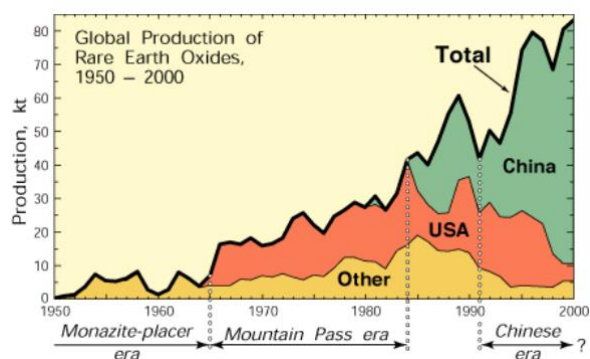


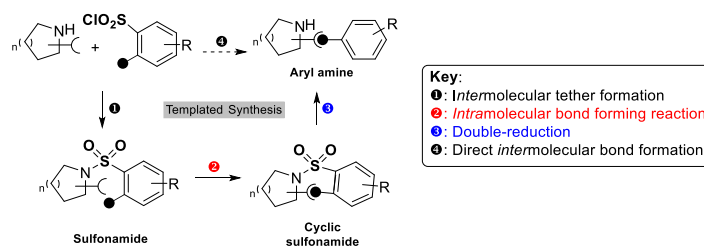


The Journal of the Institute of Chemistry of Ireland

Feature Articles:-



Global production of Rare Earth Oxides, 1950 – 2000



Use of a sulfonamide as a temporary tether: Combining N-protection and arylation

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Note: Opinions expressed in this Journal are those of the authors and not necessarily those of the Institute.

A Message from the President

Dear Fellows, Members, Graduates and Associates,

You may have noticed that 'Irish Chemical News' is now being published more frequently. This is the second issue that has appeared this year and congratulations are due to our Editor, Pat Hobbs, for his good work in sourcing such an interesting and varied selection of articles.

This issue is being published in advance of our AGM, which is due to be held on April 14th, kindly hosted by the DIT Kevin St. On that same day, Professor Hodnett of UL will give the Boyle-Higgins Award lecture. Details of this event may be found on page 7 of this journal. There will be a finger food reception immediately after the Boyle-Higgins lecture and before the AGM. During the reception, medals will be awarded to several students who obtained the top marks in last year's Honours Chemistry paper in the Leaving Certificate examination.

We are delighted that the Eurachem Analytical Measurement Competition is being hosted by Athlone Institute of Technology on April 15th. This competition is back on track this year, after a lapse of one year and The Institute of Chemistry of Ireland is pleased to be a sponsor. This is a practical contest in laboratory skills which, over the years, has helped to raise the standard of training in analytical chemistry which is being offered by our 3rd level colleges.

I appeal to members to make an effort to attend the AGM and to engage with the work of the Institute. We need more of our members to become actively involved, particularly on our committees. We have a very hard-working Education Committee, whose members have been preparing a response to the new draft Science syllabus for Junior Cycle, as well as the Leaving Cert Chemistry syllabus. Their report is nearing completion and will be published soon.

Other committees include the following: Qualifications, Professional Affairs, Membership, Recruitment, Industrial, Environmental, The Editorial Board and the Young Chemists' Group. As well as these, we have ad hoc committees to organise the Annual Congress and various awards. If you are interested in serving on any of these committees, please let us know. I look forward to meeting many of you at the AGM.

Margaret Franklin, FICI, President.

Again we thank our Sponsors:-



Editorial

Don't forget **AGM Thursday 14th** at **DIT, THE SEMINAR ROOM IN FOCAS INSTITUTE, CAMDEN ROW** and followed by:-

The Institute's Boyle-Higgins Gold Medal Public Lecture given by Prof Kieran Hodnett, UL, titled *Polymorphic Transformations in Pharmaceutical Compounds* followed by the ICI AGM will take place in DIT, Kevin St., on Thursday 14th April 2016.

In this Issue there are two academic papers. Continuing with the sustainability theme there is a paper from TCD Chemistry Department on rare earths and e-waste. The many uses of REs, their extraction from ores and WEEE, with plenty of chemistry is discussed. The second paper from UCD's School of Chemistry & Chemical Biology covers the Synthesis of Cyclic Sulfonamides using a pre-organising template, or tethering group in a synthetic sequence is discussed in some detail.

The winners of SSPC Crystal Growing Competition is reported on from UL.

A number of significant industry news items are reported on courtesy of Premier Publishing & Events Ltd publication Industry and Business.

This year's Congress will be held at Galway Mayo Institute of Technology (GMIT) in Galway City on May 27th. The theme is Chemistry and Society and will be of interest to a wide range of Chemists and Scientists in Ireland.

Maynooth hosted a seminar with WIT, CIT and AIT called Connect 2016 with the theme Knowledge Transfer highlighting the links between HEIs and industry, sources of funding and networking opportunities. This seminar was supported by Enterprise Ireland and Knowledge Transfer Ireland. A short report is included in this Issue and I expect more substantial articles to follow in later Issues.

Also carried in this Issue are advanced notices of chemistry events taking place in the coming months.

I'm sure there is much that can be done to improve ICN and I welcome your suggestions and comments. The cover layout and design needs improvement and I invite chemists and anyone with graphic design skills to contact me with your ideas.

You can sent these to The Editor at:-

<mailto:info@instituteofchemistry.org>

Patrick Hobbs MSc, FICI, CChem, CSci, MRSC.

Editor ICN,

Immediate Past President.



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ANNUAL GENERAL MEETING

Dear Member

The Sixty-seventh Annual General Meeting of the Institute of Chemistry of Ireland will be held in **THE SEMINAR ROOM IN FOCAS INSTITUTE, CAMDEN ROW, BEHIND DUBLIN INSTITUTE OF TECHNOLOGY, KEVIN STREET, AT 7.00PM ON THURSDAY 14 APRIL 2016.**

ARRANGEMENTS

FINGER FOOD RECEPTION: 6.00 – 7.00 PM

The meeting will be preceded by a Finger Food Reception outside the Seminar Room commencing around 5.45 pm.

AGENDA FOR AGM – 2016

7.00 – 7.30 PM

1. To read the Notice Convening the Meeting
2. Correspondence
3. Minutes of the 2016 AGM and Matters Arising
4. Honorary Secretary's Report
5. Honorary Treasurer's Report
6. General Resolution 2016:
Subscriptions and Charges for 2017
7. Appointment and Remuneration of an Auditor
8. Elections to Council for 2016 – 2017
9. Any Other Business
10. Presentations and Awards

All members of the Institute are invited to attend.

Yours sincerely,

Dr James P. Ryan, FICI EurChem
Honorary Secretary

Institute of Chemistry of Ireland

Boyle-Higgins Gold Medal Public Lecture

given by

Prof Kieran Hodnett

Polymorphic Transformations in Pharmaceutical Compounds

followed by the **ICI AGM**

DIT, Kevin St., Thursday 14th April



Professor Kieran Hodnett

Director

**Synthesis and Solid State Pharmaceutical Centre
Department of Chemical and Environmental Sciences
Materials and Surface Science Institute
University of Limerick**

Abstract

This lecture presents aspects of the mechanisms whereby solid state polymorphic transformations occur, with a particular emphasis on active pharmaceutical ingredients (API). Polymorphism is the phenomenon whereby chemically identical molecules can arrange themselves in the solid state to give different crystal structures. A particular polymorph will have different physical characteristics most significantly solubility, which influences bioavailability, hence the need to specify polymorphic form in all oral dose medicines.

During solution mediated polymorphic transformations (SMPT) meta-stable polymorphs convert into a more stable form through interactions with a solution phase. In principal, SMPT's involve generation of

supersaturation through dissolution, nucleation and growth phases. Metastable polymorphs will appear first in accordance with Ostwald's Law of Stages. In solution mediated transformations, supersaturation with respect to the stable phase is generated from the greater solubility of the meta-stable form(s). Eventually, the metastable polymorph in contact with the bulk solution, will dissolve and a more stable polymorph will nucleate and grow from the solution. Monitoring the solution concentration over time allows the transformation process to be evaluated by accounting for the dissolution rate of the metastable polymorph and the growth rate of the stable polymorph.

This lecture will describe aspects of the solution mediated transformation of the metastable polymorphs of Carbamazepine, Piracetam, l-Glutamic acid and Sulphathiazole. A common feature of these transformations is that the stable form nucleates on the surface of the metastable form; as the stable form grows, the metastable form dissolves, roughening in the process whereas the growing stable crystals present smooth facets and clearly defined inter-facet angles (Figure 1). The nature of the surface interactions between polymorphs are mostly unclear but there are rare striking demonstrations of epitaxy between form as such as FII and FIV in sulphathiazole (Figure 2).



Figure 1. Metastable Form II Piracetam (rough dissolving crystal) undergoing a solution mediated polymorphic transformation to FIII (smooth growing crystal).

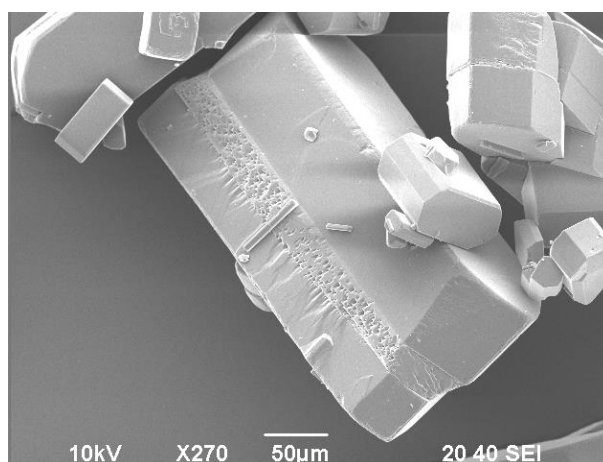


Figure 2. FIV Sulphathiazole dissolving and roughening while it is epitaxially sandwiched between two layers of FII.

This transformation can occur on timescales ranging from seconds to years. A general trend was observed; the higher the solubility, generated through choice of solvent or temperature, the faster the transformation to the stable form. From a practical perspective pure metastable forms could be isolated from solvents in which the API's were poorly soluble whereas the stable forms are readily isolated from solvents in which the API's are readily soluble.



Congress 2016: Chemistry and Society

GMIT Galway City

The Congress will take place on Friday the 27th of May with the conference dinner on the evening of Thursday 26th. The theme for this year's Congress is '**Chemistry and Society**'.

There will be speakers on the topics of medical devices and pharmaceuticals, food science and the impact of chemistry on marine science.

We are also inviting postgraduate students to present posters. There will be two prizes awarded for those presenting posters. One for the best overall poster and a second for the poster which best reflects the theme Chemistry and Society.

The timetable for the day will be:

9.15-9.45 **Registration**

9.45-9.55 **Welcome and Introductory Remarks**

10.00-11.30 **Speakers**

11.30-12.00 **Break & Trade Exhibition**

12.00-13.15 **Speakers**

13.15-14.15 **Lunch, Trade Exhibition & Poster Session**

14.15-15.45 **Speakers**

15.45-16.15 **Break & Poster Session**

16.15-16.45 **Student Research Presentations**

16.45-17:15 **Closing Remarks and Awarding of Prizes**

The rates for attending the conference are as follows:

Delegate Rate: €50 **Congress Dinner:** €40

Delegate Rate (ICI Members Only): Members of the Institute of Chemistry are invited to avail of the discount rate of €40.

Postgraduate / Post Doctoral Researchers Reduced Rate: €25 (includes free ICI membership for first time members)

Postgraduate / Post Doctoral Researchers ICI Members Rate: €15

The email address for the congress: icicongress2016@gmit.ie the congress website is at <https://iciannualcongress2016.wordpress.com> - it is currently under construction but has all the basic info in place.

www.ISC2016.ie



The International Symposium on Chromatography (ISC) represents a traditional congress series of major European Chemical Societies.

Cork is a major European centre for the life science industry with nine of the top ten global pharmaceutical companies in the world located in the greater Cork area and seven out of ten of the world's best-selling drugs produced here. If you'd like to find out more about sponsoring and exhibiting at ISC 2016, please contact the organisers at ISC2016@mci-group.com



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Scientific themes

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- Biopharmaceutical and Biologics
- Process Chromatography and PAT
- Food and Health
- New Instrumentation (LC, GC, CE, ..)
- Column Technology and Materials
- Sample Preparation
- Mass Spectrometry
- Forensic and Environmental Analysis
- Separation and Sensing
- Miniaturisation and On-Chip Devices
- Supercritical Fluid Applications
- Ion Chromatography and Trace Element Speciation
- Biomarkers, Diagnostics and Biomedical Analysis
- Metabolomics, Glycomics, Lipidomics and Proteomics



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Symposium Chairpersons
Apryll M. Stalcup & Jeremy D. Glennon
apryll.stalcup@dcu.ie / j.glennon@ucc.ie

Conference Organisers: MCI Dublin
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CHAIRPERSONS

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Dublin City University, Ireland

Prof. Jeremy D. Glennon
University College Cork, Ireland



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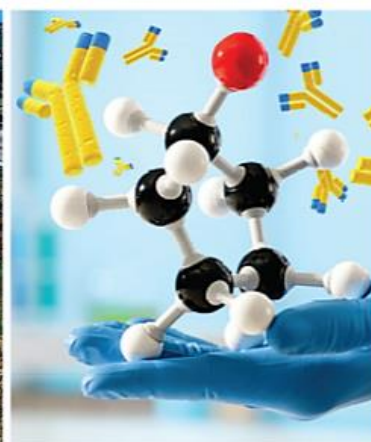


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**Abstract
Submission
Open!**

Deadlines:

Oral: 16th Feb 2016

Posters: 26th April 2016

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Department of
Chemistry

Review

Recent Advances in Rare Earth Extraction: Where Do WEEE Stand?

Harrison Omorodion and Robert J. Baker

School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland

Email: omorodih@tcd.ie

Abstract

The magnetic and optical properties of Rare Earths (REs) make these elements indispensable in green technology such as wind turbines and hybrid electric vehicles. Bastnesite, Monazite and Xenotime are the most common RE minerals. Various methods exist for extraction/separation of RE from their minerals. In general, the RE is concentrated by physical methods, then roasted with concentrated acid or alkali, leached with concentrated acids and the leachate is then extracted with various extractants. Studies on efficient RE extraction methods from the dissolved mineral leachates are increasingly popular due to projected supply issues. This threat to supply has prompted researchers to find methods which can not only extract virgin RE from its mineral but can also be applied to other sources of REs such as industrial RE scrap and waste electrical electronic equipment (WEEE or e-waste). Globally, an estimated 20-50 million metric tonnes of e-waste is generated annually and this contains a plethora of technologically relevant rare earth elements (REEs). This makes WEEE a rich source of RE as some metals have been estimated to be more concentrated in WEEE than in primary ores. Herein, we present a critical literature review on the past and current extraction methods of REs extraction from its minerals and e-waste.

Introduction

Rare earths (REs) include scandium, yttrium and the lanthanides (La – Lu, excluding Pm). Rare earth elements are extensively used in metallurgy, hard disc drives (HDDs), fluorescent light, flat screens, x-ray imaging, fibre optics, defence technology, hybrid cars and wind turbines.^{1, 2} The wide range of RE applications is due to their unique catalytic, electrical, magnetic and optical properties. Nd, Pr, Dy and Tb have found application in high performance Neodymium Iron Boron (NdFeB) magnet used in hybrid electric cars, electric cars, wind turbines, HDDs of desktop personal computers and portable devices such as tablet, mobile phones, head phone speakers.^{3, 4} Rare earth permanent magnets (REPMs) accounts for 38% of RE use in terms of volume. It is estimated that high performance NdFeBs magnets will continue to grow in demand with the highest growth rate at 10-15% which unambiguously points to potential supply issues⁵. Eu, Gd, Yb, Tb and Y have been used as phosphors in fluorescent light, flat screens, euro bank notes and imaging (MRI), while Er is used in erbium-doped fibre optics for signal amplification, (Table 1).^{2, 6}

REs tend to exist as dispersed oxide and are rarely concentrated in mineral ores (hence the name) even though they are relatively abundant in the earth crust (Table 2). This uneven geographical distribution of the REs and preference of some REs over others have led to imbalance in demand and supply of some REs including neodymium, dysprosium, terbium, and erbium⁷. Currently, 95% of the world RE supply comes from China (Figure 1). The forecasted shortages led China to announce export quotas encouraged expansion of REs relevant industries in China. As a result of this threat to supply and clean sustainable technologies REs have been labelled as “critical” metals.^{3, 7}

Table 1: Applications of Rare Earths

<i>light RE (more abundant)</i>	<i>Major End Use</i>	<i>Heavy RE (less abundant)</i>	<i>Major End Use</i>
Lanthanum	Hybrid engines, metal alloys, cheaper catalytic converter and other emission reducing technologies, energy storage in Ni Metal Hydride Batteries	Yttrium	Red colour, fluorescent lamps, ceramic, capacitors, metal alloy agent, wind and hydro power generation, medical imaging- MRI
Cerium	Auto catalyst, petroleum refining, metal alloys, cheaper catalytic converter and other emission reducing technologies, flat screen displays	Gadolinium	Magnets, phosphors for flat screen displays, medical imaging- MRI.
Praseodymium	Magnets, cordless power tools, medical imaging- MRI	Terbium	Phosphors, permanent magnets,
Neodymium	Auto catalyst, petroleum refining, hard drives in laptops, headphones, hybrid engines, cordless power tools	Dysprosium	Permanent magnet, hybrid engines, light weight and powerful motors,
Samarium	Magnets	Holmium	Glass colouring, lasers
Europium	Red colour for television and computer screens, medical imaging- MRI	Erbium	Phosphors, Erbium doped optical fibre for signal amplification
		Thulium	Medical x-ray units
		Ytterbium	Lasers, steel alloys, medical imaging- MRI
		Lutetium	Catalyst in petroleum refining

Source: DOI, U.S. Geological Survey, Circular 930-N⁶

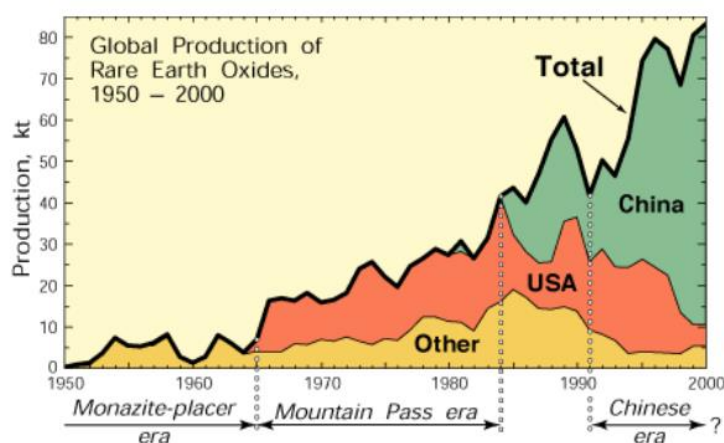


Figure 1: Global production of Rare Earth Oxides, 1950 - 2000⁸

Reduction in RE supply from China inevitably caused the prices of REs to upsurge to its all-time high in 2010 (Figure 2). Mountain Pass mine in California, USA was consequently reopened in 2012 to supply the much needed RE for green and defence technology. Although China had agreed to increase its export quotas in 2015, the recent shutdown of Mountain Pass mine in August, 2015 could be a major setback in the quest to relieve

China of its control over RE supply. There could be another huge rise in the prices of RE in the next few years if alternative source of REs is not devised. This kind of control over the resources necessary for clean and renewable technologies poses a huge threat to future development of such technology.

