerted pressure, but the idea that it might consist of different gases had not yet been conceptualised.

In 1727, botanist and chemist Reverend Stephen Hales developed a new piece of apparatus: the pneumatic trough. By passing gases into a trough of water over which was held an inverted vessel containing water, the gases could be collected and quantified. However, the potential application of this apparatus in the study of gases was not taken up by chemists until the 1770s, when there was surge of interest in gases by many prominent chemists including Antoine Lavoisier, Henry Cavendish and Joseph Priestley. By 1800, twenty different "airs" had been prepared and differentiated, including hydrogen, nitrogen, oxygen, hydrogen chloride and the various oxides of carbon.

The 1780s saw the development of 'pneumatic medicine': the use of gases to treat illness. A chemist and physician, Thomas Beddoes first used oxygen-enriched air to treat asthenic (weak) patients. In 1798, he established the Pneumatic Institution for Relieving Diseases by Medical Airs in Bristol, where patients could inhale gases produced in the basement by an enormous machine built by Gregory Watt, son of the engineer James Watt. Gas production was supervised by the young chemist, Humphrey Davy, who experimented with several gases including nitrous oxide. Upon taking nitrous oxide himself, he noted the pain-killing effects, but its potential use as an anaesthetic was not realised until 1844 when it was first used by dentist Horace Wells in Hertford, Connecticut to anaesthetise a patient before the removal of a troublesome molar tooth. Instead, prior to 1844, nitrous oxide was primarily used at "laughing gas" parties to entertain the upper classes.

Despite Wells' early success, a failed demonstration to surgeons at Massachusetts General Hospital that same year led to nitrous oxide being largely ignored for two more decades, in favour of the use of ether and chloroform. However, after dentist G. Q. Colton, demonstrated its safe use on thousands of patients without mishap in 1862, the use of nitrous oxide became common place in hospitals throughout Europe and the United States.

In addition to their medical applications, the study of gases and their reactions played a role in the development of many concepts vital to the further advancement of chemistry, including the various gas laws, the mole, molar ratios, and atomic theory.

Plant-derived medicines

Plants are an abundant source of bioactive compounds, and throughout history they have been pulped, dried, powdered, extracted and distilled in order to access the myriad of potentially beneficial compounds. However, even into the 19th century, the attribution of beneficial properties to certain plants was often based on myth rather than on science. Treatments were still described in relation to their effects on the four humours, or related to the Doctrine of Signatures (formulated in the 17th century by Jacob Bohme, a

follower of Paracelsus), whereby the curative properties of a plant were indicated by a "Divine signature" reflected in the colour, shape or other physical properties of a plant. For example, the yellow hued goldenrod was deemed to be a cure for jaundice, while the liver shaped leaves of liverwort were believed to hold the cure for liver diseases.

Astrology played a major role in the work of Nicolas Culpepper, arguably the author of one of the most famous English herbals. Published in 1653, *The Complete Herbal* incorporated many references to astrology. Culpepper's herbal remained influential throughout the 18th and 19th centuries and can still be found on bookshelves today, albeit with most of the astrological references removed.

The Doctrine of Signatures and the incorporation of astrology into herbalism reflected the religious beliefs of the time, which placed humankind at the centre of the universe. However, the Enlightenment movement of the 18th century provided an environment in which such beliefs could be challenged, particularly when scientific evidence disputed such beliefs. Chemists played a key role in challenging vitalism, the idea that living organisms possess some "vital force" that differentiates them from inorganic matter. The synthesis of urea by Wohler in 1828, acetic acid by Adoph Kolbe in 1845, and a range of organic compounds by Marcellin Berthelot in the 1850s soon removed the idea of vitalism from scientific discussion.

Prior to the 18th century a few effective treatments for disease were in use, e.g., quinine to treat malaria (first documented in 1663) and iron to treat anaemia (first described in the 1640's)), however; their discovery was largely serendipitous. In the 18th and19th centuries, a more scientific approach began to reveal many new treatments for a wide range of diseases.

The first clinical trial

In 1747, the Scottish naval surgeon, James Lind, carried out what is believed to be the first clinical trial to identify a cure for scurvy, a disease responsible for the deaths of thousands of British sailors. Taking 12 sailors suffering from the disease, he divided them into six groups, with five of the groups receiving a different daily supplement to their diet (oranges and a lemon, vinegar, dilute sulfuric acid, a herbal mix) while the sixth served as the control group. The results were clear: only the two sailors who consumed the citrus fruits responded rapidly, one of whom returned to duty after only six days. While it had previously been observed that citrus fruits had a beneficial effect in preventing scurvy, this belief was often extended to all acids. Lind's research was acted on by Captain James Cook in his second voyage, resulting in no scurvy deaths during the three years at sea.

Another physician who introduced a scientific approach to herbalism was Anton von Storck (1731 – 1803), a member of the Viennese aristocracy, and confidant to royalty, who had begun life poor and orphaned. Concerned that only the rich could afford the services of a physician, Storck sought to determine which folk remedies could be used to effectively treat disease. By testing samples on animals and then on himself, Storck studied plants such as hemlock, thorn apple, henbane, monkshood and colchicum corm. He identified monkshood as a diuretic and diaphoretic, and colchicum corm as a treatment for dropsy and pleural effusion. Later, colchicum corm would also be shown to be effective in the treatment of gout.

Folk remedies containing more than one herb could confound the search for effective herbal remedies. In 1775, physician and botanist William Withering was asked his opinion of an herbal tea which was being used to treat dropsy (fluid accumulation associated with heart failure). Examining the various herbs within the tea, Withering suspected that it was the foxglove which was causing an improvement in patients. Testing foxglove on himself, he standardised the doses to determine what would be a safe yet effective dose and then treated 158 patients, with around two thirds responding favourably.

Purification and isolation of therapeutic agents

One of the challenges of working with herbal remedies is their unreliability owing to their compositional complexity and variation. However, by the beginning of the 19th century purification methods, including acid/base extraction and crystallisation, allowed isolation of the active components of various plants with known therapeutic properties. In 1805, Friedrich Wilhelm Serturner published his isolation of an alkaline substance from opium which induced drowsiness when administered to a dog. Further research revealed that this new compound contained carbon, hydrogen, oxygen and nitrogen. When this new research was published in 1817 it drew the attention of prominent French chemist Joseph Gay Lussac who coined the term morphine to describe the new compound and predicted that similar compounds (named alkaloids in 1818) would soon be found. Improvements in purification methods would later reveal that the isolated compound was impure, and it was not until 1831 that morphine was completely purified by Professor William Gregory at the University of Edinburgh.

Other important natural products extracted at that time included emetine, which was purified enough by 1817 to demonstrate its effectiveness in treating amoebic dysentery; and quinine, in 1820. The more reliable (and more palatable) nature of quinine in treating malaria, compared to its parent natural product – powdered cinchona bark, led to great demand for this new product, and by 1826 a factory owned by Pelletier was producing 3600 kg per annum. The success of quinine in treating malaria appears to have been a pivotal point in the shift away from the use of natural products towards pure compounds to treat disease. Morphine also moved into bulk commercial production once the hypodermic syringe was invented in 1853. Thus by the mid 1850s a nascent pharmaceutical industry had been born.

Synthetic drugs

The introduction of coal gas as a source of lighting in the early 1800s provided chemists with an unwanted by-product, coal tar, to experiment with. By 1842, a German gas works chemist, Friedlieb Runge had extracted carbolic acid (phenol) and observed that this new substance could prevent the decay of organic material. This property was exploited by industrial chemist Frederick Calvert who used phenol as a disinfectant and for water purification in the

1850s. In France its use for disinfecting wounds was popularised by physician Jules Lemaire in 1862. However, its use was largely ignored by British surgeons until its use was championed by Joseph Lister, Professor of Surgery at the University of Glasgow.

The caustic nature of phenol led to the search for alternatives. A collaboration between Carl Thiersch, Professor of Surgery and Hermann Kolbe, Professor of Chemistry at Leipzig, resulted in the synthesis of salicylic acid (by the treatment of phenol with carbon dioxide in the presence of sodium) and its subsequent use as an antiseptic. This process was industrialised by 1874, and, thus, salicylic acid became the first drug to be synthesised for medical use.

A further use for salicylic acid was revealed when, on using salicylic acid as an "internal antiseptic" in the treatment of typhoid patients, Carl Buss discovered that it was an effective antipyretic. Salicyclic acid was soon being applied to other diseases, including rheumatic fever, rheumatoid arthritis and gout (owing to its anti-inflammatory properties).

Despite its myriad of applications many patients found salicylic acid irritated the stomach. In 1883, Polish physician and chemist, Marceli Nencki, attempted to solve this by reacting salicylic acid with phenol to form phenyl salicylate. Insoluble in the stomach, it was more soluble in the small intestine where it had a small therapeutic effect.

Further chemical modifications of salicylic acid, carried out by Arthur Eichengrun and Felix Hoffman at the Bayer company in Germany in 1896 resulted in the synthesis of acetylsalicylic acid (aspirin). Although initially rejected as a drug by the company pharmacologist, it eventually underwent clinical trials which demonstrated its impressive analgesic, anti-pyretic and anti-inflammatory properties. By 1899 it was being sold worldwide.

Inorganic compounds as medicines

Many inorganic compounds can either be found in relatively pure form in nature or readily extracted using physical methods. Consequently they have been applied to the treatment of disease throughout history. One prominent promoter of mineral-based treatments was Paracelsus (1493-1541), who rejected many of the herbal remedies of his time in favour of inorganic treatments. Treatments included the use of mercury, arsenic and antimony compounds. While many of these treatments had been discarded by the 18th century, some continued to be used into the 18th, 19th and even the 20th century. Some even proved successful in actually treating disease.

The treatment of iron deficient anaemia (historically described as chlorosis, "green sickness", or "love sickness") with iron compounds has been known since the 17th century; however, it was in 1832 that French physician Pierre Blaud first used ferrous sulphate to successfully treat 30 cases of chlorosis.