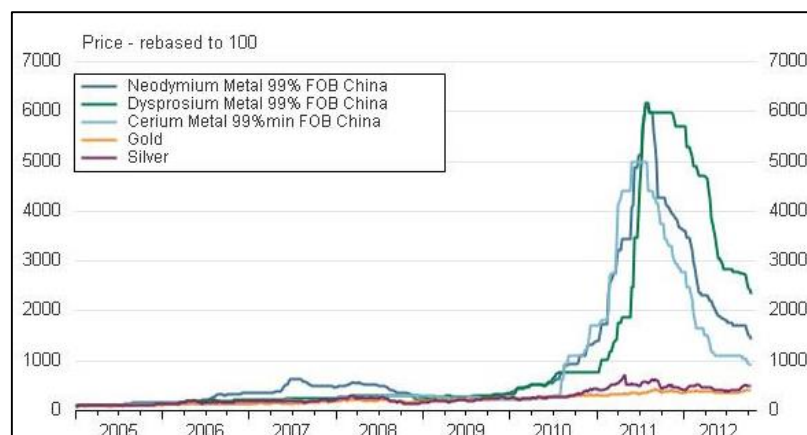


Figure 2: The Prices of Selected Rare Earths vs the Prices of Gold and Silver⁹

Rare Earth Minerals

Table 2: Rare earth abundance and contents (as a percentage of total mineral) in principal minerals

RE Oxides	Crustal Abundance (ppm)	Bastnesite %	Monazite %	Xenotime %
Light RE				
La ₂ O ₃	35	32	23	0.5
CeO ₃	66	49	45.5	5
Pr ₆ O ₁₁	9.1	4.4	5	0.7
Nd ₂ O ₃	40	13.5	18	2.2
Pm ₂ O ₃	0			
Sm ₂ O ₃	7	0.5	3.5	1.9
Eu ₂ O ₃	2.1	0.1	0.1	0.2
Gd ₂ O ₃	6.1	0.3	1.7	4
Heavy RE				
Tb ₂ O ₃	1.2		0.16	1
Dy ₂ O ₃	4.5		0.56	8.7
Ho ₂ O ₃	1.3		0.09	2.1
Er ₂ O ₃	3.5	0.1	0.13	5.4
Tm ₂ O ₃	0.5		0.013	0.9
Yb ₂ O ₃	3.1		0.016	6.2
Lu ₂ O ₃	0.8		0.006	0.4
Y ₂ O ₃	31	0.1	2.1	60.8
Total		100	100	100

Source: Mineral Facts and Problems, 1985¹⁰

REs are found in almost all mineral groups including silicates (e.g. eudialyte, allanite, zircon, steenstrupine etc.), fluoro-carbonates (e.g. bastnesite, synchisite, parasite and fluocerite), oxides (e.g. euxenite, fergusonite, pyrochlore, loparite and cheralite) and phosphates (e.g. xenotime, churchite, florencite, britholite and apatite). Bastnasite deposits in China and the USA constitute the largest percentage of the world's rare earth reserves, while monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, constitute the second largest segment. Deposits with a high proportion of heavy rare earth elements (HREE) are very rare. Although the light rare earth elements (LREE) comprise 97-99% of resources, many of the HREE play a crucial role in emerging green energy and high tech applications together with the fast growing demand in the lighting industries (LED), thereby rendering HREE much more valuable than LREE.⁸

Potential Sources of Rare Earth Elements

Due to the growing technological application of RE, there is a huge amount of RE contained in waste electrical electronic equipment (WEEE) globally such that WEEE is considered an “urban mine”. This has drawn considerable amount of interest with hopes of developing a technology that can efficiently extract RE from e-waste on an industrial scale in order to alleviate the heavy reliance on virgin RE – so called anthropogenic mining.

Rademaker et al. estimated that up to 100% of all hybrid electric vehicles, electric vehicles, desktop PCs, portable devices and 10% of wind turbines contain REPMs. The amount of REPMs in some of these devices reaches up to 700 kg. This “urban mine” was estimated to have the potential to cover up to 11-15% of REs demand. These estimates are predicted to continue growing over time as more wind and automotive technologies get to their end of life (EoL) stages.⁵ E-waste is therefore regarded as a potential source of REs that could alter the supply landscape which is currently heavily dominated by China.¹¹

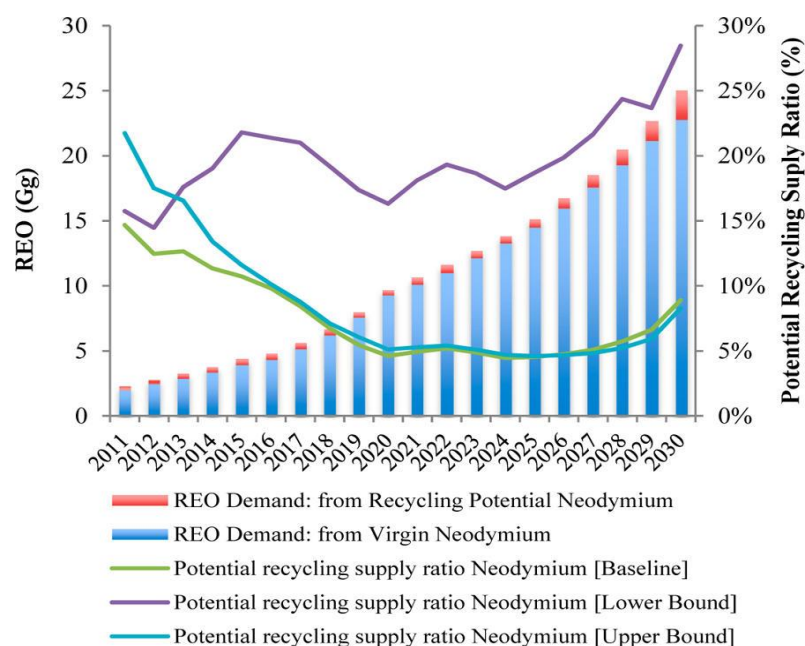


Figure 3: Potential recycling supply of Nd and predicted rise in demand of REs. [Reprinted with permission from: J. H. Rademaker, R. Kleijn and Y. Yang, *Env Sci & Tech.*, 2013, **47**, 10129-10136. © 2013, American Chemical Society].

The average life span of some of the technologies containing REs is quite long as in the case of wind turbines and electric cars. However the potential amount of REs present in EoL products with shorter life span is enough to substantially decrease dependency on virgin materials if the recovery and recycling chain is properly managed.⁵ Although RE recovery from manufacturing scrap and waste is done as industrial recycling, no commercial EoL NdFeB magnet recovery process exists for REs due to low prices of the REs in the past, dispersion of NdFeB in diversified scrap and very little or no incentive to recycling WEEE. However, the sharply rising prices for most REs, export quotas, current and forecast supply shortage and limited Chinese export have resulted in serious recycling considerations.¹²⁻¹⁴

Extraction of Rare Earths from Ores

After mining, crushing and grinding the minerals, RE is concentrated by floatation, magnetic or gravity methods which depends on the surface properties, magnetic susceptibility and specific gravity respectively. WEEE is similarly treated by crushing the electronic scrap containing RE into powder. This can be further concentrated using the physical methods listed above. The RE concentrates from mineral ores or WEEE is then subjected to hydrometallurgical treatment to obtain pure RE.

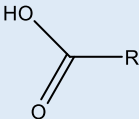
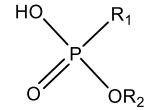
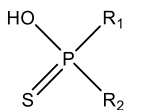
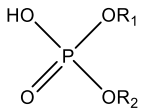
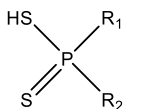
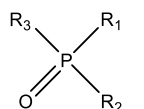
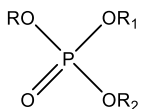
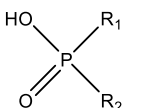
The minerals are roasted in the presence of acidic or caustic reagents. The residue is then leached with hydrochloric or sulfuric acid. The amount of acid required at this stage is minimised by the roasting at prior stage. The RE sulfates formed may be leached with water and neutralised with magnesium oxide. The leached solution is then converted to mixed rare earth chlorides by precipitation with ammonium carbonate, dissolution in HCl and crystallisation. Most commonly, the acid leached solution proceeds to one of the following extraction methods including solvent extraction or using ionic liquid, supercritical fluids; ion-exchange, membranes; microcapsules or functionalised resins and precipitation.

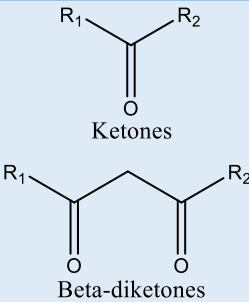
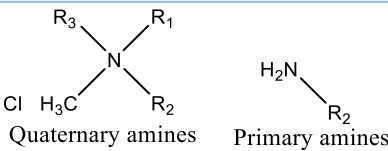
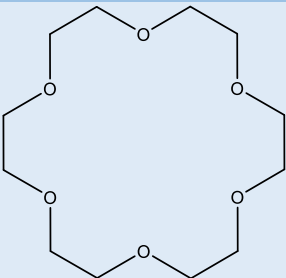
The ultimate goal is to develop a system that can efficiently extract RE from the acid leachate and easily stripped off the extractant for easy recovery of the extractants. This is why solid-liquid extraction system is more desirable as it can also solve the problem of loss of the organic extractants into the aqueous phase encountered in liquid-liquid separations.

Solvent Extraction

This technique involves the use of a biphasic system with the organic extractant dissolved in the organic layer and the RE dissolved in the aqueous phase. Ligands/extractants used in solvent extraction have been grouped by Ritcey and Ashbrook into cation exchanger, chelating exchanger, solvation extractants, and anion exchanger according to their type of interaction with the RE and the donor atoms they bear.¹⁵ Common extractants used in solvent extraction includes ligands of carboxylic acids, phosphoric acids, phosphonic acids, phosphinic acid, phosphorous ester, phosphine oxides, ketones, thiophosphates and amines.

Table 3: General Structure of Solvent Extractants.

Extractants	General structures	Targets
Carboxylic acids		Y, Ce, Pr, LREE
Organophosphoric acids and esters	 Phosphonic acids  Monothiophosphorus acids  Phosphoric acids  Dithiophosphorus acids  Phosphine oxides  Phosphorus ester  Phosphinic acids	La, Ce, Pr, Eu, Tb, Tm, Yb, Lu, Nd, Ho, Gd, Sm, Dy, Er

Ketones and β-diketones	 Ketones Beta-diketones	Ln
Amines	 Quaternary amines Primary amines	Eu, Pr, Ce, Y, Tm
Crown ethers		Y, Sc, La, Ce, Pr, Eu, Tb, Tm, Yb, Nd, Gd, Sm, Er

Carboxylic Acids

Carboxylic acids have been well investigated in extraction studies. They are regarded as cation exchangers.¹⁵ High molecular weight carboxylic acids such as cecanoic (6-Methylheptanoic acid), naphthenic (cyclohex-3-ene-1-carboxylic acid), neo-heptanoic (4,4-Dimethylpentanoic acid) and versatic acids (neo-decanoic) have been investigated in the extraction of RE by Singh et al. and Zheng et al. with similar conclusions. Yttrium was found to have extraction behaviour of HREE with sterically hindered acids (neo-heptanoic and versatic acids) and also to that of LREE (Ce, Pr) with sterically less hindered acids (cecanoic, naphthenic).^{16, 17} Preston et al. have studied the extraction of RE with naphthenic acid and versatic acids from sulfate and chloride solutions. They found a dependence of the extraction properties of the carboxylic acids on the atomic number of the lanthanide and the steric hindrance caused by the structure of the carboxylic acids.¹⁸ Other carboxylic acids such as *sec*-nonylphenoxy acetic acid (CA-100) and *sec*-octylphenoxy acetic acid (CA-12) has also been employed in the extraction of RE. Results showed that *sec*-nonylphenoxy acetic acid (CA-100) shows better extraction of RE than neo-decanoic acid at lower Ph.¹⁹ The use of multi-dentate extractants including calix[n]arene with carboxylate systems have been shown to exhibit a better extraction efficiency than the monodentate analogs.^{20, 21}

Organophosphoric Acids and Esters

Phosphoryl containing extractant are very popular in extraction due to their donor ability.^{22, 23} This family of extractant includes phosphoric, phosphonic, phosphinic, monothiophosphorous, dithiophosphorous acids, phosphorous ester, and phosphine oxides.^{22, 24, 25} Zang *et al.* reported the extraction of La(III) from chloride solution using di-(2-ethylhexyl)phosphoric acid (P204 or D2EHPA or HDEHP) and a complexing agent, lactic acid. They found that the distribution ratios (a measure of how well extracted the metal is) increased with the increase in pH value in the feed and lactic acid concentration.²⁶ Peppard et al. also showed that the distribution ratio had an inverse power dependency on HCl concentration using the same extractants. The extraction order of Ln was found to be Lu > Yb > Tm > Tb > Eu > Pm > Pr > Ce > La while distribution coefficient increase with increase in atomic number.²⁷⁻²⁹ D2EHPA has also been applied on large scale extraction of RE from bastnesite by Molycorp in 1965.³⁰

Other phosphoryl containing podands have also been studied in the separation of Th(IV) and U(VI) from La(III), Nd(III), Ho(III) and Yb(III) in low nitric acid concentration with ethyl-, butyl-, and tert-butyl substituent on the aromatic ring found to exhibit the best results.³¹ Sato reported the extraction of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium between hydrochloric acid solutions and solutions of di-(2-ethylhexyl)-phosphoric acid (DEHPA) or 2-ethylhexyl-2-ethylhexylphosphoric acid (EHEHPA marketed as PC-88A, P507, Lonquest 801) in kerosene. The extraction efficiency was found to increase with increasing atomic number and DEHPA was found to be a better extractant than EHEHPA in these conditions.²⁴ The extracted complexes have also been found to be more easily stripped.³² Commercial RE separation plant in Baotou, China uses a process which involves HEHEHP as an extractant.³³

Utilising 33 vol% dibutyl butylphosphonate in Shellsol 2325 (mixture of paraffins, cycloparaffins and aromatics) and tributylphosphate (TBP) in separate processes, Preston et al. was able to extract RE nitrates and oxides from leach liquor by the addition of 2.5 M ammonium nitrate.³⁴ The use of dialkylphosphinic acids (Cyanex 272) have been widely investigated.³⁵⁻³⁸ In a study by Talcher, the phosphorus solvent TOPS 99 (di-2-ethylhexyl phosphoric acid), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A), and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) were used in the extraction of lanthanum, cerium, praseodymium and neodymium. Terbium, dysprosium, holmium, yttrium, erbium, ytterbium, and lutetium has also been extracted from phosphoric acid solutions by Radhika et al. Results obtained indicated a decrease in extraction efficiency with increasing acid concentration and the general trend of the extractant efficiency was of the order TOPS 99 > PC 88A > Cyanex 272.³⁹ The extraction of single and binary La(III) and Nd(III) from nitrate solutions with PC88A in kerosene at 298 K has also been reported by Kao et al. A kinetic and thermodynamic study on the extraction of these RE showed higher extractability of Nd(III) over La(III). However, the stripping rate of Nd(III) was nearly two order of magnitude larger than that of La(III).⁴⁰

Ketones and β -diketones

β -diketonates are complexes of RE and β -diketones (1,3-diketones). These compounds and their derivatives were widely researched at the beginning of the 1960s at extractants.⁴¹ They have also been investigated in synergistic extractions and found to possess some extraction efficiency mostly as a mixture with other extractants.^{42, 43} β -diketones such as hexafluoroacetylacetone (HFAC) form hydrated chelate which are poorly extracted.⁴⁴ Butts and Banks concluded from their studies that hexafluoroacetylacetone in a mixture with tri-*n*-butylphosphate can effectively form solid extractable chelates. 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione have similarly been known to form chelates.^{45,46, 47}

Synergistic extraction of La(III) from chloride medium using triisobutylphosphine sulfide (TIBPS) and 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) has been reported by Jia et al. Synergistic enhancement factor of HPMBP and TIBPS was calculated to be 2.40. They concluded that mixtures have no better separation abilities for rare earth elements than HPMBP.⁴⁵ HPMBP has been further investigated by Jordanov et al. as a sole extractant in the extraction of 13 lanthanides in aqueous-benzene media. The composition of the extracted species has been determined as $\text{LnP}_3 \cdot \text{HP}$ (where P is HPMBP).⁴⁸

Synergistic extraction of RE with a polyfluorinated β -diketone 1,1,1,2,2,6,6,7,7,7-deca-fluoro-3,5-heptanedione, (H(FHD)), as the ligand, and di-*n*-butylsulfoxide (DBSO) as neutral donor has been reported by Burgett and Fritz. Individual and mixed lanthanides were obtained with 97.5 and 97.1% recovery respectively.⁴⁹ Tri-*n*-octylmethylammonium nitrate (TOMAN) and β -diketone (α -acetyl-*m*-dodecylacetophenone: LIX54) in the presence of water-soluble complexing agent (ethylenediaminetetraacetic acid: EDTA) have been studied in RE extraction by Hirai and Komasaawa. They found that only free RE which is not complexed with EDTA could take part in the extraction.⁵⁰

Amines

A multitude of amines have been used in RE co-ordination chemistry and many researchers have now extended this to extraction of RE.⁵¹ Amines are regarded as anionic exchangers.¹⁵ They have been found to poorly extract RE in chloride media but better results in sulfate media.^{52, 53}

As early as in the 1950s, Coleman et al. conducted a screening of hundreds of amines and found that simple amines are best for extraction. They attributed this to organic phase insolubility at a high pH which is less severe in simple amines with molecular weight in the range of 200-600 Da. These amines are typically of the trialkyl-, tridecyl-, iso-octyl groups.⁵⁴

Triiso-octyl amine dissolved in xylene has been used to extract actinides and lanthanides by Moore. The study showed that under certain conditions, RE can be extracted using a similar system. The extraction efficiency was found to be in the order, thorium > europium, promethium > cerium > yttrium, thulium.⁵⁵

Trialkyl methylamine (Primene JMT) has been studied in the extraction of RE and found to extract La(III) and Y(III) from sulfate media.^{56, 57} Quaternary ammonium salt (Tricaprylmethylammonium chloride, Aliquat 336) have also been investigated in RE extraction.^{58, 59} Addition of EDTA to Aliquat 336 have been shown to improve LREE separation.⁶⁰ Aliquat 336 have been shown to extract Nd, Pr in 83 and 15% respectively and other RE in 2% from didymium (a mixture of praseodymium and neodymium) nitrate solution.^{61, 62}

Crown Ethers

Crown ethers and their derivatives are a group of macrocyclic ligands with ability to form interesting complexes with a variety of metal ions. Crown ethers of various sizes and substituents has been used in the extraction of RE.⁶³ 15-crown-5, 12-crown-4 and dibenzo-18-crown-6 have been employed in the extraction of Tb³⁺, Eu³⁺, Gd³⁺, Nd³⁺, Yb³⁺, Ce⁴⁺, Sm³⁺, Dy³⁺ and Lu³⁺ from aqueous solutions containing picrate into nitrobenzene solution. A 2:1 sandwich complex with 15-crown-5 was observed for europium but 1:1 complex with 12-crown-4 and dibenzo-18-crown-6.⁶⁴

Crown ethers have been used to extract La³⁺, Ce³⁺, Pr³⁺, Eu³⁺ and Er³⁺ from acidic solution in presence trichloroacetic acid from acidic solutions. The presence of trichloroacetic acid as counter ions was shown to improve the selectivity of 18-crown-6 derivatives.⁵⁴ Ensor et al. have shown that crown ethers can be used to synergistically enhance extraction of Ce³⁺, Pm³⁺, Eu³⁺ and Tm³⁺ along with a mixture of didodecyl naphthalenesulfonic acid. The selectivity and extraction efficiency of this extractants were improved by the addition of the crown ether.^{65, 66}

The use of azacrown ether for extraction has also been studied. 1,10-diaza-18-crown-6, 15-crown-5, benzo-15-crown-5, monoaza-, and tetraazacrown have been involved in extraction studies.⁶⁷⁻⁷¹ Mono-Aza dibenzo 18-crown-6 ether have been reported to extract La(III), Nd(III) and Sm(III) in synthetic solutions with a pre-concentration factor of 120 for La(III), 131 for Nd(III) and 151 for Sm(III) with efficient extraction results achieved.⁷² Selective extraction of Y³⁺ over Sr³⁺ has been demonstrated by Wood et al. They showed that by changing the carboxylic acid at the terminal end of the lariat to hydroxamic acid, the selectivity of the extractant for Y³⁺ over Sr²⁺ is greatly increased leaving a fraction of 99% pure Sr²⁺.⁷³

Ionic-Liquids (IL) Extraction

Recently, there has been an increased interest in the used of IL in RE extraction due to their unique properties such as non-volatility, non-flammability, and wide temperature range for liquid phase. This technique, like most of the techniques discuss in this paper, have been optimised and applied to RE recycling from e-waste.^{74, 75} They are usually composed of heterocyclic organic cations and various anions. The most attractive properties of ILs with respect to separation techniques is that their physicochemical properties can be easily

tuned by changing combinations of cations and anions and thereby changing the selectivity. They can be made to be water-immiscible salts by increasing the alkyl chain length of the cation incorporating hydrophobic anions. For example, increasing the alkyl chain length of 1-alkyl-3-methylimidazolium cations, from butyl to hexyl to octyl increased the hydrophobicity.⁷⁶⁻⁷⁹ Extraction of metal ions is more efficient in IL than in volatile organic solvents.⁸⁰⁻⁸⁴ They have also been known to overcome the stripping challenges encountered in typical solvent extractions.⁷⁵

Depending on solubility in the IL and extraction efficiency in the organic solvent, a wide range of extractants in combination with the IL have been investigated in RE extraction.⁸⁵ Turanov et al. has investigated the extraction of chlorides of (Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) into organic solutions of tetraphenylmethylenediphosphine dioxide, diphenyl(diethylcarbamoylmethyl)phosphine oxide, and dibutyl(diethylcarbamoylmethyl)phosphine oxide in the presence of ILs, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. The mixture was found to extract RE far more efficiently than when the IL was absent.⁸⁶

The use of eight imidazolium ILs ([C_nmim][NTf₂] and [C_nmim][BETI], n = 4,6,8,10) and one pyrrolidinium IL ([C₄mPy][NTf₂]) as diluents using di(2-ethylhexyl)phosphoric acid (HDEHP) as an extractant for the separation of lanthanide ions from aqueous solutions of 50 mM glycolic acid or citric acid and 5 mM diethylenetriamine pentaacetic acid (DTPA) in a cation-exchange mechanism has been described by Sun et al. They reported excellent extraction efficiencies and selectivity which they attributed to the competition between the aqueous phase complexation by DTPA and the organic phase extraction by HDEHP.⁶³

Nakashima et al. reported the extraction of rare earth metals into ILs, [Bmim][PF₆] from aqueous solutions using octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) as an extractant. The IL was found to increase the extraction efficiency in a cation-exchange mechanism.⁸² The extraction of Ce(IV) along with Th(IV) and Ce(III), Gd(III), Yb(III) nitrate by pure ionic liquid, [C₈mim]PF₆ has been investigated by Zuo et al. Ce(IV) was found to be extracted better than Th(IV) and the other REs through anion exchange mechanism in the [C₈mim]PF₆ alone.⁸⁷

Modification of the alkyl chain of the imidazolium IL to obtain 1-butyl, 1-octyl, and 1-dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_nmim][Tf₂N], n = 4, 8, 12) has been reported by Goto et al. Using this as the medium, they performed the extraction using a novel extractant, *N,N*-dioctyldiglycol amic acid (DODGAA) in extraction of Eu(III) and Y(III). The REs were extracted quantitatively in a proton exchange mechanism.⁸⁸ DODGAA is a much more soluble ligand than the CMPO⁸⁹ and has a higher selectivity.⁹⁰ Shorter alkyl-chain imidazolium IL, [C₄mim][Tf₂N] was found to be a better extractant.⁹¹ Sc(III) has been separated from Y(III), La(III) and Yb(III) has also been extracted using similar IL, [C₈mim][PF₆] containing Cyanex 925 as the extractant in a cation exchange mechanism by adding EDTA to the aqueous phase.⁹²

More recent ILs includes trihexyl(tetradecyl)phosphonium chloride which acts as both the organic phase and the extractant have been developed by Hoogerstraete et al. and have been tested in the separation of copper, cobalt, iron, manganese and zinc from rare earths resulting in purer RE fractions. The high affinity of iron(III) for the ionic liquid results in very high distribution ratios with percentage extraction reaching 99.98% although the extraction efficiency of other metals such as aluminium, magnesium, nickel, calcium and chromium was low.⁷⁹

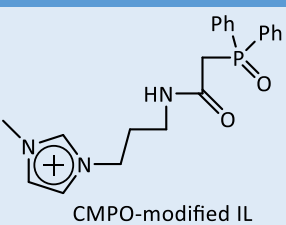
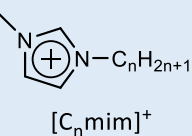
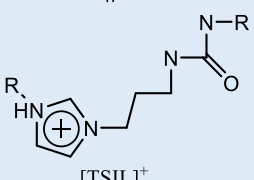
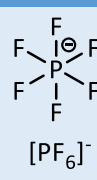
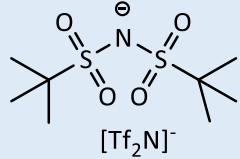
Xiaoqi et al. has further impregnated polarized XAD-7 resins with IL made up of [trialkylmethylammonium][sec-nonylphenoxy acetate] ([A336] [CA-100]) and [tricaprylmethylammonium chloride][nitrate] ([A336][NO₃]). This type of ILs are considered to be cheaper and less toxic than the imidazolium type ILs.^{93, 94} The results of this study showed that, ([A336][NO₃]) was found to have higher adsorption properties due to the presence of the cation and anion. The impregnated resin was effective in separating Sc(III) from Ce(III), Eu(III) and Y(III) by adjusting the aqueous acidity. However, the marked viscosity could be a potential hindrance to the application of these systems.

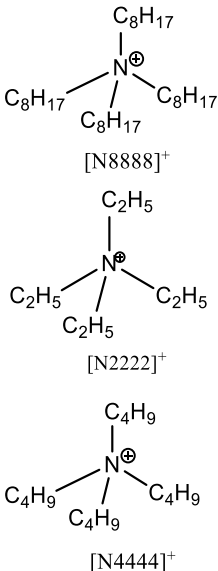
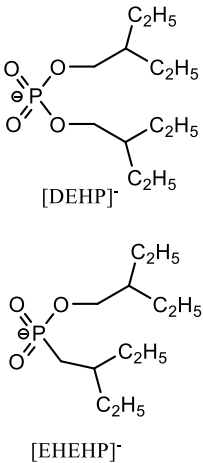
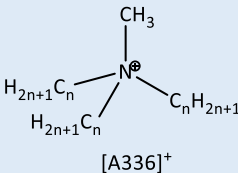
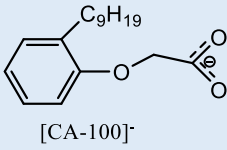
More recently, europium and other trivalent lanthanides were extracted with trihexyl(tetradecyl)phosphonium *N,N,N',N'*-tetra(2-ethylhexyl)malonate, [P₆₆₆₁₄][MA]. A good separation of the rare earths from the transition metals was achieved as the extraction efficiency increased over the lanthanide series.⁹⁵ Using tri-*n*-butylphosphate (TBP) and an electrolytic IL, triethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl)amide ([P₂₂₂₅][TfSA]), Matsumiya et al. has shown that RE can be recovered through electrodeposition with better recovery than in a typical organic solvent.⁹⁶

Several other new ionic extractant (see Table 4), including tetrabutylammonium di(2-ethylhexyl)phosphate ([TBA][DEHP]), trioctylmethylammonium di(2-ethylhexyl)phosphate ([TOMA][DEHP]), trihexyl(tetradecyl)phosphonium di(2-ethylhexyl)phosphate ([THTP][DEHP]),⁹⁷ 1-Methylimidazole (1-MIM), 2-methylimidazole (2-MIM),⁹⁸ tetraethylammonium di(2-ethylhexyl)phosphate ([N₂₂₂₂][DEHP]), tetraethylammonium bis(2,4,4-trimethylpentyl)phosphinite ([N₂₂₂₂][BTMPP]), tetraethylammonium bis(2,4,4-trimethylpentyl)dithiophosphinite ([N₂₂₂₂][BTMPDTP]), tetrahexylammonium di(2-ethylhexyl)phosphate ([N₆₆₆₆][DEHP]), and tetraoctylammonium di(2-ethylhexyl)phosphate ([N₈₈₈₈][DEHP]) have been used as extractants with bis(trifluoromethanesulfonyl)imide/bis(perfluoroethanesulfonyl)imide ([C₁₀mim][NTf₂]/[BETI]) as the IL. The effect of various conditions on extraction efficiency was investigated by Sun et al.⁸⁵ They found that increase in the size of the cation can decrease the distribution ratio and selectivity of RE. Acidity and concentration of some of the ionic extractants were also shown to affect the extractability and selectivity of the IL systems. This anion and cation influence has also been more recently described by Rout and Binnemans.⁹⁹⁻¹⁰¹

Practical application of ILs in RE extraction from phosphor powders in waste fluorescent lamps have been studied by Yang et al. After a previous metal extraction studies with *N,N*-dioctyldiglycol amic acid (DODGAA) based IL^{90, 91} these phosphorus free extractants in IL ([C₄mim][Tf₂N]) system were used in the selective extraction of Y, Eu La and Ce from Fe, Al, Zn and other impurities in electronic scrap.^{75, 102}

Table 4: General Structure of the Cation and Ionic Parts of Commercial Ionic Liquids

Cation	Anion	Extractants	Targets
 CMPO-modified IL  [C_nmim]⁺  [TSIL]⁺	 [PF₆]⁻  [Tf₂N]⁻	CMPO, TPEN, D2EHPA, Cyanex 272, Cyanex 925, Ph ₂ Et ₂ , Bu ₂ Et ₂ , TODGA, HYD, PC-88A, Htta, CMPO-modified IL, DODGAA, HDEHP	Sc, Y, Ln

 [N8888]⁺ [N2222]⁺ [N4444]⁺	 [DEHP]⁻ [EHEHP]⁻	DTPA, Glycolic acid DEHP with THTP, TOMA, TBA; 1-MIM, 2-MIM, N2222 and BTMPP, BTMPDPT	Ln
 [A336]⁺	 [CA-100]⁻	[A336][CA-100], [A336][P204], [A336][P507]	Sc, Y, Ln (fluorescent powder)

Synergistic extraction

Synergistic effect with combinations of different extractants has been a subject of many studies in the area of RE extraction. Synergism occurs when the presence of a second extractant enhances the overall extraction efficiency.¹⁰³⁻¹⁰⁸ Extraction of uranium and lanthanides from phosphoric acid using DOPPA and TOPO has been studied.¹⁰⁹ Reddy et al. has also investigated the extraction of RE with bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and trialkyl phosphine oxide (Cyanex 923) in xylene. La(III) and Nd(III) were extracted as MX₂.NO₃.TRPO complex with Cyanex 923 while Eu(III), Y(III) and HREE extracted species were MX₃.HX.2TRPO (where X is Cyanex 923 and Cyanex 301). The extraction efficiency and the selectivity were enhanced by the addition of the trialkylphosphine oxide.¹¹⁰

The use of 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP, HA) and *sec*-octylphenoxyacetic (CA12, H₂B₂) as a synergetic system in the extraction of lanthanum and neodymium have been studied. The system was found to more effectively extract the LREE.¹¹¹ The synergetic extraction of Nd³⁺ or Sm³⁺ from a sulfuric acid medium, by mixtures of di-(2-ethylhexyl) phosphoric acid (HDEHP) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (HEH/EHP) were studied. Maximum synergistic enhancement coefficient was observed with a ratio of HEH/EHP to HDEHP was 3:2. The synergistic extracted species were Nd(HA₂)₂·HL₂ and Sm·(HA₂)₂·HL₂.¹¹²

The synergistic effect in the mixtures of 8-hydroxyquinoline (HQ) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (P507) in the extraction of Pr(III) and Nd(III) has been explored by Wu et al. they found a synergistic enhancement factor to be 5.47, 3.37 and 2.86 for Pr, Nd and La(III), respectively, when the concentration ratio of HQ to P507 is equal to 3:7 at pH 3.6.¹¹³

The use of 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEHEHP, P507) and organophosphorus acids [di-(2-ethylhexyl)phosphoric acid (HDEHP, P204), isopropylphosphonic acid 1-hexyl-4-ethyloctyl ester (HHEOIPP), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301)] as mixtures of HEHEHP/HDEHP, HEHEHP/Cyanex 301, HEHEHP/HHEOIPP, HEHEHP/Cyanex 302 and HEHEHP/Cyanex 272 has been reported by Wang et al. The extraction efficiency

was found to be in the order of HEHEHP/HDEHP > HEHEHP/Cyanex 301 > HEHEHP/HHEOIPP > HEHEHP/Cyanex 302 > HEHEHP/Cyanex 272.¹¹⁴