Mercury has had a chequered medical history. Believed to be too toxic for medical use by prominent Roman physician, Galen, it was brought into use again in the 15th century, when treatments of the day had proven ineffective against syphilis. In desperation, mercury (in pure and compound forms) was applied to the treatment of syphilis, and later to a wide range of other diseases. Indeed pharmacopoeias from the 1950s can still be found which list ointments containing 30% metallic mercury, and purgatives for children made from mercury and chalk. Various attempts have been made to find less toxic mercury-based cures. Mercurous salts were found to be less corrosive than mercuric salts, and in the late 1880s mercury benzoate, the first organomercurial compounds was developed.

Arsenic compounds have been used since the tenth century when arsenic trioxide was applied to the treatment of cancer of prominent Arab physician and alchemist, Ibn Sina. In 1786, Thomas Fowler developed an alcoholic solution of potassium arsenite for the treatment of malaria. Although the solution proved less reliable than quinine, its use was expanded to other applications, including the treatment of pernicious anaemia. Unfortunately, the rosy cheeks arising from its use were less to do with a cure and more to do with capillary damage resulting from arsenic poisoning. Its use in the treatment of leukaemia proved more interesting. In 1865, Heinrich Lissauer used Fowler's Solution (1% KH_2AsO_3) to successfully (albeit temporarily – she died five months after being discharged from hospital) treat a young women with acute leukaemia. The use of Fowler's Solution for the treatment of leukaemia persisted into the 20th century, and it was used in the 1990s in China to successfully treat acute promyelocytic leukaemia, an approach which was approved for use in the USA by the FDA in 2001.

In 1863, Antoine Bechamp prepared the sodium salt of the meta-anilide of phenylarsonic acid and this compound was initially used as a treatment for skin diseases. However, in 1905 it was discovered that this compound killed the trypanosomes which caused sleeping sickness, and although it proved to be too toxic for use, its effectiveness convinced immunologist Paul Ehrlich to research analogues as potential chemotherapeutics. One of the results would be arsphenamine (Salvarsan), a potent anti-syphilitic which entered production at the end of 1910.

The time which would elapse between the identification of a new substance and its incorporation into medicine was often fairly short. Many physicians would often experiment on themselves (unlike the ancient Greeks who would experiment and often poison hapless slaves). Bismuth had often been confused with tin, lead and antimony throughout history; however, in 1753, French nobleman, Claude Geoffrey the Younger, identified bismuth as a unique substance. Within a few years various salts of uncertain composition were being applied to medicine. In 1857, bismuth subcarbonate [$(BiO)_2(CO_3)$] was used as an antacid. Bismuth subsalicylate is one of the components of modern Pepto-Bismol antacid treatments.

Magnesium sulfate was a favoured purgative in England in the 18th and 19th century. Isolated from the mineral waters of Epsom, a spa town at the time, it became known as Epsom salts. Other salts soon entered the market as antacids and purgatives, including magnesium carbonate and magnesium oxide, as well as hydrated sodium sulfate (known as Glauber's salt after Johann Glauber who isolated it from a Viennese spring).

Iodine was isolated from seaweed by Bernard Courtois in 1811. Samples of his volatile purple crystals were passed on through friends to Joseph Louis Gay Lussac, and also to Humphrey Davy.[1] Both quickly realised that it was an element similar to chlorine and rushed to lay claim to the discovery, publishing their conclusions within one day of each other, which resulted in much argument over who had made the discovery first.

By 1820, iodine was being used by Francois Coindet as a treatment for goitre. Observing that one of the natural remedies for goitre was burnt sea sponge, Coindet concluded that the active ingredient was likely to be iodine. Unfortunately, overdosing of his patients led to toxicity, and this, as well as the treatment's limited ability to treat patients with chronic goitre, led to its initial abandonment as a treatment for goitre.

Iodine was also applied to the treatment of a range of other diseases including tuberculosis, often in the form of Lugol's iodine (a 2:1 aqueous solution of potassium iodine and iodine) developed by Jean Lugol in 1829. Iodoform, synthesised by G.S. Srullas in 1822, was also used for the treatment of goitre by physician Robert Glover in 1847.

Iodine solutions were used in 1839 by J. Davies, a Hertford physician, to disinfect wounds. Although such solutions were used in the American Civil War, they were not widely applied until research by French bacteriologist Casimir Davaine in the 1870s showed that iodine solutions could kill a wide range of organisms.

Potassium bromide was first introduced into the British Pharmacopoeia in 1836, after claims that it had been successfully used to treat enlargement of the spleen. In 1857, its use as a treatment for epilepsy was described by obstetrician Sir Charles Locock. At the time, the prevalent view was that epilepsy was due to masturbation. Having read that lithium bromide could suppress the libido, Locock supposed it would be an effective treatment for epilepsy. Despite the faulty reasoning, lithium bromide proved to be an effective treatment for epilepsy, as well as being used as a sedative.

Chemistry and microbes

Elemental chlorine was first prepared and studied in 1774 by Carl Wilhelm Scheele, who mistakenly identified it as an oxide rather than an element. Within 20 years, an aqueous solution was being used as a disinfectant and for purifying water, and by the middle of the 19th century hypochlorite solutions were in common use as disinfectants.

Despite the success of such solutions as disinfectants, the medical fraternity resisted suggestions that without these solutions, they were infecting their patients with some type of "putrid particle". Both Oliver Wendell Holmes in Boston (1843) and Ignaz Semmelweis in Vienna (1847) suffered the derision of their medical colleagues when they suggested that they should wash their hands with chloride of lime (calcium hypochorite) between post-mortem examinations and dealing with patients. At the time, it was believed that infection resulted from miasma, or exposure to "bad airs".

In the 1860s Louis Pasteur published his germ theory, observing that chemical solutions could kill the infectious agent. This was applied by Joseph Lister in his use of carbolic acid (phenol) solutions to spray surgical equipment, dressings and the patient. Rates of infection dropped dramatically.

While chemistry had provided the means to kill micro-organisms, it also proved important in better understanding the structure of micro-organisms. Stains and dyes, which were first utilised in the 1870s, revealed the complex structures of the cells of microorganisms. Paul Ehrlich played a key role in the development of staining and made many important discoveries, including the identification of mast cells and a urine test to identify typhoid. Later, at the beginning of the 20th century, Ehrlich also realised that some dyes possessed the ability to kill microorganisms, and began to study their use as chemotherapeutics. As mentioned previously, this research eventually led to the synthesis of salvarsan in 1910, the first effective drug for the treatment of syphilis.

Post-1900 chemistry and medicine

By the end of the 19th century many of the theoretical foundations of modern chemistry and medicine had been laid. Therapeutic agents had been isolated from various sources, purified, quantified, tested and applied to various diseases, and the first successful attempts at the synthesis of drugs had been made. Chemistry was no longer an offshoot of medicine but a fully developed science in its own right, and was already dividing into various specialities of its own (e.g., analytical, organic, inorganic, etc.).

In the 20th century, chemists would rapidly expand on the knowledge gained during the previous two centuries. More complex drug molecules would be synthesised and the pharmaceutical industry would grow into a multi-billion dollar enterprise. The development of chromatography, mass spectrometry, nuclear magnetic resonance and other analytical techniques would reveal and identify millions of new compounds, some of which were suitable for therapeutic use.

In medicine, the discovery of DNA would bring a better understanding of diseases we now know have a genetic cause, and following the Second World War, the United States would start another war, this time on cancer. The consequences of environmental contamination would also reveal new diseases resulting from careless disregard for the effect new compounds can have on our surroundings.

Afterword

This article includes information derived from various books on the history of chemistry.[1-4]

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Enlivening science for secondary school students: interschool competitions at CPIT

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Keywords: outreach, STEM, student engagement

Introduction

Competitions for secondary schools organised by Christchurch Polytechnic Institute of Technology (CPIT) now encompasses four year levels. Two separate competitions devoted to chemistry are open to Year 11 and Year 12 students, with two other competitions across all science disciplines offered for Year 10 and Year 13 students. The competitions are all well supported by local secondary schools, with typically 15-20 schools entering. Most schools are from Christchurch, but participation sometimes extends as far north as Kaikoura and south to Timaru.

The competitions had their origin in a single competition organised by Canterbury Branch of NZIC, for Year 11 students. This competition emphasised inorganic qualitative analysis, an emphasis we retain today for the Year 11 Competition. CPIT took over responsibility around 1997. Noting that secondary school students in the humanities have long enjoyed opportunities such as debating competitions and Stage Challenge, CPIT decided to extend these competitive opportunities to science students. We wanted to reinforce the idea that science is in every sense a social occupation (Fig. 1), and to help overturn the conception that people working in science are eccentrics who beaver away on their own, in silence. We started the Year 10 Science Competition in 2000, followed by Year 13 Science in 2005, and finally Year 12 Chemistry in 2006.

The format for each competition is the same: three students per team competing in a tight time frame, with an emphasis on practical activities. The emphasis on practical activities reflects the fact that most scientific activity (at whatever level) is intensely practical, and is consistent with CPIT's emphasis on practical work in its science qualifications. One entry per school is automatically accepted, with a second team accepted to fill the available space on a first-come basis. To help organisation at the school level, start times are the same (6.45 pm) across all competitions, and each competition ends around 9.00 pm with a supper – currently food from Subway.

In recent years, we have been financially supported by NZIC and by the Canterbury Science Teachers' Association. However, the bulk of the cost (principally staff time) has been borne by CPIT. The time commitment is considerable, with one academic staff member (the author) keeping an eye out for suitable activities throughout the year. Technician time amounts to 3-4 days for each competition; two or three technicians are kept busy all day setting up the various activities on the day, and doing the clean-up next day.

Competition activities

The Year 11 Chemistry Competition typically runs in September, toward the end of the third term for schools. As noted above, the emphasis is on inorganic qualitative analysis (both solids and aqueous solutions) using simple test tube reactions (Table 1).

Table 1. Information given to participants for the Year 11 Chemistry Competition, to allow identification of calcium carbonate, sodium sulphate, sand, sodium carbonate, sodium salicylate and sodium chloride as unknown white powders.

Litmus paper indicates whether a solution is acid, alkaline or neutral.
Barium carbonate, chromate and sulfate are insoluble in water.
Barium chloride and nitrate are soluble in water.
Group I carbonates are soluble in water and turn litmus blue, but **Group II carbonates** are insoluble in water.
All carbonates dissolve in dilute acid with the evolution of bubbles of a colourless gas (CO_2).
Sand is neutral to litmus.
Sodium salicylate is soluble in water and insoluble in dilute acid. When a few drops of ferric chloride are added to an aqueous solution, the colour changes to violet/red.
Sodium sulfate is soluble in water and in dilute acid; it is neutral to litmus.

A similar approach is used for the series of colourless solutions. There is nothing particularly complicated, but participants get tubes mixed up, do not follow instructions carefully, or run out of time. We have recently added pH buffer preparation as an additional activity. In this case, we deliberately choose buffers with one component that is slow to dissolve (such as oxalic acid).The Year 12 Chemistry Competition usually runs in May, shortly after the start of the second term. This competition focuses on organic chemistry, but assumes no background knowledge. Like the Year 11 Chemistry Competition, the emphasis is on problem-solving, following instructions, attention to detail, etc. Most of the evening is taken up with organic qualitative analysis of both solids and liquids, using simple test tube reactions of solubility in water, acid, and base; reaction to litmus; and decolourisation of potassium permanganate alongside a simple functional group test (e.g., precipitate formation with 2,4-DNP). As for the Year 11 competition, participants get tubes mixed up, do not follow instructions carefully, or run out of time. We often include a molecular model isomerism activity (e.g., make non-superimposable mirror images of $C_2H_3Br_2Cl$), an activity in which participants usually score well.

Fig. 1. Participants in the 2012 Year 12 Chemistry Competition

The Year 13 Science Competition is in mid-March, before the year's NCEA assessment load kicks in. Similarly, the Year 10 Science Competition (November) is timed to occur after senior students go on NCEA study leave. The Year 13 Competition deliberately introduces competitors to equipment that they will encounter at tertiary level. In 2012, we included spectrophotometric measurement of reducing sugar in an energy drink, gram staining of bacteria, and measuring the dimensions of a soil micro-invertebrate using a microscope. For the Year 10 Competition, activities have included calibrating a thermometer by measuring ice point, and calibrating an autopipette. These activities are sufficiently portable that we now offer the Year 10 Competition for South Canterbury schools, based in Timaru (courtesy of Timaru Girls' High School).

Both of the Year 10 and Year 13 competitions include a multiple-choice quiz covering all areas of science (including the history of science). Questions reward participants who are able to problem-solve, for example this question from the 2011 Year 10 Science Competition:

The radioisotope caesium-137 is an important environmental contaminant released from the incident at the Fukushima nuclear plant in Japan earlier this year. The electronic charge on an ion of caesium-137 is +1; the electronic charge on caesium-135 will be: (A) -2, (B) +1, (C) +2 or (D) +3.

Who won?

The intent behind running the Competitions has never been to sort out the "best school in Christchurch"! Nevertheless, schools (and their students) are often intensely competitive. Noting that league tables are currently controversial, some schools take the competitions more seriously than others, and not all schools participate every time. Over the years:

Eight schools have won more than once (Burnside High School, Cashmere High School, Christchurch Girls' High School, Christ's College, Hillmorton High School, Rangi Ruru Girls' School, Riccarton High School, St Andrew's College);

Thirteen schools have won at least once (the above plus Avonside Girls' High School, Darfield Hgh School, Lincoln High School, Papanui High School, Shirley Boys' High School);

Twenty four schools have been placed in the top five at least once (the above, plus St Thomas of Canterbury College, Christchurch Boys' High School, Hagley Community College, Kaiapoi High School, Kaikoura High School, Middleton Grange School, Oxford Area School, Rangiora High School, St Margaret's College, Unlimited Paenga Tawhiti, Villa Maria College).

From this it is clear that winning schools are spread across both private and state schools, single-sex and co-ed, town and country, and a wide decile range.

Conclusion

Competitions are a key part of CPIT's outreach to secondary schools, and unlike many "marketing" activities, the competitions have benefits to all parties. As well as meeting marketing outcomes (CPIT's brand; CPIT as a science provider; key institutional qualities such as an emphasis on 'hands-on'), we believe that the competitions enhance the position of science in secondary schools.

When plants bite back: A broadly applicable method for the determination of cyanogenic glycosides as hydrogen cyanide in plant-based foodstuffs

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Keywords: cyanide, cyanogenic glycoside, cassava, colourimetric analysis

Cyanide uses and toxicity

Cyanide is extensively employed in a variety of industrial processes including the extraction of gold and silver from ores, electroplating baths, insecticides, case hardening of steels, analytical chemistry and the manufacture of other cyanides.[1]

Many cyanides are extremely toxic to terrestrial vertebrates and aquatic life. The cyanide anion is an inhibitor of the enzyme cytochrome *c* oxidase (a trans-membrane protein complex found in mitochondria and bacteria), attaching to the iron within this protein and preventing the transport of electrons from the enzyme to oxygen. Consequently, the eukaryotic cell can no longer aerobically produce ATP for energy and cellular respiration is greatly reduced, affecting those tissues most dependent on, especially the central nervous system and the heart.

Following oral administration, soluble cyanide salts at the pH encountered in the stomach, form predominantly HCN which rapidly penetrates mucous and cell membranes. Acute exposure can result in nausea, anxiety, confusion, vertigo, dizziness, lower jaw stiffness, convulsions, spasms, paralysis, coma, irregular heat beat, cyanosed (blue-grey coloured) skin, increased rate of breathing and death. The oral LD_{50} (rats) for potassium cyanide is 5 mg/kg body weight, the oral LD_{Lo} (lowest dose known to have resulted in fatality) for humans is 2.8 mg/kg body weight (or approximately 1 mg/kg body weight as HCN). The primary means the body employs to detoxify cyanide is its conversion to thiocyanate, mediated by the enzyme rhodanese.[2]

Cyanide as a plant defense mechanism – cyanogenic glycosides

Plants use cyanide as a poison to deter predators. Cyanide in plants appears mostly in the form of cyanogenic glycosides (CNG), (i.e., a sugar attached to a cyanide group). At least 2650 species of plants produce CNGs and the corresponding hydrolytic enzyme which are bought together when the cell structure of the plant is disrupted by a predator. This results in the rapid breakdown of the cyanogenic glycoside to a sugar and a cyanohydrin that rapidly decomposes to form HCN.[3] There are approximately 25 CNGs known, some of which are found in major food crops and other edible plants including cassava, sorghum, lima beans, bamboo shoots, stone fruits, and almonds (Table 1, Fig. 1). Cassava (also known as manioc, yuca and tapioca) is by far the most important CNG-containing food crop for humans, being the most important food in the tropics after rice and maize.[4]

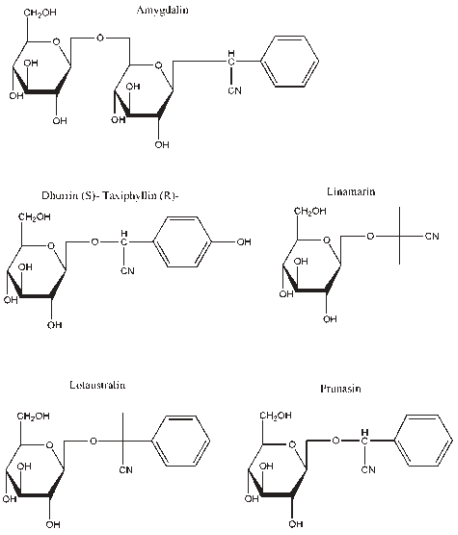

Fig. 1. Chemical structures of the major cyanogenic glycosides

Effect of chronic exposure to cyanogenic glycoside containing foodstuffs

Liberation of hydrogen HCN from CNGs usually occurs after mastication and ingestion and arises from enzymatic degradation of the latter to produce HCN, resulting in acute or chronic cyanide poisoning. The enzyme responsible (β-glucosidase) may arise from the plant material or from gut microflora. HCN can also be produced to a lesser extent by glucosidases in the liver.[5]

While cyanide poisoning from CNGs most commonly occurs following ingestion, hydrolysis may also occur during food preparation. One graphic example involved a series of failed rescue attempts resulting in the poisoning of eight individuals exposed to HCN gas produced by bamboo shoots left to pickle in a well in Thailand (cyanide content of the bamboo ranged from 39 to 434 mg/kg, well volume was 27 m^3). All victims lost consciousness, two died following cardiac arrest, four recovered with supportive care, and two regained consciousness soon after the event.[6]

Chronic exposure to food containing CNGs has been linked to several diseases primarily affecting the central nervous system. Tropical ataxic neuropathy (TAN) describes several neurological symptoms affecting the mouth, eyesight, hearing and gait that present clinically as sore tongue, optical atrophy, angular stomatitis (in-

Table 1. Cyanogenic glycosides in various foodstuffs.[1,3]

Plant	Part containing cyanogenic glycoside	Cyanogenic glycoside	Cyanide content as Total HCN mg/kg
Cassava (*Manihot esculenta*)	Roots, leaves	Linamarin (~95%) and lotaustralin (~5%) (Nambisan 2010)	Leaves (bitter-sweet) 300 and 451 Tubers (bitter and sweet) 380 and 445 Dried root cortex 2360[3]
Sorghum (*Sorghum vulgare*)	Young leaves	Dhurrin	2400 whole immature plant[1]
Flax (*Linus usitatissimum*)	Seed (linseed)	Linamarin, linustatin, neolinustatin	360-390[3]
Giant taro (*Alocasia macrorrhizos*)	Stem, leaf	Triglochinin	29-32[3]
Bamboo (*Bambusa arundinacca*)	Young shoot	Taxiphyllin	7700 immature shoot tip[1]
Lima beans (*Phaseolus lunatus*)	Bean	Lotaustralin	2000-3000 depending on species and source[1]
Apple (*Malus* spp)	Seed	Amygdalin	690-790[3]
Peach (*Prunus persica*)	Kernel	Amygdalin, prunasin	710-720[3]
Almonds bitter (Prunus dulcis)	Kernel (depending on cultivar)	Amygdalin	4700[3]
Apricot (*Prunus armeniace*)	Kernel	Amygdalin, prunasin	89-2170[1]
Plum (*Prunus* sp.)	Kernel	Amygdalin, prunasin	696-764[3]
Nectarine (*Prunus persica var nucipersica*)	Kernel	Amygdalin, prunasin	196-209[3]

flammatory lesions at corners of the mouth), neurosensory deafness, skin desquamations (peeling or shedding of outer skin layers) and sensory gait ataxia (deviation from normal walking). It occurs only rarely in children under 10 years of age and the diet of patients is usually comprised of a monotonous intake of cassava derivatives.