Mono- and dithiophosphinic acids in combination with ammonium salts have also been investigated in synergistic extraction systems by Belova et al. Salts of trioctylmethylammonium with dialkylphosphinic, dialkylmonothiophosphinic, and dialkyldithiophosphinic acids were employed in the extraction of RE. Extraction efficiency of binary extractants towards lanthanum chloride as well as lanthanum nitrate decreases in the series: dialkylphosphinate > dialkylmonothiophosphinate >> dialkyldithiophosphinate of quaternary ammonium base (QAB).¹⁰⁷

Supercritical Fluids

Supercritical fluids (SCF) have been adapted in the extraction of metal due to its unique properties. Above certain temperature and pressure (critical point), SCF is neither in its liquid or gas phase. It can diffuse like a gas and dissolve material like a liquid. Its extraction selectivity can be enhanced by tuning the temperature and pressure.¹¹⁵ These properties have been harnessed by a number of researchers to extract metals from industrial or electronic scraps. SCF can be modified by adding an appreciable amount of polar solvents such as methanol in order to improve the polarity of the organic phase and solubility of the extractants or the extractant-metal complex.¹¹⁶

Supercritical carbon dioxide (scCO₂) is an example of SCF which have received a lot of attention due to its low toxicity and is environmentally acceptable, cheap and low critical temperature and a moderate critical pressure. Unlike organic solvents, scCO₂ is inert to the extraction conditions; its solvency can be tuned to improve selectivity by small change in temperature and pressure. Residual contamination of aqueous phase by the organic phase is not an issue with scCO₂.¹¹⁷

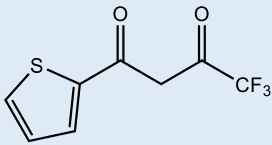
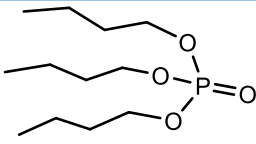
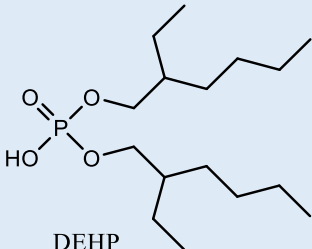
ScCO₂ containing various extractant have been investigated by a number of researchers.¹¹⁸ There exists a number of extractant including TTFA (Thenoyltrifluoroacetone), ACAC (Acetylacetonate), LiFDDC [Lithium bis(trifluoroethyl)-dithiocarbamate], TBA(tert-butyl alcohol), HFOD (1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione), that have been widely used as various metal extractants in scCO₂.¹¹⁹⁻¹²⁶ Unfortunately, only a few of these extractants have made it to RE extraction. There is a general problem of solubility of these ligands and/or their metal complexes when using scCO₂. Although some ligands including CMPO, CMP, TBP, TOPO are more soluble in scCO₂¹¹⁵ only a handful of data on the solubility of CMPO, CMP, TBP, TOPO (Trioctylphosphine oxide) complexes exists in the literatures. However it has been shown that fluorinated ligands and their metal complexes are more soluble in SCF than non-fluorinated analogs. For example, fluorinated DCC and HFA and their metal complexes have been found to be very soluble in scCO₂.¹¹⁹

Lin and Wai studied the extraction of La³⁺, Eu³⁺ and Lu³⁺ from aqueous solution using TTFA as the chelating extractant in scCO₂. They obtained extraction efficiency of 30, 38 and 51% for La³⁺, Eu³⁺ and Lu³⁺ respectively. However, the use 50 mg of extractant in 40 ml of scCO₂ for the extraction of ≤50 % of 0.01 mg of lanthanide suggests very low efficiency of the system used in this study.¹²⁷ Laintz and Tachikawa has extended scCO₂-TBP extraction system to La³⁺, Ce³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Dy³⁺, Yb³⁺ and Lu³⁺ and obtained extraction efficiency of 43.6 for La³⁺, 60.5 for Ce³⁺, 85.1 for Sm³⁺, 86.7 for Eu³⁺, 86.9 for Gd³⁺, 91.8 for Dy³⁺, 71.9 for Yb³⁺ and 69.2 for Lu³⁺ with 30% TBP.¹²⁸ This indicates significant improvement to scCO₂ extractions. Using the same extractant and DEHPA, in scCO₂, Dehgani et al. was able to extract Ce³⁺, Pr³⁺, Nd³⁺, Ho³⁺, Eu³⁺, Y³⁺ from aqueous phase comprised of 0.05 M Ln(NO₃)₃, 0.1 M HNO₃ and 3M NaNO₃ at 40 °C and 150 bar with 7 mole% TBP. The extraction efficiency for the LREE increased with increasing atomic number.¹²⁷

Laintz and Tachikawa have studied the effect of adding TTFA to TBP in a synergistic system and obtained slightly improved efficiency of RE extraction.¹²⁹ Dehgani has also investigated the use of TBP and DEHPA for Ln extraction. Most interestingly, they found that addition of 2.5 mole% DEHPA to 3 mole% (instead of 7 mole%) TBP significantly increased the extraction efficiency from 1 to 99% extraction of Yb³⁺.

Using TBP- HNO_3 complex has been adapted by Tomioka et al. for the extraction Nd from several oxides such as Nd_2O_3 , ZrO_2 , MoO_3 , and RuO_2 ; and binary mixtures of the oxides such as $\text{Nd}_2\text{O}_3\text{-ZrO}_2$, $\text{Nd}_2\text{O}_3\text{MoO}_3$, and $\text{Nd}_2\text{O}_3\text{-RuO}_2$. Selective extraction of Nd from 0.01 mole Nd_2O_3 powder was obtained quantitatively using scCO_2 containing TBP- HNO_3 (TBP) at 313 K and 12 MPa, while Zr, Mo, and Ru were not extracted.¹³⁰ The application of scCO_2 containing tri-*n*-butyl phosphate (TBP) complexes with HNO_3 and H_2O in the extraction of Y, Eu, La, Ce and Tb from waste fluorescent lamp has also been investigated by Shimizu et al. Over 99% extraction efficiency was obtained for some of the metals from the fluorescent lamp.¹¹⁸

Table 5: General Structures of Extractants used in SCF

Extractants	Structure of Extractants	Targets
Thenoyltrifluoroacetone	 TTFA	La^{3+} , Eu^{3+} and Lu^{3+}
Tributyl phosphate	 TBP	Y, Eu, La, Ce and Tb, Nd oxides, La^{3+} , Ce^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Dy^{3+} , Yb^{3+} and Lu^{3+}
Di-(2-ethylhexyl)phosphoric acid	 DEHP	Ce, Pr, Nd, Ho, Eu, Y

Ion-Exchange Resin

Ion exchange was once the only practical to separate RE on large scale. As solvent extraction is now capable of large scale separation, ion-exchange is now only used to obtain high purity RE for analytics and electronics.¹³¹ The simplicity and convenience makes this method particularly attractive for separation and purification of RE.¹³²⁻¹³⁴ Commercial ion-exchange resins include amberlite, amberlyst, amberjet, dowex, and Duolite. They can be weak or strong cation, anion exchangers, mixed bed, chelating, or polymeric resins.¹³⁵

RE in red mud, the by-product of the alumina production, could be selectively separated from the main and minor elements, as well as from yttrium and the lanthanides using a combination of ion exchange-solvent extraction method. After a suitable borate/carbonate fusion of red mud, the sample solution was passed through the ion exchanger Dowex 50W-X8 and Fe, Al, Ca, Si, Ti, Na, Ni, Mn, Cr and V were removed by elution with 1.75 M HCl. Sc, Y and the lanthanides were quantitatively obtained by a subsequent elution with 6 M HCl. Scandium could then be selectively and near quantitatively extracted in the organic phase using di(2-ethylhexyl)phosphoric acid in hexane, while yttrium and the lanthanides remained in the aqueous phase.¹³⁶

The separation and analysis of RE using a mixed solvent ion-exchanger in a batch separation process has been described by Roelandts. After dissolving samples of RE containing Apatite in HNO_3 , a basic anion-exchanger,

Dowex 1X8 100-200 mesh (nitrate form) RE mixed with the resin were then adhered to a cellulose support and analysed by X-ray fluorescence spectrometry.¹³⁷

Faris et al. has investigated the extraction of yttrium and scandium from methanol-nitric acid solution using a strongly basic anion-exchange resin in a column elution technique. The REs were eluted from the column in order of increasing atomic number with little individual separation for those higher than dysprosium. Large separation factor was found for those lighter than terbium. Scandium was not adsorbed in appreciable amount while yttrium behaved like lutetium. The extraction system has been extended to macro-scale process for fractionation of crude RE to obtain extremely pure RE.¹³⁸ Although with slightly different aim, Koopman and Witkamp were able to efficiently separate lanthanides from phosphoric acid processes using Dowex C-500 ion exchange resin functionalized with sulfonic acid functional groups.^{139, 140} Using AG50WX4 cation-exchange resin and CMPO, (16 wt.%) dissolved in TBP (24 wt.%) and supported on the inert porous polyacrylic substrate Amberchrom CG-71ms, lanthanides were quantitatively recovered.¹⁴¹ Lanthanum along with uranium and thorium were separated individually using Amberlite XAD-16 (AXAD-16)-N,N-diethylcarbamoylmethyl phosphonic acid quantitatively in >99.8% efficiency from nuclear spent fuels as well as from geological and natural water resources.¹⁴²

Synthesised resins has also been used in extraction of RE. Draye et al. described the alkaline polycondensation of 8-hydroxyquinoline with formaldehyde to obtain a polymeric resins. The selective uptake of Eu^{3+} from aqueous solutions containing La^{3+} was found to be due to the incorporation of 8-hydroxyquinoline in the molecular matrix of the phenolic resins.¹⁴³

High pressure ion-exchange has been applied to separation of adjacent lanthanides by chromatographic elution from Dowex 50 resin showing that this system can be equally used to obtain pure lanthanides.¹⁴⁴

Microcapsules and functionalised resins

Microcapsules

The use of microcapsules to encapsulate extractants allows for easy recycling of the extractant¹⁴⁵, recovery of various metals,¹⁴⁵⁻¹⁴⁷ and ease of metal sorption unto microcapsule.¹⁴⁸⁻¹⁵⁰ This results in a solid-liquid system as opposed to the conventional liquid-liquid systems in hopes of overcoming the challenges posed by liquid-liquid system. Kondo et al. have shown the extraction process of lanthanum, cerium, neodymium, promethium and samarium in separate studies using encapsulated 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA). Encapsulated EHPNA use in metal extraction is controlled by both the chelating complex formation reaction between the metal and extractant as well as the diffusion of the complex in the microcapsule pores.¹⁵¹⁻¹⁵³ They also reported the use of dibenzoylmethane encapsulated into MC by *in situ* radical polymerization of divinylbenzene. The results showed that the amount of metals adsorbed onto the MC increased as the pH increased. Also, the separation of dysprosium and gadolinium was achieved as only dysprosium was extracted at pH 6.0.¹⁵³

Extraction of RE using MC consisting of styrene (St)–divinylbenzene (DVB) copolymer and containing bis(2-ethylhexyl)phosphinic acid (PIA-226) has been studied by Nishihama et al. A mixture of Pr/Sm was efficiently separated using a column packed with these MC as Pr with high purity was obtained initially from the aqueous effluent solution, and Sm with high purity was obtained in the microcapsules.¹⁵⁴ After an earlier successful study with microcapsules containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA),¹⁵⁵ Kamio et al. investigated the use of EHPNA in a microcapsule in the extraction of lanthanum, samarium and erbium. The initial extraction rates of lanthanides in the microcapsule system were found to be affected by the external aqueous conditions, such as the pH and metal concentration. It was found that the initial extraction rate for the microcapsule system varied in the same way with pH and metal concentration as it does in a liquid–liquid extraction system.¹⁵⁶ Selective extraction of neodymium using EHPNA encapsulated in magnetic alginate MC was reported by Zang et al.¹⁵⁷

Jing et al. reported the use of polysulfone microcapsules in RE extraction. The pierced polysulfone microcapsule was functionalised with EHPNA using ultrasonic method. Results revealed a high extraction of Sm^{3+} and Er^{3+} whilst La^{3+} extraction levelled off after 50%.¹⁵⁸ Wang et al. has investigated the optimisation of polysulfone MC preparation. The results EHPNA was imported at high loading ratio. The maximum uptakes of La^{3+} , Sm^{3+} and Er^{3+} were 3.02×10^{-4} mol/g, 8.05×10^{-4} mol/g and 5.58×10^{-4} mol/g, respectively.¹⁵⁹

Reagent impregnated resins (RIRs)

The use of RIRs in extraction of RE offers simplicity, coordination, a wide range of application and facile extractant recovery.¹⁶⁰⁻¹⁶⁸ Using 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (PC-88A) and Amberlite XAD-2, XAD-4, XAD-16 and XAD-7 as a polymeric support has been studied by Matsunaga et al. and results showed that the extraction rate is affected by amount of PC-88A impregnated into XAD-2, XAD-4 or XAD-16 resins with respect to their pore volume while the amount of PC-88A impregnated into XAD-7 had only little effect on the extraction rates.¹⁶⁹

Taking a step further, Sun et al. has reported the extraction of yttrium from other RE using IL impregnated resin. The IL was mixed with Cyanex923 and immobilised on a XAD-7 resin. Results showed a shorter equilibration time, 80% separation efficiency and yttrium was selectively extracted from Ho, Er, Yb and Sc by adding a water soluble complexing agent (EDTA) to the aqueous phase.¹⁷⁰

Merrifield chloromethylated (MCM) resin has been grafted with octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methylphosphine oxide (CMPO) (MCM-CMPO) for the purpose of metal extraction. The resin showed very high sorption capacity values of $0.960 \text{ mmol g}^{-1}$ for U(VI), $0.984 \text{ mmol g}^{-1}$ for Th(IV), $0.488 \text{ mmol g}^{-1}$ for La(III) and $0.502 \text{ mmol g}^{-1}$ for Nd(III) under optimum HNO_3 medium.¹⁷¹ Ionic imprinted resin bearing diethylenetriamine pentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA) derivatives have been reported in RE extraction with Gd(III)-imprinted polymers found to be more selective.⁵¹

Ion-imprinted polymer based on picolinic derivative have been shown by Chauvin et al. to be particularly well adapted for yttrium extraction, having a sizeable capacity ($8.9 \pm 0.2 \text{ mg g}^{-1}$ resin) and a fast rate of extraction ($t_{1/2} = 1.7 \text{ min}$). The group prepared the resin by copolymerization with styrene and divinylbenzene and subsequent acid treatment to remove the metal ion. The resin displayed high selectivity for yttrium and lanthanide cations against alkali and alkaline earth metals.¹⁷²

Liquid Membrane Extraction

This technique involves the use of *Liquid surfactant membrane* or *Supported liquid membrane*. It generally involves the selective permeation of metal ions through a very thin liquid membrane and a huge interfacial area for the separation of metal ions.¹⁷³ This technique generally utilised the concentration gradient in extraction of metal ions from the feed solution to the stripping solution. A thin liquid film made up of the extractant and a suitable solvent can be supported on a micro-porous hydrophobic hollow fibre and then used to transport the solute from the feed to the product side.¹⁷⁴

Using a liquid membrane system, the synergistic separation of yttrium ions from rare earths mixture using an acidic extractant, Cyanex 272, and a neutral extractant TBP mixed in kerosene has been investigated by Ramakul et al. The selective extraction of yttrium is thought to be due to the decrease in equilibrium constant with an increase in atomic number or decreases with the ionic radius of the lanthanides.¹⁷⁴ The use of other membranes including hinokitiol (4-Isopropyltropolone) and flavonol (3-hydroxy-2-phenylchromen-4-one)¹⁷⁵ and carriers including calix[4]arene,^{176, 177} 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA),^{88, 178, 179} crown ether carboxylic acids,⁶³ PC-88A,¹⁸⁰ di(2,4,4-trimethylpentyl)phosphinic acid,¹⁸¹ diethylenetriaminepentaacetic acid,¹⁸² *N,N,N',N'*-tetraoctyl diglycolamide (TODGA), *N,N*-di-*n*-hexyl

octanamide (DHOA),¹⁸³ Cyanex-301 (bis(2,4,4-trimethyl pentyl)dithiophosphinic acid)¹⁸⁴ for the transport and separation of RE have also been reported to exhibit remarkable RE extraction coefficients.

Case Studies

Industrial RE extractions from host minerals

Molycorp is an American mining co-operation. Their process of europium extraction has been described by Gupta and Krishnamurthy. Calcination and leaching with HCl result in a RE chloride solution. 10% v/v D2EHPA in kerosene is used in the extraction at five different mixer and settler stages to obtain a raffinate of Nd with the LREE and Sm and the HREE in the organic phase. Further treatment of the raffinate with the extractant and precipitation with ammonium and hydrogen sulfide results in 98% extraction of europium. The extracted europium can then be stripped by addition of 4 mol/L HCl. Neutralisation to pH 3.5 precipitates the iron impurities. Further rounds of treatment of the europium solution with other HREE with 10% D2EHPA is required to separate the LREE. The europium is extracted along with other HREE while the remaining LREE remains in the raffinate. After stripping europium and the other RE, the europium(III) strip liquor is reduced to europium(II) which is then precipitated out as europium sulfate and calcined to europium oxide.¹⁸⁵

AS Megon is a mining company whose process for yttrium extraction has been described by Gaudernack.¹⁸⁶ Xenotime processing involves extraction of yttrium from concentrates of xenotime. Solvent extraction cycles with D2EHPA, scrubbing and stripping results in La, Ce, Pr and Nd and impurities which include Fe^{2+} in the raffinate. Selective washing results in the separation of the yttrium mixture into three groups. Tri-capryl methylamine is used as an extractant in the second yttrium extraction stage. The LREE contained therein are extracted while Y, Tm, Yb and Lu remains in the raffinate. A third stage involves the use of tri-capryl methylamine- NH_4SCN to produce high purity yttrium oxide.¹⁸⁶

A Monazite processing plant in Yue Long Chemical Plant in Shanghai, China uses an adaptation of the Rhône-Poulenc (Rhodia Solvay Group) process. Monazites have high contents of HREE. Therefore acidic extractants are preferable as HREE have high affinity for acidic extractants. The monazite is digested in NaOH, filtered and leached with HCl. D2EHPA is used to extract the chloride solution. The extracted RE are split into three groups to produce carbonate, chlorides and oxides. Cation exchangers such as HEHP and naphthenic acid are typically used in extraction of RE from the HCl or H_2SO_4 leachates. Controlled stripping results in individual RE oxides or chlorides.^{67, 68}

Industrial Recycling of Rare Earths

Opening/expansion of RE mines and recycling of REs from RE-containing EoL products, industrial pre-consumer scrap and industrial residues have been suggested as a ways of possibly mitigating the risk to REs supply. To this end, mining from old, new or reopened RE deposits including Mountain Pass Mine in California have been explored.¹⁸⁷ However, there is a question of whether these mines can compete with cheaper Chinese REs (one of the reasons some of these mines were shut down in the first place) and how long these mines will remain in operation as Mountain Pass Mine recently shut-down. Obviously, alleviating china's dominance over RE through opening of mines in other countries is not working as expected. Recycling of RE is therefore another viable alternative to Chinese REs that could be explored.