Spastic paraparesis (called mantakassa in Mozambique and konzo in the Democratic republic of Congo) is a motor neuron disease charaterised by weakness or paralysis of the legs. It often has an abrupt onset and most frequently affects children and women of child-bearing age. The condition can sometimes affect the arms and speech. Epidemics of konzo have all been associated with chronic intake of cyanogenic glycosides at sub-lethal concentrations from cassava or cassava flour in combination with a low intake of sulphur amino acids.

Goitre and cretinism attributed to iodine deficiency can be exacerbated by chronic consumption of inadequately processed cassava. Cyanogenic glycosides are converted to thiocyanate during the detoxification process, which reacts with iodine which is subsequently unavailable to the thyroid, increasing the dietary requirement for iodine.[7]

Methods of reducing or eliminating toxicity

While genetic manipulation of CNG metabolism or selective breeding of cultivars offer a potential means of controlling the formation of CNGs and their distribution in plants, processing to remove CNGs remains the most practical method of reducing the levels of these toxic compounds in foodstuffs.

A plethora of different techniques are employed by communities for whom cassava represents a substantial portion of their diet. These techniques include peeling and slicing followed by boiling, baking, steaming, drying, deep frying, fermentation, grating/pounding, followed by drying and roasting. These processes differ in their effectiveness, but remove CNG either by enzymatic hydrolysis with the subsequent loss of the volatile HCN produced or by being leached out with water. Cutting cassava into small pieces and boiling in water can remove up to 80% of CNGs which are leached into the water, which is decanted repeatedly. The removal of CNG during drying is affected by the enzyme linamarase which can act on the cassava for a protracted period. In contrast, baking, steaming and frying are the least effective means of removing CNG (approximately 20% removed), owing to the inactivation of linamarase and the stability of the CNG linamarin. The most effective means of removal are crushing and sun-drying (<5% retained) and grating/fermentation, dewatering and drying (<2% retained).[8]

Method of analysis of total cyanide in cassava

The analysis of CNGs generally involves three steps: (i) extraction from foodstuff, (ii) hydrolysis of cyanide and (iii) analysis of cyanide. Extraction is normally carried out in dilute acid followed, in the case of cassava, by enzymatic hydrolysis using linamarase. The enzyme, however, is expensive, while acid digestion is cheaper and can hydrolyse all of the CNGs. Acid hydrolysis based primarily upon the method of Haque & Bradbury[3] was chosen because, being non-specific, the technique can accommodate a greater diversity of foodstuffs than autolysis or enzymatic hydrolysis.

Table 2. An inter-laboratory comparison of cyanide detected as HCN in cassava.

Sample	Division of Analytical Laboratories using picrate kit (Total cyanide as HCN mg/kg)	ESR Method using colourimetric method described above (Total cyanide as HCN mg/kg)
I	26	33
II	84	83
III	28	32
IV	58	56
V	32	34

Preparation of standards

Standards were prepared fresh for each analytical run from KCN. Approximately 12 mg was weighed accurately into a 5 ml volumetric flask and made up to volume with 0.1 M H_3PO_4. A 100 mg/L as HCN working standard was prepared from this solution using a conversion factor KCN to equivalent HCN of X 0.415. The working solution was used to prepared standards in the following concentrations: 0.5, 1.0, 2.5, 5.0, 10.0 and 20.0 mg/L as HCN in 0.1 M H_3PO_4. These solutions were treated as for the sample extracts but without being heated in a water bath. They equate to approximately 5, 10, 25, 50, 100 and 200 mg/kg cyanide as HCN in the original sample prior to extraction/dilution.

Extraction

Samples were homogenised in a blender (raw foodstuffs were frozen or assayed immediately to avoid break-down of CNGs due to endogenous enzymes), and approximately 10 g accurately weighed into a 100 ml Schott bottle. 100 ml of 0.1 M H_3PO_4 was added, the contents were shaken for two minutes and then left overnight at 5 °C. The resultant solution was then centrifuged at 3000 rpm in a 50 ml centrifuge tube.

The method of Haque and Bradbury[3] does not give an extraction time for the initial extraction into 0.1 M H_3PO_4. Comparison between the ESR determination and that performed by an Australian laboratory on the same samples (Table 2) found that samples left to extract overnight gave comparable results.

Digestion

1.6 ml portions of the interstitial layer were pipetted into multiple 8.0 ml capacity, sealable glass vials labelled respectively 0, 20, 40, 60, 80, 120, 180, 240, 300 and 360 minutes corresponding to the length of time the vial thus labelled was to remain in the water bath. 1.6 ml of 4 M H_2SO_4 was added and the vials immediately sealed. The vials were then placed in a water bath heated to 100 °C. Upon removal (or in the case of time (t) = 0 minutes, immediately) the vials were placed in an ice bath and 4 ml of 3.6 M NaOH added to halt the digestion process and convert cyanide to the stable NaCN.

Linamarin requires approximately 60 minutes under the conditions described above for complete hydrolysis. However, during the hydrolysis the vial is losing HCN gas at a slow rate. The rate of loss is determined by graphing equivalent HCN concentration in each digest against time spent digesting and extrapolating to $t = 0$.

Upon standing following the addition of 3.6 M NaOH it was noted that a brown precipitate formed. The precipitate was removed from each solution by filtering through a 0.45 µm syringe filter, removal being essential as any remaining precipitate can occlude light passing through the sample from the plate reader, thus resulting in a false positive or excessive result.

Colourimetric analysis

Aliquots (210 µl) of 0.2 M acetate buffer pH 5.0 were pipetted into the wells of a 96 well microtitre plate followed by 12 µl of chloramine-T (5 g/L in deionised water). 30 µl of neutralised digestion solution was then added, followed by 48 µl of isonicotinic/barbituric acid colourimetric reagent (prepared by making 0.85 g of isonicotinic acid and 0.90 g of barbituric acid up to 40 ml with deionised water and adjusting the pH to 11.0 with 3.6 M NaOH before making the volume up to 50 ml with deionised water).

The solutions were allowed to develop for 60 minutes before having their absorbance read at 600 nm on a plate reader.

Results

Salt and vinegar potato chips were also assayed by the method above and found to contain <10 mg/kg cyanide as HCN.

Standard curves

Standard curves were linear across the range 0.5 to 20.0 mg/L as HCN with r^2 values ranging from 0.998 to 1.000.

Spiked recovery

The recovery of pure linamarin from a 59 mg/L linamarin solution in 0.1 M H_3PO_4 (equivalent to 6.4 mg/L as HCN) under the conditions described above was 96.0%.

The recovery of cyanide as HCN from cassava spiked with linamarin at concentrations from 52-64 mg/kg as HCN ranged from 87 to 100% (n=5).

Inter-laboratory comparison

As part of the method validation procedure, sub-samples of cassava assayed by the ESR chemistry laboratory were submitted to The Division of Analytical Laboratories, Sydney West Area Health Service, New South Wales, Australia for confirmatory analysis.

Limit of detection

The limit of detection for this analysis was <2 mg/kg total cyanide as hydrogen cyanide.

Discussion

According to the Australia New Zealand Food Standards Code, Standard 1.4.1 Contaminants and Natural Toxicants 4(3) Table 2, clause 4, the maximum permitted levels of hydrogen cyanide (mg/kg) in various foodstuffs are: confectionary (25 mg/kg), stone fruit juices (5 mg/kg), marzipan (50 mg/kg) and alcoholic beverages (1 mg per 1% alcohol content).[9] In 2008 a limit of 10 mg/kg total cyanide as hydrogen cyanide in cassava chips was set by Food Standards Australia New Zealand (FSANZ) owing to concerns about very young children consuming ready-to-eat cassava chips.[10]

In our opinion, the method described in this paper is sensitive enough and sufficiently reproducible to be applied to the quantitative determination of CNG content in foods for regulatory purposes.

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The Olympic rings and the chemistry of Olympicene

The London 2012 Olympic games and Paralympic games have been enthralling audiences all over the world. It was fascinating to watch international and home team athletes competing against each other in a wide variety of sports.

In 1890 Baron Pierre de Coubertin founded the International Olympic Committee and the first modern games were held in Athens in 1896. He was responsible for designing the Olympic symbol used today, which comprises five coloured interlocking rings (blue, yellow, black, green and red) on a white background. The colours represented the colours of the flags of the nations, which took part in the games at that time. The modern view of the rings is that they represent the union of the five major nations of the world and the meeting of athletes from all over the globe.

Scientists have recently designed and imaged a molecule named Olympicene whose structure resembles these Olympic rings.

Professor Graham Richards, (former head of Oxford University's Chemistry Department) and member of the RSC, came up with the idea while he attended an RSC meeting thinking of ways of how the RSC could celebrate the London 2012 Olympics.

"When doodling in a planning meeting, it occurred to me that a molecular structure with three hexagonal rings above two others would make for an interesting synthetic challenge," said Professor Graham Richards CBE, RSC Council member. "I wondered: could someone actually make it, and produce an image of the actual molecule?"

A collaboration with chemists Dr David Fox and Anish Mistry at Warwick University resulted in the synthesis of Olympicene (2*H*-benzo[*cd*]pyrene).

Olympicene is related to graphene and has interesting electric and optical properties, which could be of potential use in solar cells and in lighting sources such as LEDs. The molecule's structure was initially observed at the University of Warwick using scanning tunnelling microscopy. However, to obtain a better resolution image, non-contact atomic force microscopy (AFM) was required and this led to a collaboration with the Physics of Nanoscale Systems Group at IBM in Zurich.

Dr Leo Gross of IBM-Zurich is an expert on non-contact AFM, an imaging technique that measures the interaction between electrons on a scanning probe with electrons in a molecule. A single carbon monoxide molecule attached to the scanning tip detects the strength of the short-range chemical bonds between the atoms. Dr Gross states "The key to achieving atomic resolution was an atomically sharp and defined tip apex as well as the very high stability of the system. We prepared our tip by deliberately picking up single atoms and molecules and showed that it is the foremost tip atom or molecule that governs the contrast and resolution of our AFM measurements."

A picture of the image can be seen at *www.rsc.org/AboutUs/News/PressReleases/2012/olympicene-resources.asp* A video discussing the story of Olympicene can be seen at *www.youtube.com/watch?v=dFp8Eoh_Vqo&feature=youtu.be*

Implications of a novel interpretation of the isosbestic point

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Keywords: Isosbestic point, degree of freedom, solvolysis, phase rule

In an earlier article we articulated the isosbestic point from an entirely novel perspective,[1] (i.e., from the stand point of the steady state principle). Here we would like to report a new finding in the solvolysis[5] reaction that the isosbestic point is invariant, contrary to the conventional belief that there is one degree of freedom.[6] Furthermore, we find that many of the conventional descriptions of isosbestic point in the literature and allied websites appear to need reconsideration or revision.

Introduction

The existence of isosbestic point(s) in UV-visible spectra is demonstrated with the solvolysis of dichloromethylbenzene.[2, 5] From the time dependent spectra of solvolysis of dichloromethylbenzene (Fig. 1) two distinctly visible isosbestic points are observed.

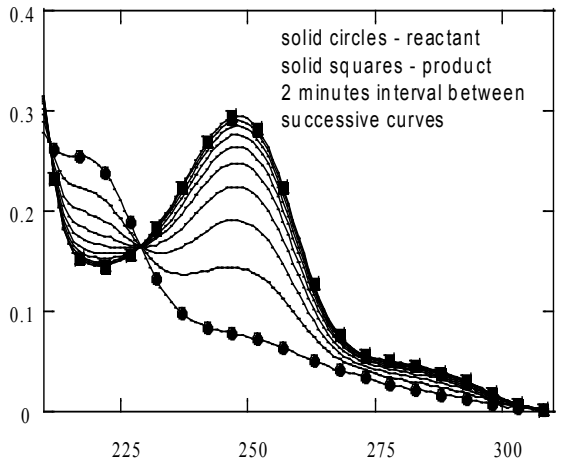


Fig. 1. Time-dependent UV-VIS spectrum of dichloromethylbenzene in water at 25°C.

In our recent new interpretation[1] we explained the reason for the appearance of isosbestic point at 233 nm from the stand-point of steady state approximation. In the following discussion, we address the implications of our new interpretation.

Discussion

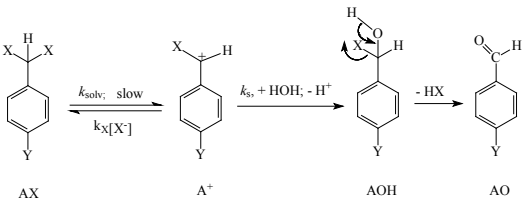
The term 'isosbestic point'[7] is usually employed with reference to a set of absorption spectra, plotted on the same chart for a set of solutions in which the sum of the concentrations of two principal absorbing components, A and B, is constant. The curves of absorbance against wavelength for such a set of mixtures often all intersect at one or more points, called isosbestic points**.** Isosbestic points commonly appear when electronic spectra are determined on (a) a solution in which a chemical reaction is in progress (in which case the two absorbing components concerned are reactant and product); or (b) on a solution in which the two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component, typically the concentration of hydrogen ions, e.g., in acid base indicator equilibrium.

$$A \rightleftharpoons B^- + H^+_{aq}$$

The effect may also appear (c) in the spectra of a set of solutions of two unrelated non-interacting components having the same total concentration. If absorption spectra of the types considered in the foregoing three cases intersect not at one or more isosobestic points but over progressively changing wavelength, this is *prima facie* evidence in case (a) for the formation of a reaction intermediate in substantial concentration A→C→B.

Our findings (Fig. 1 and the corresponding Scheme 1) report two distinctly visible isosbestic points for the solvolysis of 1,1-dichlorotoluene/dichloromethylbenzene with α-chlorobenzyl carbocation as intermediate.

Scheme I



where X = Cl or Br or N_3

This does not conform with information available in the 1997 edition of the IUPAC Compendium of Chemical Terminology[7] (in the absorption spectra in question, intermediate α-chlorobenzyl carbocation is observed in spite of the absence of intersection of spectra at progressively changing of wavelengths).

Furthermore, from a physical chemistry point of view,[8] the isosbestic point has been defined as: during a chemical reaction, a point occurs in the absorption spectrum (i.e., a wavelength) where at least two chemical species (for example, reactant and product) have identical molar absorption coefficients, which remain constant as the reaction proceeds. A stable isosbestic point is evidence that a reaction is proceeding without forming an intermediate or multiple products. Against the backdrop of our findings (Fig. 1 and Scheme 1) of two isosbestic points in the solvolysis reaction and with the unequivocal evidence of presence of α-chlorobenzyl carbocation,[2, 5]again this description of the isosbestic point appears to need revision.

In addition, it has been reported[9] that when a one-to-one (one mole of reactant yeilding one mole of product)

chemical reaction (including equilibrium) involves a pair of substances with an isosbestic point, the absorbance of the reaction mixture at this wavelength remains invariant, regardless of the extent of reaction (or position of the equilibrium). This occurs because the two substances absorb light of that specific wavelength to the same extent, and the analytical concentration remains constant (at isosbestic point both molar absorbtivities are the same). The isosbestic is defined[10] as the wavelength, wave number or frequency at which the total absorbance of a sample does not change during a chemical reaction or physical change of the sample. A simple example occurs when one molecular entity is converted into another that has the same molar absorption coefficient at a given wavelength. As long as the sum of the concentrations of the two molecular entities is held constant there will be no change in the absorbance at this wavelength as the ratio of the concentration of the two entities is varied. The essence of these two descriptions [9, 10] is that the concentrations of the two substances remain constant at the isosbestic point, and their molar absorption coefficients are same. Again, against the backdrop of the interpretation of isosbestic point in our earlier publication,[1] even these descriptions need to be reconsidered. According to the interpretation[1] from the stand-point of steady state approximation, the concentration of the intermediate α-chlorobenzyl carbocation (Scheme 1) is constant; and as a consequence of this intermediate remaining constant, the absorbance (at 233 nm) is invariant (and not because the concentration of the two molecular species is constant). Thus, the popular blanket assertion that at the isosbestic point the concentration of the two molecular species remains constant, again, has to be redefined, at least for the solvolysis reactions described in Scheme 1.

Pouest *et al.*[6] summarized the general conditions for the occurrence of the isosbestic point. Even though there is no general agreement on the conditions required, two major trends can be found concerning the number of absorbing components in the system:

1) A specific case was studied for a maximum of six absorbing species,[11] then simplified for an even more specific case of a complexation reaction with a maximum of four absorbing species.[12] These cases gave special conditions between products of molar absorptivities and stoichiometric coefficients.

2) More general cases without any limitation on the number of components were also studied. One study gave the most complete conditions on the system,[13] stating that an isosbestic point can be shown when:

   (a) the system is closed or results need to be corrected to correspond to a fixed overall concentration;

   (b) the spectra of the limiting states of the system (e.g., before and after reaction) intersect; or

   (c) the changes in the concentrations of the various components are linearly related, i.e., there is only one degree of freedom (e.g., the extent of reaction).

Returning to our system shown in Scheme 1 and the time-dependent spectra Fig. 1, in which we have interpreted the isosbestic point on the basis of presence of the intermediate α-chlorobenzyl carbocation,[1] we can now calculate the number of components using the phase rule,[14] viz., $F = C - P + 2$, where F is the number of degrees of freedom, C is the number of components and P is the number of phases However, since our system is closed, the '2' (which represent the temperature and pressure variables) can be neglected; thus, the expression reduces to $F = C - P$. If this simplified phase rule is applied to our system at the isosbestic point, the number of components is 1 (intermediate α-chlorobenzyl carbocation); the number of phases is 1; and, as a result, the number of degrees of freedom is 0. Thus, in our system the isosbestic point is an invariant system (analogous to the triple point of water). In the conventional description of isosbestic point wherein we have two components and one phase, the number of degrees of freedom is 1. We infer that Pouest *et al*.'s conclusion that the number of degrees of freedom at the isosbestic point is one appears to be wrong, at least for our solvolysis reaction system.

Furthermore, Pouest *et al*.[6] have concluded that when a reaction is followed by spectrophotometer, the appearance of one component is usually linked to the disappearance of one intermediate component, which can be highlighted by the fact that at some point during the reaction, the spectra no longer participates in the isosbestic point. A useful application of such a phenomenon could be the detection of the occurrence of an unknown or unusual component in an analyzed effluent for the process control or environmental purposes. Thus the use of the isosbestic point can be utilized for water quality monitoring. However, this application would again be erroneous with respect to our spectra (Fig. 1), as there is no observation of spectra which no longer participates in the isosbestic point.

According to Powles and Williams[15] an isosbestic point may be found when some quantity is conserved in spite of the variation of other physical parameters. In our system (UV-spectroscopy) the absorbance is conserved in agreement with the observations of Powles and Williams. But again, with the backdrop of our new interpretation of isosbestic point the concentration of intermediate α-chlorobenzyl carbocation is also conserved with respect to time, i.e., there are two quantities which are conserved: absorbance and concentration of the intermediate α-chlorobenzyl carbocation.