However, less than 1% of rare earths are being recycled commercially despite the vast amount of literature on (Lab scale) RE recycling.^{12, 13} Binnemans et al. has extensively reviewed the recycling of REs from RE permanent magnets, nickel metal-hydride batteries, lamp phosphors, glass polishing power, CRT phosphors, fluid cracking catalysts and optical glass in small and large scale.¹⁴ On a commercial scale, there is a lot of talk amongst manufacturers such as Honda, Mitsubishi Electric, Umicore, Japan Metals & Chemicals (JMC)

etc. to recycle REs from NiMH batteries, air conditioning units, waste lamps etc., although the exact recycling process is unreported in a lot of cases.

Umicore's NiMH batteries recycling operations include NiMH and Li-ion batteries. The batteries go in through a vertical shaft furnace, along with a small amount of coke and a slag former. Oxygen is injected at the bottom of the shaft furnace. The metals form alloys of Ni-Co-Cu-Fe and a slag which consists mainly of oxides of Ca, Al, Si, and Fe, and also contains Li and the rare earths.¹⁸⁸ Li as well as rare-earth concentrates can then be recovered from these oxide slags.^{189, 190}

Hitachi has developed a technology for commercial scale recycling of rare earth magnet from HDDs and air conditioner compressors.¹⁹¹ The HDD dismantler removes voice coil motors (VCMs) from the HDDs. The VCMs disassembled by the HDD dismantler are then demagnetized in an electric furnace, but the external yoke and rare-earth magnets that make up the VCM remain joined by a carbonized adhesive. The magnet recovery machine then separates the rare-earth magnets from the yoke, using a machine for performing the process. Recycling of RE magnet in air conditioners involves the use of a mechanical unit for cutting open the casing, a rotor removal machine that extracts the rotor from the motor, a demagnetizer that operates at room temperature using resonance damping demagnetization, and a magnet removal machine with a drop impact mechanism.

The actual separation RE from waste magnet is a much more complicated process. Ames Laboratory have developed and received commercial licensing for its RE magnet recycling technology. In principle, REs, particularly neodymium are very soluble in magnesium while the other components of magnets, like iron and boron are poorly soluble in magnesium.¹⁹² The process involves melting and dissolving neodymium with molten magnesium leaving behind the other components of magnets, like iron and boron which are less soluble. Sintered, uncoated magnets that contain neodymium, praseodymium and dysprosium are broken up using an automated mortar and pestle until the pieces are 2-4 mm long. The tiny magnet pieces go into a mesh screen box, which is placed in a stainless-steel crucible. Technicians then add chunks of solid magnesium. A radio frequency furnace heats the material. The magnesium begins to melt, while the magnet chunks remain solid. Rare-earth magnet scraps are then melted in a furnace with magnesium. All three rare earths leave the magnetic material by diffusion and enter the molten magnesium. The iron and boron that made up the original magnet are left behind. The molten magnesium and rare-earth mixture is cast into an ingot and cooled. Then the magnesium is boiled off leaving just the rare earth materials behind.^{192, 193}

Conclusion

As innovation tends towards clean and renewable technology, it will become more imperative that sourcing of materials necessary for this purpose needs to be from green and efficient processes. More so, ease of access to RE is vital to sustain the growth of renewable technologies as the subject of future supply is met with a lot of uncertainty.

Efficient extraction of RE from their host minerals and e-wastes has been discussed. All of the methods discussed in this paper have seen major optimisation and some of which are now being applied on industrial scale in extraction facilities. Researchers seek to find a good balance between the environmentally friendly and efficiency in their extraction technique. However, the concentrated acids used in leaching can be environmentally expensive. An efficient recycling, neutralisation or disposal of the acid waste is vital. Solvent extraction has made significant advances but still retains its limitations such as contamination of the aqueous phase by the extractants. Supercritical fluids, ionic liquids, ion exchange and membrane extractions hold promise of greener methods. A hybrid of techniques could be the future of extraction as it has been shown to be effective and environmentally benign. Extractant that have been proven in solvent extraction can be used in other techniques such as IL, scCO₂, and membrane in order to eliminate the need for organic solvent. Solvent extractants and IL can also be used in liquid membranes and resins thereby encouraging facile recover and reuse.

There is a need to translate the success of lab scale RE extraction to commercial scales RE extraction from RE containing e-wastes to meet the growing need for RE. Commercial scale RE extraction from mineral ores using proven extraction methods have been efficacious. Similar success can be expected if applied to RE recycling from e-waste.

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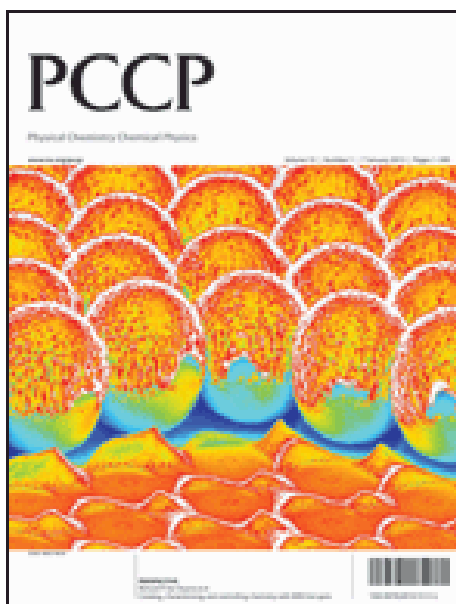


Harrison Omorodion, from Nigeria, graduated with an Honours BSc. degree in Medicinal Chemistry from University College Dublin (UCD) in 2013. He moved in 2013 to Trinity College Dublin, (TCD) for his PhD working under the supervision of Professor Robert J. Baker. His PhD research is based on New Approach to WEEE recycling of rare earths and platinum group metals and is funded by the Environmental Protection Agency (EPA).



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There Has Never Been a Better Time to Collaborate with Universities

John Scanlan, Maynooth University Director of Commercialisation

Up until about 15 years ago, universities understood their contribution to the knowledge economy as mainly confined to teaching with limited and poorly funded research activity. Top level, highly qualified graduates were streamed from our institutions into the jobs market and formed a talent pool that represented one of the great draws of Foreign Direct Investment into Ireland. This contribution was widely feted. With the establishment of Science Foundation Ireland in 2003, a much stronger focus on research emerged and funding for basic science grew dramatically. In the last number of years, and particularly since the publication of the Innovation Taskforce Report in 2010, and more recently the Innovation 2020 Report, the role of universities has been re-evaluated in terms of how this investment in research can impact our economy.

The Innovation Taskforce Report outlined a new strategy for investing in research to drive economic growth and foster a culture of collaboration between companies, entrepreneurs and academics. This coincided with a widespread growth in confidence amongst business leaders in the value of investing in research: between 2008 and 2013, industry investment in R&D grew by 31% to just over €2 billion.

The growing desire of universities to support national policy and work with entrepreneurs and companies to commercialise research has resulted in significant changes in the profiles and activities of Irish universities. This represents a huge opportunity for companies that are willing and able to engage with the sector. Not only can they leverage the broad range of supports offered by universities to access world-class expertise and state-of-the-art services and facilities, but they can also avail of significant funding supports from Enterprise Ireland, Science Foundation Ireland, and the EU. The much talked about “Knowledge Development Box” that will guarantee a favourable tax rate for income generated through R&D investment only serves to make the proposition more attractive.

Furthermore, entrepreneurs and companies can benefit from a shift in intellectual property management and dissemination making it very favourable to industry. The National Intellectual Property Protocol published in 2012 called for universities to avoid retaining exclusive control of intellectual property rights. It put the infrastructure in place to make it easy for businesses to exploit and commercialise discoveries. The establishment of Knowledge Transfer Ireland (KTI) has made it even simpler to for entrepreneurs and companies to utilise this system. KTI gives prospective collaborators access to lists available expertise at all Irish universities, “how-to” guidelines, and model intellectual property agreements.

Maynooth University recently hosted its biennial knowledge transfer demonstration event, *Connect 2016*. This event included clinics outlining how companies can navigate this national system to optimise their benefits and hear the stories of companies who have succeeded through doing so. Guest speakers included University collaborators *Sigmoid Pharma* which develops new therapies for immunological and gastrointestinal diseases and *Treemetrics*, a company focused on forest management.

The upshot of all this is that there has never been a better time for entrepreneurs to work directly with universities. Research collaboration, consultancy, use of facilities and equipment, engagement with the undergraduate and postgraduate student pool all provide opportunities for companies at various stages of development and growth.

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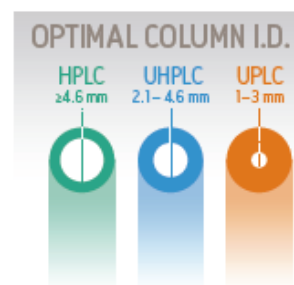
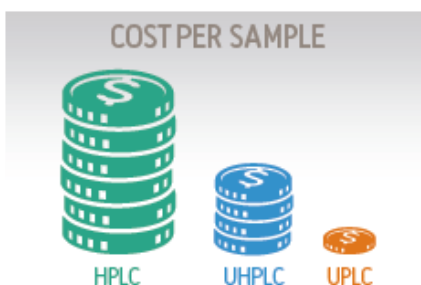
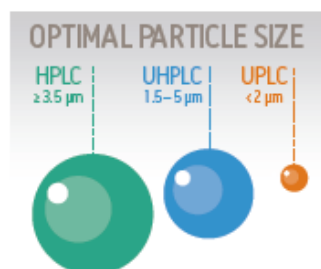
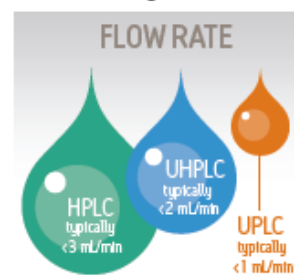
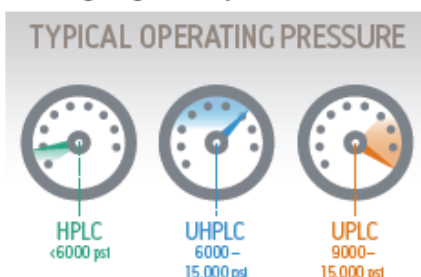
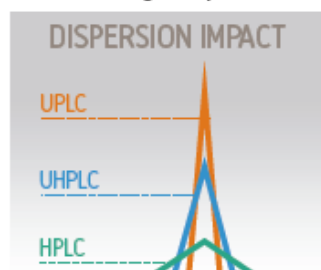


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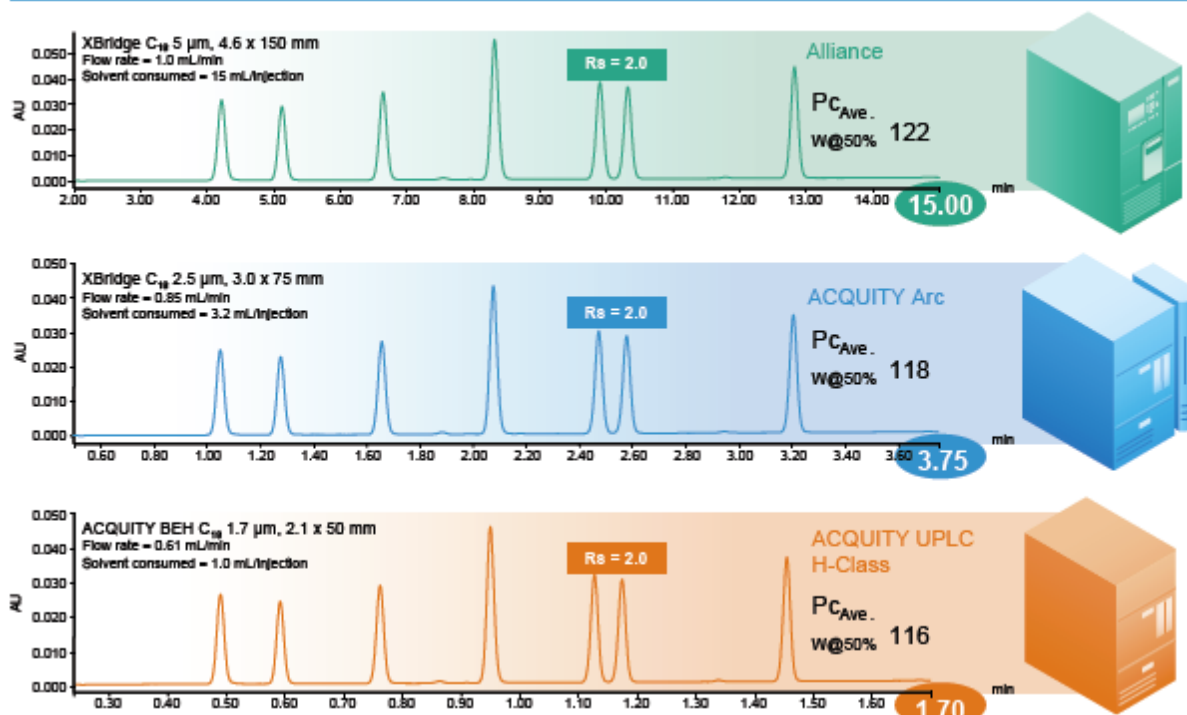
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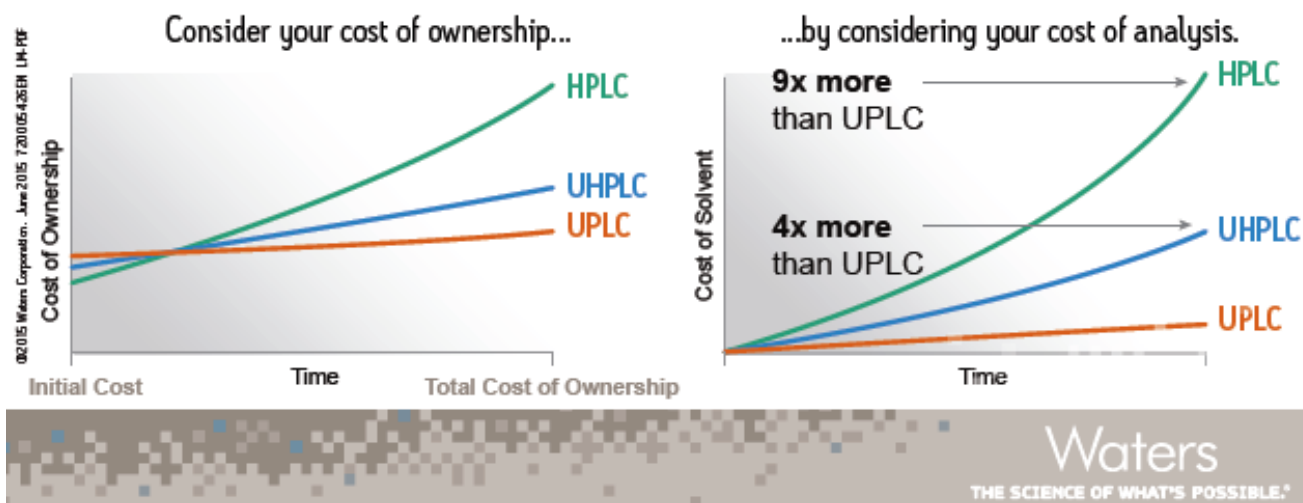
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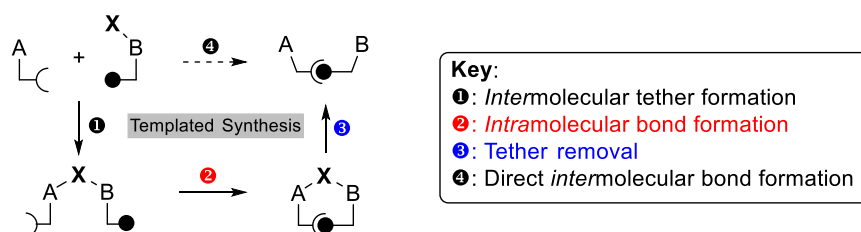
Templated Synthesis of Cyclic Sulfonamides and Applications in the Synthesis of Aryl-substituted Nitrogen Heterocycles

Kimberly Geoghegan and Paul Evans

School of Chemistry and Chemical Biology, University College Dublin

Introduction

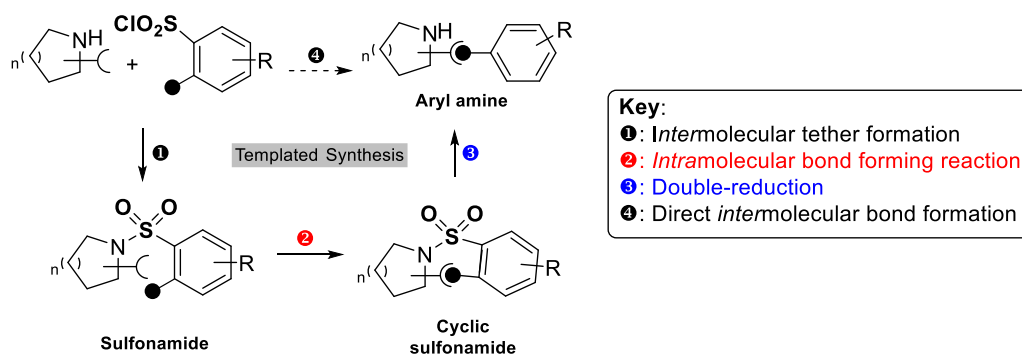
The concept of using a pre-organising template, or tethering group in a synthetic sequence is outlined in Scheme 1.¹ The tether or organising element, **X**, coupled to both A and B (Step 1), essentially brings the two fragments into close proximity to each other, facilitating their coupling. Thereafter, an intramolecular bond formation reaction occurs producing a cyclic compound (Step 2). Finally, removal of the organising element, **X**, leads to the ultimate coupled compound (Step 3). This templated synthetic strategy has several potential advantages compared to the direct intermolecular bond formation, which may not proceed in the same fashion in the absence of the tether (Step 4).