An extremely important point with regard to interpretation of isosbestic points in this system (solvolysis of dichloromethylbenzene) is that at 233 nm the conventional definition of isosbestic point[10] and our alternative interpretation[1] are applicable. However, when it comes to isosbestic point at 212 nm, the conventional interpretation of isosbestic point[4] fails miserably. It can be easily perceived from the UV-spectrum of benzaldehyde that benzaldehyde would possibly not absorb at 212 nm and as a consequence there is no probability of its existence at this isosbestic point, i.e., 212 nm. According to the conventional definition, both dichloromethylbenzene and benzaldehyde should be present in constant ratio with their molar extinction coefficients identical. Since there is no

likelihood of existence of benzaldehyde at the isosbestic point of 212 nm, the conventional definition fails to explain the isosbestic point. At this stage of the development of interpretation of isosbestic point, our own interpretation[1] also fails to explain the presence of isosbestic point. In fact, this is unexplored territory: the challenge remains in front of us.

Acknowledgement

Rachuru Sanjeev would like to dedicate this manuscript to his late mother, Rachuru Vijaya, a conscientious teacher who saw to it that "the nature and nurture" that he received groomed him into a teacher with the same kind of quality.

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Obituary

Professor Martin Fleischmann, March 1927 — 3 August 2012.

Martin Fleischmann was one of the giants of 20th century electrochemistry. He was always stimulating and challenging, interesting, creative, iconoclastic and great fun.

Martin started his research career at Imperial College in 1947. He was supervised by Herrington; Bockris was the charismatic, hugely energetic personality driving the effort, and other students included Conway and Parsons who both became very influential figures in electrochemistry.[1] The Faraday Discussion of 1947 gives a flavour of the intense interest in electrode kinetics and mechanism that developed at this time with Bockris as one of the leading figures: arguably the cradle of modern electrochemistry.[2] Martin studied the diffusion of electrogenerated hydrogen through thin palladium foils.[3] His first published work came after he had moved to Newcastle in 1951, to work with H R Thirsk. This first paper[4] has many of the hallmarks of Martin's later work. First, there was the need to design and build a new instrument, in this case a fast and accurate potentiostat. (Such instruments did not exist then; it was a bold move to recognise that, as electrode potential was the important control variable, the design problem had to be tackled – controlled current experiments were much easier and were the norm at the time.) Then, there is a comprehensive set of careful experimental measurements; there is a carefully worked-out theoretical development – Martin was a consummate mathematician and liked nothing better than a good calculation – which was fitted to the experimental data to derive insight into the fundamentals of the electrode reaction mechanism. Finally, the paper is beautifully and clearly written. The series of papers on electrocrystallisation, electrochemically-induced solid-state transformations and the anodic deposition of insoluble phases [5,6,7] are classics, and have defined the field ever since. Martin, with Alan Bewick, was a pioneer in the design of the fast potentiostats and pulse and ramp generators needed for accurate kinetic studies.[8] Nowadays, when the potentiostat is a black box with a computer connection, it is easy to forget that it is a complex instrument whose behaviour in conjunction with the electrochemical cell to which it is connected has to be understood thoroughly if results are to be believable: it is very instructive to re-read these early papers. Spurred by the interests of Wynne-Jones in Newcastle, Martin had moved to the study of electro-organic reactions, [9,10] and so potentiostats also had to have high output voltages. The potentiostat designs were commercialised first by Chemical Electronics and then by Hi-Tek. A Chemical Electronics instrument was in the lab in Auckland in the early 1970s. It was a beast and a formative and instructive experience in practical electrochemistry: a big blue box with 70V/1A output and 1 μs rise time – much faster and more capable than most modern instruments: a Ferrari of potentiostats. The chart recorder had to be connected in a particular way, otherwise the capacitance across the cell was altered critically and the potentiostat turned into a high-powered radio station, eventually frying the output transistors, which then took some time to replace. This must have been a second generation instrument, with solid-state electronics. Laurence Peter recounts that

> *The output stage of the blue box potentiostat was driven by tuned pentodes[8] to give the exceptional performance that is difficult to beat with transistors. They did indeed fry things if corrected incorrectly.*

He recalls having a student in floods of tears in his office after she had blown the front off the potentiostat by putting a wire wound resistor across the terminals!

For electrosynthetic reactions to be practical, cells have to be designed that have sufficient throughput, so Martin naturally moved to the design of efficient electrochemical cells. His mathematical proficiency was a great advantage in the

analysis and optimisation of the designs.[11,12] When he moved to Southampton in 1967 he took with him a group of exceptionally talented people and soon attracted more. The whole gamut of electrochemistry was covered, from big electrochemical engineering projects to photoelectrochemistry and the first *in-situ* spectroelectrochemistry: uv-visible, infra-red and Raman, as well as early attempts at *in-situ* X-ray diffraction measurement. The spectroscopy projects were driven by the desire to drill down from the observed kinetics and understand the chemical nature of the intermediates present on the surface. Of course, these studies again needed advances in instrumentation and the lab was a hot-bed of experimentation around that. To visit Southampton Electrochemistry in the mid-1970s was a revelation: the place fizzed with energy. Graham Hills was a calming presence who led his own outstanding research and also took care of the administration, and Martin was free to be himself, churning out ideas by the bucket-load and then turning the ideas into great experiments. He was surrounded by creative people who sparked off one another and the lab – bigger than many entire Chemistry Departments at the time – was a mecca for anyone wanting to study at the frontiers of the subject.

Of Martin's great output from Southampton in the 1970s and 1980s, four particular strands stand out. The first is the discovery of the surface-enhanced Raman effect;[13] the second is the development of microelectrodes;[14] the third is the study of stochastic effects as a means to derive basic information about electrochemical reactions;[15]and the fourth is the systematic development of concepts of electrochemical engineering. The first two of these, carried out contemporaneously with developments in the US, are recognised as amongst the most significant recent developments in electrochemistry. The atmosphere at Southampton at the time is captured in Jim McQuillan's recollection:[16]

I was a postdoctoral fellow at Southampton with Martin Fleischmann and Pat Hendra from June 1972. Physical chemistry at Southampton was a whole new world. Both Martin and Pat were innovative scientists, enjoyed competing with each other in scientific brainstorming, and were excited by the prospect of audacious experiments. I well remember those sessions when ideas were flying. One evening in August 1973 the extraordinary data from pyridine adsorbed to an electrochemically roughened silver electrode was obtained. The signals were much more intense than expected from calculations and this aroused great excitement tempered with scepticism.

The SERS phenomenon is now understood as the outstanding example of a plasmon resonance effect[17] and its discovery led to the field of plasmonics - a current hot topic in physical chemistry (e.g., single molecule spectroscopy) and in near field optics. Additionally, the original SERS paper gave Ron Shen the idea that led to sum frequency generation spectroscopy – the current pre-eminent vibrational spectroscopic technique for surfaces.[18] Martin was rightly honoured for these discoveries by the award of the Palladium Medal of the Electrochemical Society and by election to the Fellowship of the Royal Society of London. Pat Hendra recalls that which for his friends and colleagues was the essence of the man:

Through the 70s and on until he left Southampton, Martin used me as an intellectual 'punch bag'. I well remember one morning (and there were many others) I was giving a tutorial to a small group of undergraduates. Suddenly, the door crashed open unseating my secretary whose desk was behind the door and in advanced the Great Man as I always called him- eyes slightly glazed, in a world of his own, with those oh so familiar words "I've had an idea". He was, of course, bearing a coffee cup in his left hand most of the contents of which was slopping into the saucer and whence onto the floor. Once he had slurped the contents of the saucer, he excitedly pushed the student at the board aside, rubbed off his efforts and started to explain and illustrate his latest wheeze. Several minutes later after repeated reassurances that I would find him after I had finished teaching, we managed to get him out of the door and sent him off to acquire another coffee and I returned to my students. No more tutorial – they were gob-smacked. "Who was THAT?" I explained that they had been privileged to see how genius worked.

In the 1970s, the headship of the Department of Chemistry circulated every two years between the full professors and Martin fulfilled this role in his own particular style. He was not a natural administrator. Derek Pletcher describes how his office was always covered with stacks of reports/correspondence, etc. If your interest dropped below a certain level you were wise to sneak in and return it to the top of the pile. His secretary, Kate, had a system where piles were regularly moved to a box in a cupboard and then destroyed if Martin had not noticed in two years! Derek also commented that he used to tease Martin by saying, "The only thing that you do efficiently is to book your skiing holidays." Despite these shortcomings, Martin was an effective leader with a great talent for inspiring novel research activity. Eventually, however, the stress got to him. He described how he used to get home in the evening and would then have to walk around the garden for an hour, breaking wind, he was so wound up. Hence, he took early retirement in 1983. He then arranged to split his time between Southampton, Utah and Harwell, enjoying the different collaborations. I had asked Martin on a staircase during a scientific meeting whether he'd like to think about applying stochastic modelling to the problem of pitting corrosion. It piqued his interest and led to a wonderful and career-defining time for me.[19]

One day he asked for a confidential meeting with senior physicists at Harwell and described in outline some experiments he was directing in Utah, involving electrochemical loading of deuterium into palladium, where there seemed to be some excess heat being produced that did not apparently have any explanation other than a nuclear reaction. There was obviously scepticism, but he was supplied with a neutron safety monitor, and, at his request, preparations were made to do careful and sensitive measurements looking for any excess neutron emission from his system. About a week later, Martin suddenly asked for these experiments to be started immediately: the cells were set running but no neutrons appeared. Experimentation was driven by a sense of urgency and safety considerations were perhaps not as prominent at first as they should have been – there was subsequently a reminder of the dangers of stoichiometric mixtures of hydrogen and oxygen in the of presence of palladium when a cell exploded inside the neutron counter. Then late one night there was a telephone call from Martin: he

could not keep the lid on any longer and he had become convinced that the effect that he had hypothesised was real. The next day the press conference at Utah happened and things went crazy. Martin came to Harwell about a week after that and presented his results. First, there were the heat measurements: clearly these had to be repeated to seek confirmation; then there were results from the neutron monitor: clearly these were marginal and within the limits of noise for that device; finally there was the gamma-ray spectrum. There was an expert in the room who said simply, "That is not a gamma-ray peak." There was a silence. It was not that the peak was at the wrong energy – something that caused a great fuss later – but that the peak was too narrow. It might have been an instrument artefact at the limit of the measurement range. Was this the result that had convinced Martin: a sloppy measurement by someone else using an instrument that was outside Martin's normal domain of expertise? We will never know, but it is a trap we can all fall into. By then it was too late and the world was baying. All of the results in the original paper turned out to be of insufficient accuracy to support the claims that had been made. Although the results from the simple calorimeters of the original design could be interpreted to indicate some excess heat, measurements in instruments without the major error sources in the simple design showed nothing unexpected.[20] The idea, though, continues to attract serious and very careful measurement. The thermal measurements have been hugely refined.[21] The magnitude of the claimed effects has become much smaller as the calorimetric methods have been improved. However, the idea continues to intrigue and has not died out, although it seems that irreproducibility still plagues the study, despite some fairly detailed specifications of the conditions required to achieve the effect.[22] It seems that trace impurities in the electrolyte, such as silicate leached from the glass cells, may be of importance: intriguingly a reminder of some of the key considerations in the subject in 1947[1] that continue to jump up and bite the unwary,[23] and represent another connection to the beginning of Martin's scientific career.