Scheme 1. Templated Synthesis Utilising Tether **X**.

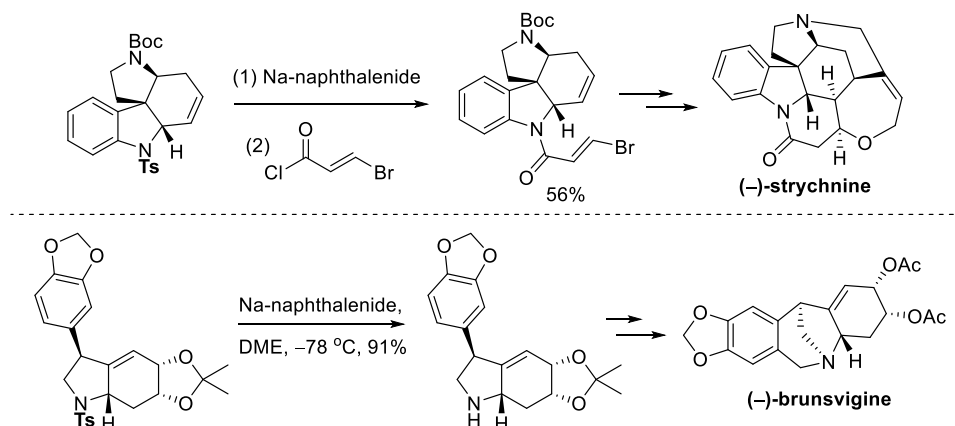
Cyclic Sulfonamides

For several years we have studied the synthesis of cyclic sulfonamides and have investigated their reactivity under reductive conditions. Our central concept in relation to the templated synthesis strategy was to use a sulfonyl group ($-\text{SO}_2-$) as the tether, represented by **X** in Scheme 1. We envisaged that the *sulfonyl tether* would perform three tasks: Firstly, it would protect the nitrogen atom, effectively removing its basicity, nucleophilicity and ability to coordinate to metal atoms. Secondly, the robust sulfonamide functionality would serve as a unit that could facilitate an intramolecular bond forming event. Finally, reductive excision of the sulfonyl tether (**X**), whereby both S-N and C-S bonds (coined double-reduction) are reductively cleaved, would provide a functionalised amine (Scheme 2). It is perhaps noteworthy to point out that sulfonamides are typically air and bench stable crystalline materials, properties which make for easy handling!



Scheme 2. The use of a sulfonamide as a temporary tether: Combining *N*-protection and arylation.

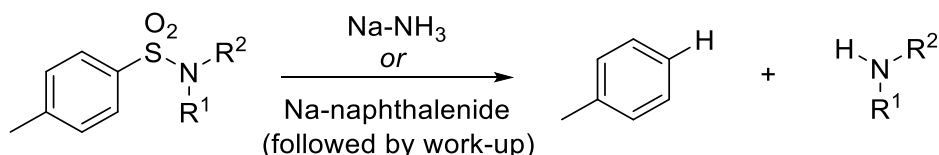
The literature contains a plethora of examples in which sulfonyl halides (usually chlorides) react with amines to form sulfonamides (Step 1). Numerous examples and strategies also exist for cyclising acyclic sulfonamides into their cyclic sulfonamide congeners – also known as sultams (Step 2).² A variety of reductive methods exist for the cleavage of sulfonamides (Step 3),³ allowing them to be routinely employed as nitrogen protecting groups in organic synthesis (Scheme 3).



Scheme 3. Examples of sulfonamides as protecting groups in total synthesis. Ts = Tosyl.

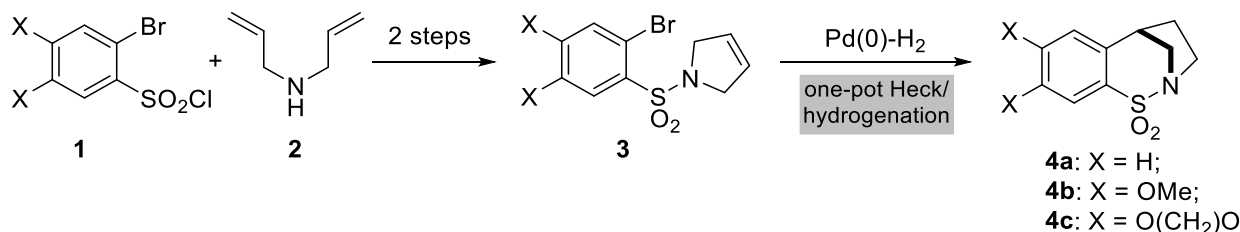
Double-Reduction of Cyclic Sulfonamides

Typically, however, the fate of the C-S bond in the type of process outlined in Scheme 3 is immaterial, since, in a typical *N*-deprotection strategy, such as the examples selected in Scheme 3, the nitrogen fragment is the molecule of interest.⁴ However, there are two reports suggesting that, for simple sulfonamide-containing compounds, under reductive conditions, *both* the N-S and C-S bonds undergo cleavage (Scheme 4),⁵ coined by us as the *double-reduction* of sulfonamides. These findings served as the basis for our templated synthesis strategy depicted in Scheme 2. To demonstrate if we could truly apply this sulfonamide tether approach as a means of intramolecularly transposing an R-group to our amine moiety (Step 2) and thereafter extrusion of “SO₂” (double-reduction) affording substituted amines, the Evans lab investigated the preparation of suitable, and more elaborate amine substrates - namely cyclic sulfonamides (cyclic sultams).



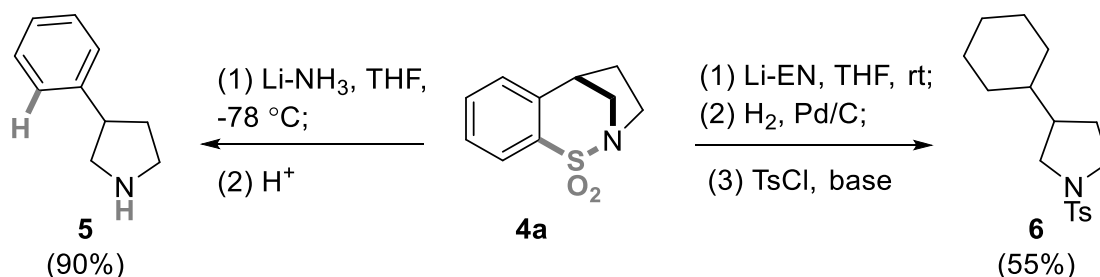
Scheme 4. Toluene formation from *N*-tosyl-based sulfonamides.

Initial studies employed the Intramolecular Heck Reaction (IHR) to form the cyclic sulfonamide (see Scheme 5).⁶ The Heck precursors can be rapidly accessed *via* coupling of sulfonyl chloride **1** with an appropriate amine **2** (Step 1, Scheme 2). Ring closing metathesis was then utilised to generate *N*-sulfonyl dihydropyrroles of the type **3**.⁷ This sequence enabled the preparation of a range of dihydropyrroles **3**, in which the substituent X was varied. A key step in this overall strategy was then the execution of an intramolecular Heck reaction of the family of sulfonamides **3** (Step 2, Scheme 2). This process, as applied to cyclic sulfonamide synthesis, has been studied in depth by our group. The alkene product resulting from the initial IHR must be hydrogenated to provide saturated sulfonamides of the type **4**. For this purpose we developed a one-pot Heck-hydrogenation protocol, whereby the Pd(0)-catalyst used for the cyclisation was re-used, *in-situ*, to mediate the hydrogenation of the alkene. This type of assisted tandem reaction was achieved simply by switching the atmosphere to H₂.⁸ Thus using this sequence substrates (**4**) required for the proposed double-reduction study were rapidly accessed.



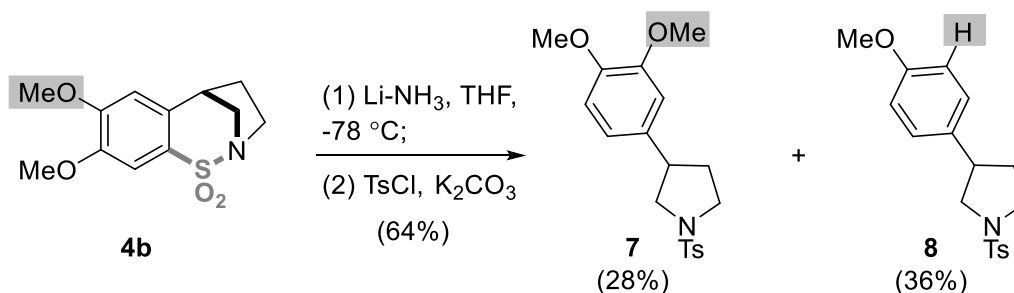
Scheme 5. Intramolecular Heck-based synthesis of cyclic sulfonamides.

Pleasingly, treatment of these benzo-fused cyclic sulfonamides (**4**) under standard desotylation conditions, sodium, or lithium-ammonia at -78°C , led to the isolation of 3-substituted pyrrolidines of the type **5-8** (Schemes 6 and 7).^{6b} For example, **4a** underwent conversion into **5** in a rapid process that involved at least 4 equiv. of the alkali metal and without an acidic additive (eg. *t*-BuOH) no Birch-type reduction was observed. In contrast, use of the more powerful reductant combination: Li in ethylene diamine (EN), termed Benkeser's conditions, led to dearomatisation in conjunction with sulfonamide double reduction. The 3-cyclohexylpyrrolidine **6** can be thus isolated in reasonable yield.



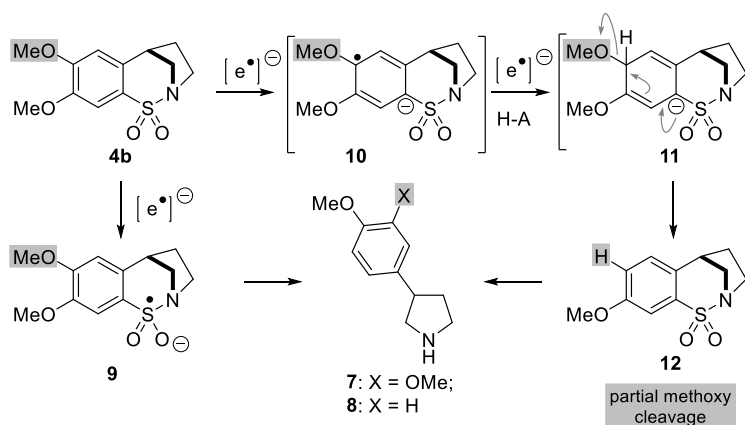
Scheme 6. Double reduction of cyclic sulfonamides. Ts = Tosyl.

Interestingly, when dimethoxy-substituted sulfonamide **4b** is treated under the reductive conditions the anticipated dimethoxy-pyrrolidine **7** formed along with the unexpected product **8**, resulting from a regioselective methoxy cleavage.⁹ These compounds were formed in approximately a 1:1 ratio (Scheme 7).



Scheme 7. Regioselective partial methoxy cleavage of **4b**. Ts = Tosyl.

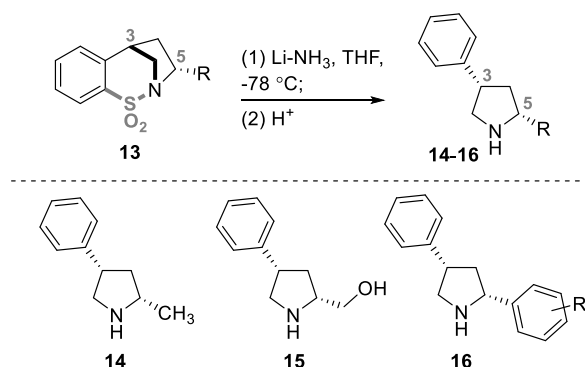
In the light of the findings described above some hypotheses concerning the reaction mechanism for the double reduction can be made (Scheme 8). Single electron transfer to **4b** is expected to generate radical anions of the type **9** and **10**. In the case of the former N-S bond cleavage would be expected to generate an aminyl radical and a sulfinate. Further reduction would lead to the dimethoxy-aryl substituted pyrrolidine **7**. In contrast, it seems plausible that the Birch-type radical anion **10** provides a means for methoxide elimination, *via* intermediate **11** and thus the ultimate formation of **8** may be understood.



Scheme 8. Possible competing pathways for the formation of **7** and **8**.

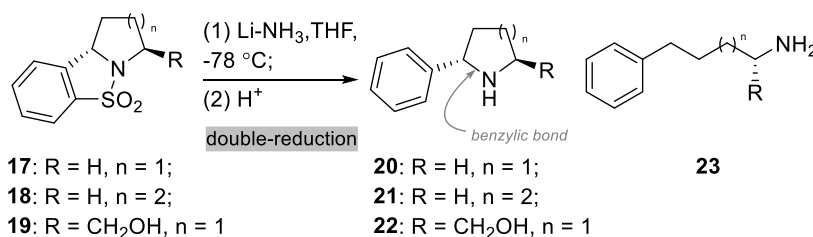
In the future additional work is planned to attempt to elucidate and better understand these possible pathways. In relation to this endeavour we briefly investigated the use of an alternative reductive method and employed sodium naphthalenide under aprotic conditions. In this instance only dimethoxy-substituted compound **7** was isolated, albeit, in poor chemical yield (25%).

Alternative cyclic sulfonamide substrates were next prepared using the IHR-based tactic and as Scheme 9 depicts the use of the sulfonyl moiety as a nitrogen protecting group and as a *disposable tether*, was used to access a number of 3-aryl-5-substituted pyrrolidines (eg. **14-16**), some examples of which are enantiomerically pure.



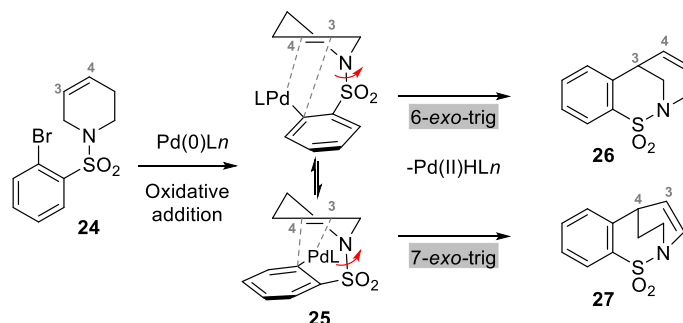
Scheme 9. Double reduction of substituted benzo-fused cyclic sulfonamides.

2-Phenyl pyrrolidines and piperidines can be similarly assembled (Scheme 10). One aspect concerning this type of product is that the secondary amine products possess a benzylic bond and it was noted that if a large excess of reductant was employed the reduction of the benzylic bond took place (*i.e.* forming **23**). Fortunately by controlling the amount of reductant (4 equiv.), good yields of the hoped for cyclic amines were achieved. Use of pyroglutamic acid derived starting materials led to the formation of optically active products.



Scheme 10. Synthesis of 2-Phenyl pyrrolidines and piperidines.

Next we investigated Δ^3 -piperidines (**24**) and as described in previous literature¹¹ no regioselectivity could be achieved in the IHR (Scheme 11). The resultant adducts, **26** and **27**, stemming from C-C bond formation at both C-3 and C-4, were formed in approximately equal amounts and proved inseparable by recrystallization and chromatography. In this example clearly both modes of cyclisation occur competitively and under the reaction conditions the difference in energies between reactive conformers (**25**) are not significant enough to obtain selectively.



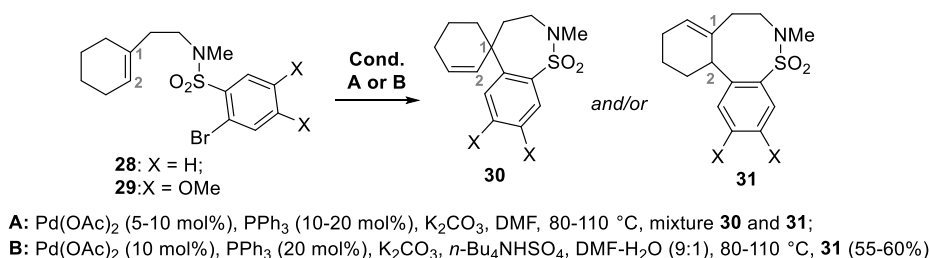
Scheme 11. Non-regioselective Intramolecular Heck Reaction of **24**.

Although this outcome proved synthetically not useful, thoughts concerning the lack of selectivity spurred further research into the regiochemical outcomes of the type of intramolecular, cyclic sulfonamide generating Heck reaction.

Regioselectivity in the Intramolecular Heck Reaction

It is well-appreciated that electronic and steric factors govern the outcome of Heck reactions and for intermolecular reactions C-C bond formation typically occurs at the more electrophilic carbon and the less hindered carbon (although alteration of reaction conditions can influence these preferences).¹⁰ These factors, unsurprisingly, also influence the outcome of intramolecular Heck reactions. However, results clearly indicate that for reactions in which new cycles are formed it is size of the newly formed ring that is the crucial in determining the regiochemistry observed and Baldwin's rules and nomenclature are often applied to describe reaction outcomes (see Scheme 11 for example). The significance of the ring size in governing the process can be traced back to how efficiently the sp^2 hybridised C-Pd bond can align with the alkene leading to alkene insertion (carbopalladation). Clearly the conformational constraints placed on the system by the atoms linking the reactive centres influence this event. It should be noted that current consensus is that the alkene insertion is irreversible.

Following on from Scheme 11 in which the size of the ring and the *exo/endo* mode of ring closure may control isomer distribution, the monosubstituted alkenes **28** and **29** were prepared and separately subjected to a range of reaction conditions.¹²

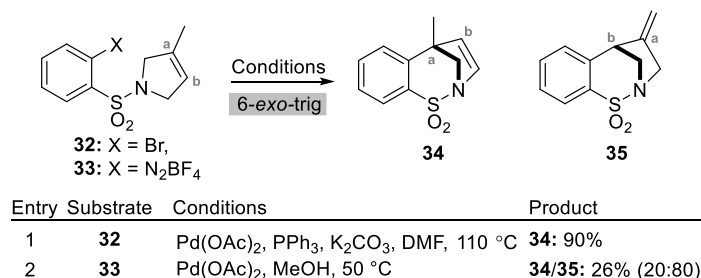


Scheme 12. Reagent controlled regioselectivity in the IHR of sulfonamides **28** and **29**.

Roughly equivalent results were obtained for both substrates **28** and **29**. A mixture of spiro-cyclic **30** and bicyclic **31** were isolated when standard Heck conditions were employed (Conditions A). However, when

Genêt's adaptation of Jeffery's conditions (Conditions **B**) was utilized, the reaction provided exclusively **31**, demonstrating, in this case, reagent controlled regioselectivity.

In another process where one might anticipate poor regioselectivity, methyl substituted pyrrolidine based Heck precursors, e.g. **32**, were studied.^{13, 14} This type of unsymmetrically substituted alkene substrate is fundamentally different from the examples shown in Schemes 11 and 12 since cyclisation can only proceed in this instance *via* a 6-*exo*-trig mode. We felt that it would be interesting to observe what effect a substituent on the alkene has on the regioselectivity of the IHR for these tethered substrates.

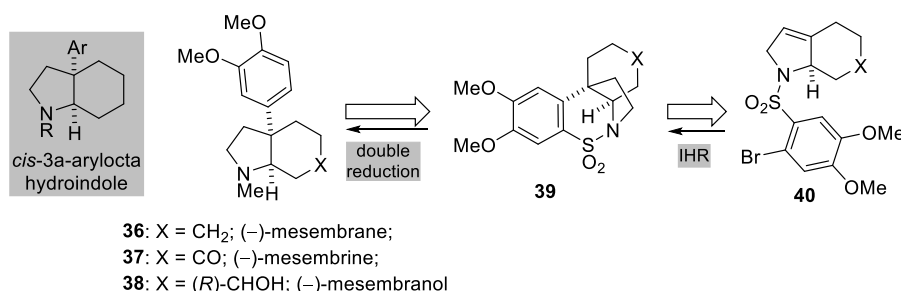


Scheme 13. Substituted alkenes in the IHR.

Under standard Heck conditions (Entry 1, Scheme 13), **32** regioselectively cyclises to provide the all-carbon quaternary isomer **34**, with only trace amounts of regioisomer **35** detected by proton NMR spectroscopy. A study was carried out to identify conditions that would successfully influence regioselectivity, or indeed overturn this inherent regioselectivity completely. An extensive screening of catalysts, ligands, solvents, bases, temperature and time, and also use of different halides or *pseudo*-halides, proved unsuccessful, demonstrating a significant bias for the formation of **34**. However, the most promising result is outlined in Scheme 13, Entry 2. A Matsuda-Heck cyclisation of diazonium salt **33** afforded a mixture of **34/35**, with the previously elusive tertiary compound **35** as the major isomer, albeit in a poor 26% isolated yield (the majority of the mass balance was the *N*-phenylsulfonyl pyrrole). While this is a promising result, the material is not sufficient for synthetic use and sparks further investigation and optimisation (these ideas are revisited in Schemes 15 to 17 below).

Templated Synthesis of Natural Products

The combination of the highly regioselective Heck reaction followed by a double-reduction provided a potential strategy for the preparation of aryl-substituted bicyclic *N*-heterocycles.¹⁵ Our particular interest concerned the preparation of a class of bioactive nitrogen compounds (*Sceletium* alkaloids) in which the application of the templated cyclic sulfonamide strategy would access the core *cis*-3a-aryloctahydroindole skeleton. Scheme 14 summarises key steps in our syntheses of the alkaloids: (±)-mesembrane **36**¹³ and (+)-mesembrine **37** and (+)-mesembranol **38**.¹⁶



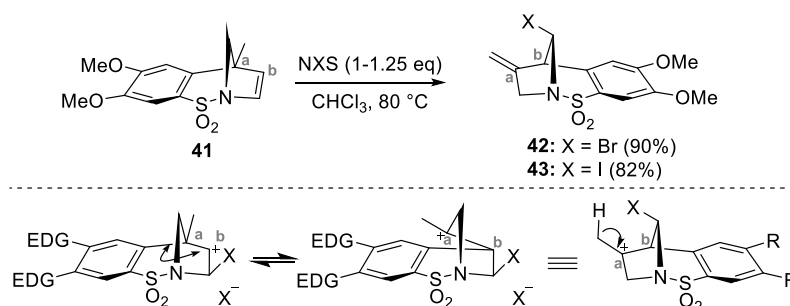
Scheme 14. Retrosynthetic schematic for *Sceletium* alkaloids synthesis.

There are a few points of interest that occur during the IHR in this sequence. Again, substrates of the type **40** display high regioselectivity in the formation of the required quaternary centre, **39**. Of equal importance

is that the new C-C bond formation event occurs on the same side as the methine adjacent to the nitrogen atom making this reaction highly diastereoselective. These features are key for accessing the correct relative stereochemistry in the final products. The application of the templated sequence, combining the IHR with the double reduction, proved a reliable method for the preparation of substituted saturated N-heterocycles.¹⁷ Of particular interest is access to material for the *unnatural* enantiomer of mesembrine **37**, whose biological evaluation would be interesting for future documentation.

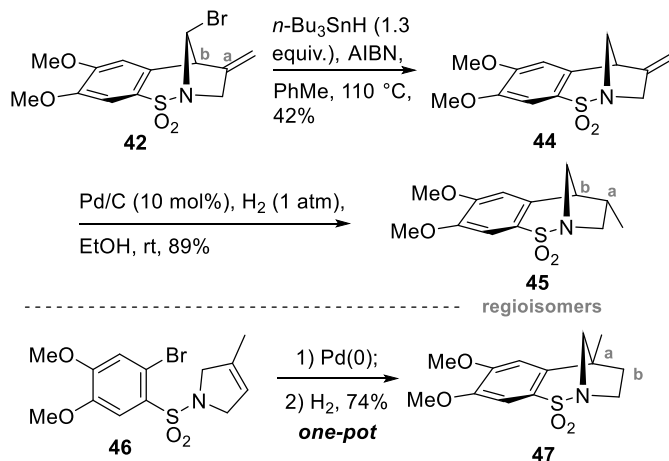
Halonium-Mediated Rearrangement

As described in Schemes 13 and 14 the regiochemical outcome of the intramolecular Heck reaction on sulfonamide precursors is selective for the formation of a quaternary centre from an unbiased system in terms of the size of the newly formed ring. Unsuccessful in identifying Heck conditions that would overturn this inherent regioselectivity (see Scheme 13) we recognised an alternative opportunity to access regioisomeric material. Based on reports by Paquette¹⁸ and Evans^{7, 19} a halonium ion-mediated rearrangement (Wagner-Meerwein type rearrangement) could be evoked on Heck products of the type **41** and would, after *walking* of the benzylic carbon to carbon b (Scheme 15), provide **42/43** - the halogen containing regioisomer of the major product of IHR.



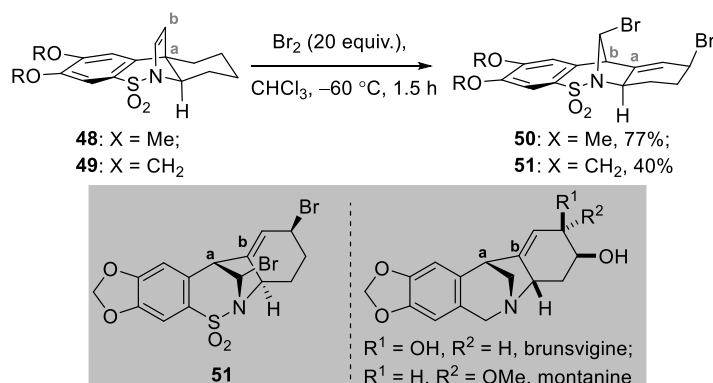
Scheme 15. Wagner-Meerwein rearrangement of **41**.

Heating a chloroform solution of alkene **41** with a halide source provided the rearranged products in excellent yields. The best sources of halides were found to be the succinimides (NBS and NIS). No conversion was observed using *N*-chlorosuccinimide. The electron-donating groups on the aromatic ring greatly accelerate this rearrangement, and ‘unactivated’ substrates give no conversion. The products from the Wagner-Meerwein rearrangement contain an alkyl halide, which is a synthetically useful functional group. However, for our studies we transformed **42** into **45**, the alkene reduced regioisomer of **47** which can be directly obtained from the IHR sequence (Scheme 16).



Scheme 16. Accessing regioisomer **45** from **42**.

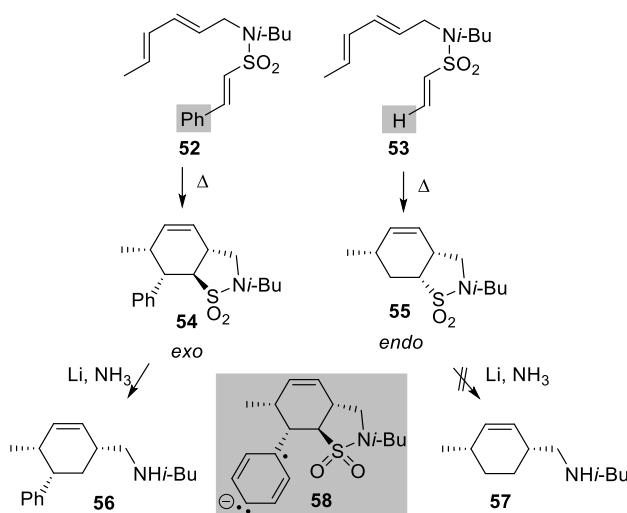
In terms of a potential application, the tricyclic core within compound **51** is found in a variety of naturally occurring alkaloids, and, in particular, could be applied in conjunction with the double reduction to the synthesis of the montanine alkaloids²⁰ (Scheme 17).



Scheme 17. Accessing regioisomer **51** from the halonium-based rearrangement of IHR product **49**.

Conclusions and Future Work

Currently, we are screening a variety of alternative reduction conditions (eg. Mg-MeOH, RaNi etc.). In order to see if a protocol can be developed which avoids the use of liquid ammonia. Additionally, we aim to probe and uncover whether the sulfonamide must be aromatic in order for the double reduction to occur. This will shed light on mechanistic aspects (Scheme 8). As Scheme 18 indicates we have initiated investigations in this area. Diels-Alder cycloaddition of trienes **52** and **53** gave bicyclics **54** and **55**.²¹ In both instances a mixture of adducts resulting from a formal *endo* and *exo*-cycloaddition were observed. In the case of styryl sulfonamide **52** (R = Ph) predominantly the *exo*-adduct **54** was isolated. Conversely, in the case of vinylic sulfonamide **53** diastereoselectivity favoured the *endo* adduct **55**.



Scheme 18. Synthesis of cyclic sulfonamides via an intramolecular Diels-Alder reaction and behaviour of the adducts under reductive conditions.

Treatment of both adducts with the dissolved metal reductions conditions successfully used in the previous studies (see above) led to interesting results. Aromatic adduct **54** did indeed undergo clean double reduction and secondary amine **56** could be isolated in good yield (75-90%). In contrast, **55**, under identical conditions, was resistant to double reduction and only starting material was recovered. We speculate that this difference stems from the proximal aromatic group and that the Birch-type intermediate **58**, reversibly formed, serves as the source of electrons for the double reduction.

Acknowledgments

We would like to thank the NUI for the provision of a travelling studentship (Dr. Kimberly Geoghegan). The contributions from Dr. Susan Gaffney (née Kelleher), Dr. Johannes Klein, who worked on their PhD and MSc respectively in this area, are acknowledged. Additionally, numerous visiting and undergraduate project students also contributed, helping us to better understand this topic. We would like to acknowledge our collaborators Prof. Isabel Rozas (Trinity College Dublin, Ireland) and Prof. Ibon Alkorta (Instituto de Quimica Medica (IQM-CSIC), Spain). Dr. Helge Müller-Bunz is thanked for his efforts in solving numerous X-ray crystallographic structures for many of our nicely crystalline sulfonamides. The support from UCD and the various Heads of School over the years is gratefully acknowledged. And finally, this is an opportunity to sincerely thank all current and previous postgraduate students who enthusiastically and skilfully worked on the sometimes crazy ideas I suggested, mostly with smiles on their faces – I am very grateful to you all! They are as follows: Patricia Duffy, Yvonne Kavanagh, Susan Kelleher, Maciej Stefanko, Noel McLaughlin, Aisling O’Byrne, Johannes Klein, Elizabeth Dunny, Niamh Murphy, Kimberly Geoghegan, Eimile Sheehy, William Doherty, Shaun Smullen, Raed Zaidan, Aaron Keeley, Brian Leavau and Aisha Khalifa.



Paul Evans graduated with a B.Sc. in Chemistry (1994) from the University of East Anglia. Following that he undertook a D.Phil. (1998) with Prof. Richard Taylor working on sulfone chemistry, specifically the Ramberg-Bäcklund reaction. Paul then worked as a Postdoctoral Research Associate, firstly with Prof. Ron Grigg in Leeds, and then Prof. Jim Thomas in Manchester before moving in 2001 to University of Liverpool to begin his independent research. In 2003, Paul moved to Trinity College Dublin taking a Lectureship in Organic and Medicinal Chemistry. Then in 2006, Paul and his research group moved to University College Dublin, where he is currently Senior Lecturer in Organic Chemistry.



Kimberly Geoghegan, a native-born Dubliner, graduated from University College Dublin (UCD) with a B.Sc. in Chemistry in 2009. She continued on in UCD, joining the research group of Dr. Paul Evans. Kimberly was awarded a National University of Ireland (NUI) Travelling Studentship to undertake her doctoral studies on the regioselective Heck reaction and its applications in the synthesis of natural products, and graduated in 2013. Thereafter, Kimberly travelled to Switzerland and joined the research group of Prof. Jeffrey W. Bode at ETH Zürich, where she developed a new class of ‘SnAP’ reagents, specifically for the synthesis of spirocyclic and bicyclic scaffolds towards drug discovery. In September 2015, Kimberly joined the fragrance division of Givaudan as a Process Research Scientist.

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MASTER CLASS: PROCESS DEVELOPMENT & SCALE UP IN THE PHARMACEUTICAL INDUSTRY

MODULE CH510
SCHOOL OF CHEMISTRY, NUI GALWAY
21st and 22nd April 2016

As part of their structured PhD programme, the School of Chemistry in NUI Galway, in association with the Synthesis and Solid State Pharmaceutical Centre (SSPC) in the University of Limerick, are providing a 2-day course on the development and scale-up of organic syntheses for the commercial manufacture of drug substances. The course will be run immediately before the 2014 Irish Universities Chemistry PhD colloquium, which is being held in NUI Galway on June 19 and 20. The course will:

- Be delivered by expert industrial practitioners
- Focus on synthetic processes for "small molecule" drugs and address the organic, physical and analytical chemistry involved.
- Cover process selection and development, technology transfer and on-going optimisation with reference to the safety, environmental, engineering, quality and regulatory disciplines involved.
- Use real examples to illustrate the subject

The course is aimed at:

- PhD students in chemistry and related disciplines. On completion of associated assignments the course is valued at 5 ECTS credits.

There will be a fee for non-NUIG attendees of €100. More information is available on the NUI Galway, School of Chemistry website.

REGISTER NOW @

<https://www.eventbrite.ie/e/master-class-in-process-development-and-scale-up-tickets-21459944271>

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Winners announced for SSPC National Crystal Growing Competition at the University of Limerick

“Crystals come in all different shapes and sizes and can be found everywhere in nature. Most of the medicines we take are made up of compacted powders and the individual particles of the powders are in fact tiny crystals.” Prof Kieran Hodnett, SSPC Scientific Director.