Beyond the controversy, we hold memories of a wonderful warm, kind and engaging personality, full of insight and of energy, enthusiasm and quirky humour. As Laurence Peter recalls:

> *Martin was a real European intellectual with broad interests in the arts (and wine) as well as science. I first met him in 1966 – needless to say I was absolutely captivated by Martin – the accent, the dynamic personality. That is what turned me into an electrochemist.*

Martin was a formative influence on a whole generation of electrochemists, who will all remember those wonderful ideas sessions, a kind gesture ("I've taken a house at Villars: come skiing!") and the love of a good wine and a good joke. Martin taught that science is great FUN. He is much missed.

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Australia Raising the Bar

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In the April issue of *Chemistry in New Zealand* we discussed the new patent law being passed in the United States. Now it is Australia's turn. The Intellectual Property Laws Amendment "Raising the Bar" Act[1] passed into law in April 2012 and results in a number of changes to the Patents Act 1990. Here we discuss the more important amendments to the Patents Act from a practical perspective.

Improving the quality of granted patents

A patent application undergoes examination by IP Australia for a range of patentability criteria before it becomes a granted patent. The focus of many of the amendments made by the new Act is to strengthen the key tests for patentability and ensure rigorous scrutiny of patent applications during examination. The amendments also seek to allay concerns that patentability thresholds in Australia are too low, thus making patents too easy to get and discouraging follow-on innovation. By improving scrutiny during examination, the new law should also give patentees and the public greater certainty in the validity of granted patents.

While the amendments are likely to make it harder to get a granted patent in Australia, they should ensure that patents are only granted for inventions that add significantly to what was previously known and available to the public.

Examining for inventiveness

Patent applications are examined by the patent office to see if the invention they describe is *inventive*. This means the invention must be more than just an obvious extension of what is already known in order to be granted a patent. In general terms, *revolutionary* new developments are inventive, whereas *evolutionary* incremental-type developments are less likely to be inventive.

Currently the background information (prior art) by which inventiveness is assessed is information that a person familiar with the subject area could be reasonably expected to have *ascertained, understood and regarded as relevant*. One of the changes to the law will mean the invention must be inventive over *any* publicly available information. For example, currently it could be argued the information in a document in Japanese would not be likely to be combined with the information in a document in Russian, because it is unlikely the documents would both be found and understood by a person in Australia. This type of argument will no longer be as relevant under the new law. This change takes Australian patent law closer to the law in the United States and Europe and means that the threshold of inventiveness that the invention must reach is slightly higher.

If you have an invention which does not quite meet this threshold for inventiveness, i.e. the invention is novel but is *evolutionary* rather than *revolutionary*, there is another form of patent available in Australia called an innovation patent. This type of patent only lasts 8 years (compared to 20 years for a standard patent), and only requires that the invention is *innovative*, rather than *inventive*. In effect, if the invention has a meaningful difference over what is already known (i.e. is *evolutionary*, not necessarily *revolutionary*) it is likely to be considered *innovative*. The rights conferred by innovation and standard patents are the same; they provide the right to stop another party from making, using, importing or selling an invention covered by the claims of the patent in Australia.

Innovation patents can be a great option for incremental advances in technology or for fast-moving areas of technology where a shorter patent term is of less concern. Apple Corp. have made extensive use of innovation patents in Australia and are in the process of enforcing them in their continuing legal action against Samsung.

Experimental use of patented inventions

In the April 2011 issue of *Chemistry in New Zealand* we discussed whether experimental use of a patented invention in New Zealand or Australia would constitute infringement of the patent. At that time, there was no legislative basis for experimental use exceptions in either country. One of the amendments to the Australian law which came into force immediately was to formally legitimise the use of a patented invention for *experimental purposes*. However, this is not as broad an exception as it may sound and certainly does not legitimise the use of patented invention for *any* research/experimental purposes.

In very general terms, if a person is experimenting *on* the invention, this would be deemed experimental use. If a person is experimenting *with* the invention, this would be infringement of the patent. *Experimental purposes* include determining the properties of the invention, determining the scope of a claim of the patent, improving or modifying the invention, determining the validity of the patent or claims of the patent or determining whether an act would infringe the patent. The wording of the amendment makes it clear there may be other experimental purposes other than the ones listed above, but we suggest caution should be exercised if venturing outside these.

Expansion of regulatory approval exception to infringement

Previously the law allowed acts carried out for the purposes of obtaining regulatory approval for a patented pharmaceutical. This means that before the patent has expired, competitors such as generic manufacturers of pharmaceuticals can obtain the necessary clearance to market

and sell their product. This exception to infringement allows competitors to hit the ground running and get their product on the market as soon as possible after the expiry of the patent and not have additional lag time while approval is granted. The exception, which previously only applied to pharmaceutical patents, has now been extended to apply to any patent where the patented product requires regulatory approval. This will be useful for generic manufacturers of agrochemicals and medical devices (or any other field where regulatory approval is required).

When does the law change?

Most of the law changes come into effect in April 2013, although the new *experimental use* and *regulatory approval* exception are already in effect. However, the true extent of the reforms will probably only become clear in due course once a court has had to decide a case granted under the new laws.

If you have an Australian patent application or you are thinking about filing one, you should consider requesting examination of the application prior to April 2013 to avoid being held to the more rigorous standards.

New Zealand bringing up the rear

New Zealand patent law has changed little since the introduction of the current Patents Act in 1953. The Labour government introduced a new Patents Bill back in 2008, but the bill has moved at a snail's pace through the corridors of power in parliament. It seems that the political will to move it forward is lacking and there is speculation that the inter-play between the Bill and the Trans-Pacific Partnership (TPP) negotiations have conspired to slow its progress.

Despite this, recently there does appear to have been renewed impetus. A supplementary order paper was released on 28 August 2012 clarifying a point in the Patents Bill relating to software patents. Whether or not this indicates that the Bill will advance and put New Zealand patent law on a par with other developed nations remains to be seen.

If you have any queries regarding intellectual property related matters (including patents, trademarks, copyright or licensing), please contact: *tim.stirrup@baldwins.com or katherine.hebditch@baldwins.com*

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1. Intellectual Property Laws Amendment (raising the Bar) Act 2012, No. 35, 2012

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Dates of Note

Frank Harold ***Spedding***, the American chemist who, during the 1940s and 50s, developed processes for reducing individual rare-earth elements to the metallic state, was born on 22 Oct, 110 years ago. *Arthur* ***Kornberg***, the American biochemist and physician who shared the 1959 Nobel Prize for Physiology or Medicine (with Ochoa) for the discovery of the mechanisms in the biological synthesis of DNA, died on 26 Oct, five years ago. On 31 Oct 1992 the Vatican admitted erring for over 359 years in formally condemning *Galileo* ***Galilei*** for entertaining scientific truths such as the Earth revolves around the sun, which the Roman Catholic Church long denounced as anti-scriptural heresy.

On 1 Nov 1772 *Antoine* ***Lavoisier*** reported in a note to the French Academy of Sciences that in the previous week he had discovered that sulfur and phosphorus increased in weight when burned because they absorbed air, while the metallic lead, formed when litharge (PbO) was heated with charcoal, weighed less than the original litharge because it had lost air. The 60th anniversary of the marketing of frozen peas by *Clarence* ***Birdseye*** is on 3 Nov. The Canadian-American metallurgist, mining engineer and philanthropist, *James* ***Douglas***, who developed the copper mining industry in the US, was born on 4 Nov, 175 years ago. *Claude Louis* ***Berthollet*** died on 6 Nov 1822. He was a French chemist and the first to note that the completeness of chemical reactions depends on the masses of the reacting substances. The Bodleian Library was established in Oxford on 8 Nov 1602. *Chaim* ***Weizmann***, the Russian-British-Israeli chemist who used bacteria for the synthesis of organic chemicals, died on 9 Nov 1952.

Nobel physics laureate Sir *John* ***Rayleigh***, the English

scientist who made fundamental discoveries in the fields of acoustics and optics, was born on 12 Nov 1842. On the same day in 1912, the body of Sir *Robert Falcon* ***Scott*** was discovered in the Antarctic, the day that, in 1847, Sir *James Young* ***Simpson***, employed chloroform for the first time as an anaesthetic in an operation. *Elmer* ***McCollum***, the American biochemist who originated the letter system of naming vitamins, died on 15 Nov 1967, the same day that *Franciscus* ***Sylvius***, the Dutch physician, chemist, physiologist and founder of the seventeenth century's "iatrochemical school of medicine" (iatrochemistry seeks to provide chemical solutions to diseases and medical ailments), died in 1672. This is also the day, 125 years ago, in 1887, that the German scientist, *Carl* ***Gassner***, was issued with US patent 373,064 for the first dry cell. It was also the day in 1492 that *Christopher* ***Columbus*** noted the use of tobacco among Indians in his journal. The 90th birthday of *Stanley* ***Cohen***, the US biochemist who shared (with Levi-Montalcini) the 1986 Nobel Prize for Physiology or Medicine for their discoveries of growth factors, will be celebrated on 17 Nov. *Niels* ***Bohr***, the Danish physicist who was the first to apply quantum theory, died 50 years ago on 18 Nov. *James B.* ***Sumner***, the American biochemist who shared (with Northrop and Stanley) the 1946 Nobel Prize for Chemistry as the first to crystallise an enzyme and show it to be a protein, was born 125 years ago on 19 Nov. *James Bertram* ***Collip***, the Canadian biochemist who co-discovered insulin, was born on 20 Nov 1892, 120 years ago. *Johannes Diederik* ***van der Waals***, of equation fame, was born on 23 Nov, 175 years ago. *Robert A.* ***Swanson***, the American chemist who co-founded Genentech, Inc., the research-based company that pioneered the biotechnology industry, was born on 29 Nov, 65 years ago; he died in 1999. *Vladimir Nikolayevich* ***Ipatieff***, one of the first to investigate high-pressure catalytic reactions of hydrocarbons and who developed a process for manufacturing high-octane gasoline, died on 29 Nov, 60 years ago.

Luis Federico ***Leloir***, the Argentinian biochemist who won the Nobel Prize for Chemistry in 1970 for his discovery of sugar nucleotides and their role in the biosynthesis of carbohydrates, died on 2 Dec, 25 years ago (1987). It is also the day 135 years ago (1877) that *Louis-Paul* ***Cailletet*** liquefied oxygen for the first time. *Johannes* ***Wislicenus***, the German chemist whose pioneering work with lactic acid led to the recognition of the importance of the spatial arrangement of atoms within a molecule, died on 5 Dec 1902. *Carl Wilhelm* ***Scheele***, the Swedish chemist who discovered oxygen in 1772, and after whom the calcium tungstate ($CaWO_4$) mineral, scheelite, was named, was born on 9 Dec 1742. *Thomas Robert* ***Cech***, the American biochemist and molecular biologist who (with Altman) was awarded the 1989 Nobel Prize for Chemistry for discoveries concerning RNA, has his 65th birthday on 7 Dec. *Johannes Nicolaus* ***Brønsted***, the Danish physical chemist known for his acid-base concepts, died 65 years ago on 17 Dec. On 21 Dec, 75 years ago, the animated Disney film *Snow White and the Seven Dwarfs* opened in Los Angeles, while 23 Dec 1947 saw the transistor was first demonstrated by Brattain and Bardeen at Bell Laboratories. *Vladimir Vasilyevich* ***Markovnikov***, the Russian organic chemist known for his addition rule, was born on Christmas Day 175 years ago in 1837, while Sir *Isaac* ***Newton*** was also born on 25 Dec, but in 1642. *Louis* ***Pasteur*** was born on 27 Dec 1822. The 60th anniversary of the sale of the first hearing aid occurs on 29 Dec. *Vaughan Frederick Randal* ***Jones*** is the New Zealand mathematician who was awarded the Fields Medal in 1990 for his study of functional analysis and knot theory; 31 Dec marks his 60th birthday.

New Year's Day, 225 years ago (1788), saw the first publication of *The Times* newspaper, while 125 years ago *Robert* ***Kane***, then a 24-year-old Irish chemist, published the first proposal of the ethyl radical ($-C_2H_5\bullet$) in the *Dublin Journal of Medical and Chemical Sciences*. National film censorship commenced on 1 Jan, 100 years ago. The 125th anniversary of the wax drinking straw is on 3 Jan. The first picture newsreel in colour was shown in the US on 5 Jan 1948, 65 years ago, the day British Railways came into existence with the nationalization of the four founding railways corporations. On 6 Jan, 100 years ago, *William M.* ***Burton*** patented a process to crack petroleum to produce gasoline that was used by Standard Oil. *Valdimir* ***Prelog***, the Yugoslavian-born Swiss chemist, who shared the 1975 Nobel Prize for Chemistry (with Cornforth) for work on the stereochemistry of organic molecules and reactions, died on 7 Jan 1998, while *Fukui* ***Kenichi***, the Japanese chemist who shared the 1981 Nobel Prize for Chemistry (with Roald Hoffmann) for the concepts of conservation of orbital symmetry, died on 9 Jan of the same year. The superfluidity of liquid helium at a temperature near absolute zero was reported in *Nature* on 8 Jan, 75 years ago. *Isidor Isaac* ***Rabi***, the Austrian-American physicist who was awarded the Nobel Prize for Physics in 1944 for his invention of the atomic and molecular beam magnetic resonance method of measuring magnetic properties of atoms, molecules, and atomic nuclei, died on 11 Jan, 25 years ago. *Joseph Farwell* ***Glidden***, the US inventor of barbed wire who formed the Barb Fence Company of De Kalb, Illinois, was born 200 years ago on 18 Jan. On 20 Jan 1838, 175 ago, the first Travelling Post Office in Britain left London for Birmingham. It was a converted horsebox in which the mail could be sorted on the Grand Junction Railway.

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Chemistry conferences

AsCA 12/Crystal 28

2-5 December 2012, Adelaide Convention Centre

Held in association with the Bragg Symposium, 6 December 2012, Elder hall University of Adelaide

A Joint Meeting of the Asian Crystallographic Association (AsCA), Society of Crystallographers in Australia and New Zealand (SCANZ) and the BRAGG Symposium.

See: www.sapmea.asn.au/conventions/crystal2012/index.html

11th International Conference on materials chemistry (MC11)

8-11 July 2013, University of Warwick, UK.

Themes: Energy Materials, Environmental Materials, Biomaterials, Magnetic, Electronic and Optical Materials

Oral abstract deadline: 9 November 2012; Poster abstract deadline: 10 May 2013

See : www.rsc.org/ConferencesAndEvents/RSCConferences/MC11/index.asp

23rd International Symposium: Synthesis in Organic Chemistry

23 - 25 July 2013, University of Oxford, UK

The Synthesis in Organic Chemistry Symposium traditionally provides an international showcase for the core area of organic chemistry - synthesis - covering all aspects of contemporary organic synthesis and providing a forum for the ever more exciting methodologies and strategies that continue to emerge.

See: www.rsc.org/ConferencesAndEvents/RSCConferences/OS23/Index.asp

IC'13, the Royal Australian Chemical Institute's 2013 Inorganic Chemistry Divisional Conference

8-12 December 2013, University of Queenstown, Australia

The meeting embraces all aspects of inorganic chemistry.

Plenary Speakers include: Professor Michael Graetzel (EPFL, Lausanne, Switzerland); Professor Chuan He (Chicago, USA); Professor Annie Powell (Karlsruhe, Germany); Professor Phil Power (UC, Davis, USA); Professor Dongyuan Zhao (Fudan, China)

See: www.scmb.uq.edu.au/ic13

Grants and Awards

MacDiarmid Institute for Advanced Materials

Competition for the best nanotechnology research images

A competition is being organized to find the best New Zealand images from nanotechnology research. Entries are encouraged from any researcher or research student based in New Zealand.

$2000 in prizes will be awarded and the best images will be displayed in a prominent Auckland gallery, the Gus Fisher Gallery, for three weeks in February 2013.

Look through your files, find your best images, and start to think about how you would explain them to a lay audience – the rules and entry form will be available soon.

The deadline for entries to be received will be in October 2012. For more information please contact Prof Simon Brown, Deputy Director, MacDiarmid Institute for Advanced Materials and Nanotechnology.

See: www.macdiarmid.ac.nz/

Bayer Primary School Science Fund

The is sponsored by Bayer and administered by the Royal Society of New Zealand. This fund is to support primary schools to teach and enhance both environmental science and 'nature of science' activities.

A primary school can request a maximum sum of up to $2,000 to help fund activities. A school that has been successful in being funded may only apply for funding once every three years.

Applications due 31 October 2012. Please send to Debbie.Woodhall@royalsociety.org.nz or post to Debbie Woodhall, Royal Society of New Zealand, PO Box 598, Wellington.

See: www.royalsociety.org.nz/programmes/funds/bayer-primary-school-science-fund/

FREESTA (Freemasons Student Travel Award)

FREESTA is funded by Freemasons New Zealand and administered by the Royal Society of New Zealand. It has been established to support travel and registration costs for Yr12 – Yr13 (as at 2012) secondary school students who have been selected for Hands-on-Science, Dunedin. Hands-On Science will run from Sunday the 13th to Friday the 18th of January 2013.

Email your application to Debbie.woodhall@royalsociety.org.nz or post to Debbie Woodhall, Royal Society of New Zealand, PO Box 598, Wellington. Applications due 23 November 2012.

See: www.royalsociety.org.nz/programmes/funds/freemasons-secondary-school-student-travel-fund/

Indices for Chemistry in New Zealand, Vol. 76, 2012

Author Index

Subject Index

Chemistry in the News

Continued from p. 117

University of Otago senior science quiz

More than 600 students from all over New Zealand entered the University of Otago Senior Science quiz, which took place on 13 June 2012. The quiz contained 45 multiple-choice questions and was aimed at Year 11, 12 and 13 students. It tested their analytical ability and general science knowledge.

Robert Tucker, a James Hargest College (Invercargill) pupil, achieved the top mark for Year 13. He was also part of the winning team at the University of Otago interschool chemistry quiz last year that went on to compete at the national competition science. Robert plans to start a Bachelor of Science in chemistry next year at Otago and then would like to study for a Chemistry PhD.

Certificates and cash prizes were awarded to the winners for Year 11,12 and 13. An Otago Boys' High School pupil was the winner of the Year 11 quiz, while the Year 12 quiz, was won by a girl from Nayland College, Nelson.