Following the great success of the 2014 SSPC National Crystal Growing Competition, which was launched as part of Science Week to celebrate the International Year of Crystallography 2014, the Synthesis and Solid State Pharmaceutical Centre (SSPC), announced the winners of the 2015 SSPC National Crystal Growing Competition at the University of Limerick on Friday, March 4th, 2016. The competition was open to primary and post-primary schools in Ireland and aimed at students who were challenged to grow a single crystal from a variety of compounds such as: Salt (Sodium Chloride), Alum, Sugar, or Copper Sulphate.

Professor Kieran Hodnett, SSPC Scientific Director said:

“The SSPC National Crystal Growing Competition is of significant importance as not only has it enabled students to grow their own crystals, but it has also increased students’ awareness and understanding of the importance of crystals in our lives today.”

At the award ceremony, Professor Michael Zaworotko, SSPC collaborator and University of Limerick's Bernal Chair of Crystal Engineering, announced the winners of the SSPC National Crystal Growing Competition. First place prizes were awarded to Aoife Ryan, Coláiste Bhaile Chláir, Galway and Keat's 5th class from Scoil Ide primary school, Limerick. Second runner-up prizes were awarded to Dominika Dacus, Cabinteely Community School, Dublin and Billy Clarke, Coláiste Bhaile Chláir and third runner-up prizes were awarded to both Dean Byrne, Cabinteely Community School and Megha Theresa James, St Paul's Secondary School, Dublin. This year an additional prize was awarded to Rachel Scarry, of Coláiste Bhaile Chláir, for the most innovative crystal.



Celebrating their SSPC National Crystal Growing Competition win at the Analgo Devices Building, University of Limerick were, Coláiste Bhaile Chláir, Galway students, first place prize winner, Aoife Ryan, second runner-up prize winner Billy Clarke and Rachel Scarry, for the most innovative crystal. Picture: Alan Place/Fusionshooters

Professor Michael Zaworotko said:

“As someone who appreciates the beauty and importance of crystals, it excites me to see the high level of energy and dedication shown by the students and their teachers involved in the SSPC National Crystal Growing Competition. Congratulations to all our winners as the standard of crystals were of a very high quality.”



Attending the SSPC National Crystal Growing Competition winners event, were, Lucy Fogarty, Eimear Begley and Nadia Scalast, Scoil Ide, Corbally. Picture: Alan Place/Fusionshooters

Growing crystals takes time and the best crystals are those which have grown slowly. The final judgement is based largely on fundamentals such as the crystal definition, clarity, size and overall quality. The judging panel for the SSPC National Crystal Growing Competition complimented the excellent standard of entries.

The crystals submitted to the SSPC National Crystal Growing Competition will be kept on public display at SSPC headquarters at the University of Limerick. This event was supported by the University of Limerick.



Sophie Ryan and Abi Dowling, Scoil Ide, Corbally with Dr. Sarah Hayes, SSPC Education and Outreach Officer. Picture: Alan Place/Fusionshooters

To find out more information go to http://www.sspc.ie/crystal_growing or contact SSPC Education and Outreach Officer Dr Sarah Hayes: sarah.hayes@ul.ie

Point of contact for media query – Louise O'Neill, SSPC Communications Officer Phone +353 (0)61 234675

Email: louise.oneill@ul.ie



InterTradelreland Meet the Funder Events 2016

Tuesday 26th April 2016

Europa Hotel, Belfast

Thursday 28th April 2016

Croke Park, Dublin

Following on from the successful launch and roll out of InterTradelreland's Funding for Growth Programme in 2015 two Meet the Funder events will be held in April 2016.

Both events are aimed at companies with ambitions to grow providing information on and access to a range of funding providers and advice on how to approach the funding process.

Conference Programme

- 7.30 Refreshments & Networking
- 8.00 Welcome
- 8.05 Opening Address, Martin Cronin, Chairman InterTradelreland
- 8.10 The Funding environment, Grant Thornton
- 8.30 Panel 1 Bank Finance
- 9.00 Panel 2 Private Equity
- 9.30 Panel 3 Alternative Sources of Finance
- 10.00 Closing Remarks
- 10.10 Network with Finance Providers
- 11.30 Close

*Programme subject to change

[REGISTER FOR BELFAST](#)

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Please note that as a number of the funding providers are different north and south it is recommended that Republic of Ireland companies register for the Dublin event and Northern Ireland companies for the Belfast event.



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**Eurachem Ireland Workshop
TrainMiC Metrology in Chemistry Part II**

20 April 2016

**The State Laboratory,
Backweston, Celbridge, Co.Kildare**

Eurachem Ireland will host a TrainMiC workshop on Metrology in Chemistry. The workshop will be delivered by TrainMiC trainers and covers Part II of the TrainMiC syllabus. Note that attendance at Part I is not required to attend Part II or Part III.

The workshop will be of interest to early-career chemists; chemists interested in refreshing their metrology knowledge; post-graduate chemistry students; scientists and engineers working in chemistry metrology.

Agenda

9.45-10.15	Registration with tea/coffee
10.15	Introduction to TrainMiC and Eurachem Ireland update
10.30	Introduction to Metrology
11.30	Selection and use of Reference Materials
12.30	Sandwich Lunch
13.15	Interlaboratory Comparisons
14.15	Internal Quality Control
15.15	End

TrainMiC Trainers: Éidín Christie, Gerry McCaffrey and Oonagh Quinn.



Completed registration forms should be emailed to eurachem@statelab.ie by 6 April. Registration forms can be requested by emailing eurachem@statelab.ie.

Fee €90 Students/Unwaged: €50

Workshop Materials An electronic copy of the presentations will be provided to participants on a USB key on the day. A hard copy of the presentations is available on request to participants registered before 20 March 2016.

Transport

There are two Irish Rail stations close to the laboratory: Leixlip Louisa Bridge (Maynooth/Sligo line) and Hazelhatch (Celbridge) (Kildare/Limerick/Cork line).

Dublin Bus services 67 and 67X between Dublin and Maynooth stop within a 10 minute walk from the laboratory. (From Dublin: Bus stop no. 3899; From Maynooth: Bus stop no. 3939).

The State Laboratory is located 5 minutes from Junction 5 on the N4 in the direction of Celbridge. Carparking is available.



Eurachem Ireland is an organisation for people working in chemistry in Ireland, with a focus on analytical chemistry. Chemistry students are welcome too. Eurachem Ireland promotes the objectives of Eurachem (www.eurachem.org) in Ireland including good quality practices. Other objectives of Eurachem Ireland include, but are not limited to:

- Facilitate networking among Irish analytical chemistry laboratories from the public sector, private sector and education sector;
- Provide a forum for the discussion of common issues;
- Encourage Irish participation in Eurachem working groups;
- Increase awareness of opportunities for organisations to participate in research;



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Registration

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<https://www.eventbrite.ie/e/8th-conference-on-analytical-sciences-ireland-2016-tickets-20890754810>

Costs

Registration Fees	General	Student
Early Bird – before 5th April 2016	100.00	75.00
Fees after 5th April 2016	150.00	100.00

****Registration fee includes conference materials, T/C breaks, 1 lunch and conference dinner on Thursday 14th April 2016.**

More Information

<http://www.ncsr.ie/news/casi2016/about/>



EcoBalt 2016



EcoBalt 2016 is an international research conference that will be held on **9.–12. October 2016** in **Tartu, Estonia** (in Dorpat conference centre). The conference will focus on the most recent scientific and technological developments in the field of environmental analysis, environment and its protection. With the support by the EcoBalt conference series, EcoBalt 2016 is organized by the *University of Tartu* with *Tallinn University of Technology* and *Estonian Environmental Research Centre*.

!Great news! EcoBalt2016 has received grant for organisation of international events and conferences from Estonian Ministry of Economic Affairs and Culture in cooperation with the Enterprise Estonia tourism development centre. This means that a lot is included in the conference fee, most notably, conference dinner and excursions.



Please download the [Second Circular!](#)

EcoBalt2016 will:

- bring forward **most recent** scientific and technological developments in the field of environmental science
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- **be of interest** to anybody interested in the environmental analysis (air, water, soil etc) or any other issue in relation to environment and its protection.
- be a **great chance for scientists, industry and students** in the Baltic region and further to come together and share knowledge and discuss issues in relation to our environment.

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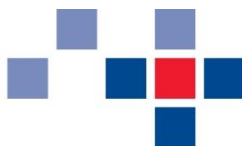
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[Key dates and deadlines!](#)

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[The Organising Committee](#) is committed to providing the most wonderful conference experience and **if any** questions, please contact the local organising committee at riin.rebane@ut.ee.



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AMBER researcher awarded €2.5m grant

Posted on 17 February 2016. Tags: [Consolidator Grants](#), [European Research Council](#), [Prof. Valeria Nicolosi](#)

Source: Industry & Business Premier Publishing & Events.



Professor Nicolosi has been awarded €2.5million ERC Consolidator Grant to create an innovative new type of energy storage device

An AMBER, the Science Foundation Ireland funded materials science centre, researcher, Prof. Valeria Nicolosi, has been announced as a recipient of the European Research Council's (ERC) Consolidator Grants. The 'ERC Consolidator Grant' is one of the most sought-after competitive research grants in Europe and will provide Prof. Nicolosi with €2.5 million in funding over 5 years for her project "3D2DPrint". The project focuses on creating a new type of extremely long lasting battery – one that can come in any shape or size and can be camouflaged within any type of material – whether that's clothing, your mobile phone, your car dashboard or even implanted inside your body (e.g. for an Implanted Cardiac Device). This funding will enable her to establish a multidisciplinary research group to develop this unique class of energy storage devices. Prof. Valeria Nicolosi is Ireland's only four-time ERC awardee, and has been awarded over €11million in funding for her research in the past 5 years at Trinity.

Imagine a family of batteries that recharge in a few minutes, that can come in any shape or size and can be disguised within any type of material – whether a piece of clothing or the hard plastic shell of a mobile device. These are revolutionary batteries that could be customised just for you and could even be implanted within your body to power a device that monitors your health – they could be hidden and integrated to the extent that you might not really know they were even there. From there, consider that these batteries won't die after a year's worth of repeated recharging – they could last 50 times longer than the normal battery life as they are "smart" batteries – they harvest energy from their surroundings and are actually charging themselves. These are a new type of battery that Prof. Nicolosi and her team are working to create.

The project Prof. Nicolosi and her team are working on will develop fully customisable batteries – they will be custom made and formulated for whatever specific application needed. They will be able to be used for general fitness (e.g. within a 3D Printed smart fitness watch), as well as being manufactured and fully integrated within a 3D printed Implanted Cardiac Device. These batteries will also, compared to the current Li-battery technology, be fully non-harmful and non-flammable.

The aim of this project is to develop a new energy storage technology using a unique combination of Prof. Nicolosi's novel 2-Dimensional nanomaterials and 3D printing processes. It is hoped that this innovative

approach will produce a range of energy storage devices by exploiting 3D printing to develop complex material shapes, which may offer further performance enhancement at low cost.

This grant will enable Prof. Nicolosi to employ 6 researchers (3 Senior Post Doctorates and 3 PhD candidates). This is her 4th ERC Award, she has previously received an ERC Starting and two Proof of Concepts grants worth €4.3 million in total.

Prof. Valeria Nicolosi, Professor at the School of Physics and the School of Chemistry, Trinity College Dublin and Principal Investigator at AMBER, said, “I am delighted to be awarded the European Research Council’s (ERC) Consolidator Grant. Since 2011, the first year of my ERC Starting Grant, my group has grown from 3 to 25 people. The ERC Grants I have been awarded were not only important in helping fund our research and grow our team, but to also help leverage more funding and realise partnerships with large multinationals. What is key is that these Grants allow us to take the next step with our research – whether it is the licencing of technology or starting-up a new company.”

Prof. Michael Morris, Director of AMBER, commented on the announcement, saying, “The awarding of this Consolidator Grant to Prof. Nicolosi is an excellent acknowledgement of the research work she and her team are currently undergoing. The work Prof. Nicolosi and her team are doing is at the fore front of their fields, and this grant will help them take the next step in combining the team’s expertise of advanced materials methods to integrate nanomaterials into 3D printed energy storage devices. During her time at Trinity, Prof. Nicolosi has received over €11 million in funding, including €4.3 million to date from the ERC, and now an additional €2.5 million to further her research. She is an exceptional asset to the AMBER team and this funding also reaffirms how competitive Ireland is as a place for research.”

The European Research Council awards these competitive ERC research grants to top researchers who engage in pioneering research, at the frontier of knowledge in their field.



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GE Healthcare invests \$40m to create 140 jobs in Cork

Posted on 01 December 2015. Tags: [Cork](#), [GE Healthcare](#), [investment](#), [Jobs](#)

Source: Industry & Business Premier Publishing & Events.

GE Healthcare today announced a \$40 million investment in its manufacturing facility in Carrigtwohill, Cork.

Employment at the Cork facility, which currently stands at almost 500 people, is expected to increase by 140 people. The investment which is supported by the Department of Jobs, Enterprise and Innovation through IDA Ireland, will double the Carrigtwohill facility's production capacity of medical imaging contrast media – from 22.5 million to 43 million units per year.

This significant investment will position GE Healthcare globally for growth in developing precision medicine and biopharmaceuticals.

Paschal McCarthy, Managing Director, Global Supply Chain at GE Healthcare said: "Today's announcement represents a key development in the journey of our facility here in Carrigtwohill. We are proud to be part of GE Healthcare's Life Sciences division as it grows and positions itself to meet the international demand for precision medicine, biologics and other advanced medicines such as cell and immunotherapies. Most importantly, this investment in our facility represents a significant vote of confidence in our people and their commitment to delivering the very best possible products available in the market".

Minister for Jobs, Enterprise and Innovation, Richard Bruton TD said: "Manufacturing is a key sector which we have targeted as part of our Action Plan for Jobs. This is an area which was neglected in recent decades but we have put in place a range of measures to support growth and in recent years we have seen a strong jobs performance. Today's announcement that GE Healthcare is investing \$40 million and creating an extra 140 jobs in Carrigtwohill is a great boost for Cork and for manufacturing in Ireland. I wish Paschal and the team every success with this project".

Welcoming the expansion, Martin Shanahan, CEO, IDA Ireland said: "The life sciences sector continues to thrive in Ireland. This increase in the production of this diagnostic tool of almost 100% is a real endorsement of the Carrigtwohill facility by GE Healthcare. IDA Ireland will continue to target further investment in this sector in the coming months".

Established in 1992, GE Healthcare's Cork facility fills, packs, and distributes contrast media used in medical scans to aid the diagnosis of disease to more than 80 markets internationally. Contrast media is commonly used during MRI scans and may be ingested by or injected into a patient in order to improve the visibility of the body's internal structure. Today's announcement builds on the development of a \$10 million production suite at the Carrigtwohill facility in 2012 which saw the site's manufacturing capacity increase by over fifty percent at that time.

Headquartered in the United Kingdom, GE Healthcare is a unit of General Electric Company (NYSE: GE). Worldwide, GE Healthcare employees are committed to serving healthcare professionals and their patients in more than 100 countries. GE Healthcare provides transformational medical technologies and services to meet the demand for increased access, enhanced quality and more affordable healthcare around the world.

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 **Agilent Technologies**

GSK to invest €12m in Cork manufacturing plant

Posted on 26 February 2016. Tags: [Cork](#), [GSK](#), [laboratory](#), [manufacturing](#), [pharmaceutical](#)

Source: Industry & Business Premier Publishing & Events.



Multinational pharmaceutical giant GSK has announced a new €12m investment at its manufacturing plant outside Cork city in Currabinny.

GSK said that €9.5m will be spent on its Kilo Scale Facility, while the remainder will be used in its technical laboratory in Cork.

The new purpose built Kilo Scale Facility will allow the site to begin manufacturing highly specialised active ingredients for newer, targeted oncology drugs.

GSK employs 450 people at its Cork facility. It produces a range of drugs and medicines for diseases such as cancer, HIV and depression.

The global healthcare company employs over 1,800 staff across four locations in Ireland – Cork, Dublin, Waterford and Sligo.

Kevin O’Keefe, Head of Engineering at GSK Cork said the new facility represents an important new opportunity for the company in Cork.

Mr O’Keefe said the plant will expand the company’s operating scale to allow it introduce new targeted medicines that require highly specialised manufacturing equipment.

“This investment opens up new potential for Cork to produce these in the future,” he added.



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Ranbaxy Pharmaceutical to close with the loss of 100 jobs

Posted on 31 March 2016. Tags: [Jobs](#), [Loss](#), [pharmaceutical](#), [Ranbaxy](#), [Sun Pharma](#), [tipperary](#)



Ranbaxy pharmaceutical is to close its plant in Cashel, Co Tipperary with the loss of 100 jobs. The plant which has been in business for over 30 years on the Cork Road, make and package generic drugs.

The facility is owned by Sun Pharma which is the fifth largest drugs producer in the world. Sun Pharma took over Ranbaxy's international operations last year.

Negotiations over the future of the facility had been taking place for a number of months, with the owner Sun Pharma looking to sell the plant.

Sun Pharma had stated that it intended to scale down or divest itself of certain operations worldwide, with the Cashel site said to be one of the locations to be either sold or divested.

In a statement Sun Pharma said it decided to cease operations at its Cashel unit as part of an ongoing operations network review.

It added it expects "to cease operations at Cashel by end of current calendar year"

The company said it will move certain roles to other facilities within its global operations network.

It will engage with trade unions and employee representatives in the coming months and "at the end of this period, if necessary, the company may proceed with redundancies".

Co Tipperary Chamber expressed its disappointment with the decision to close the plant, saying it has been a "consistent employer in the local economy for many years".

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Bristol-Myers Squibb and NIBRT Launch €1 Million Collaboration

Posted on 31 March 2016. Tags: [Biologicals](#), [Bristol-Myers Squibb](#), [NIBRT](#)

Bristol-Myers Squibb has announced a collaboration with the National Institute of Bioprocessing Research and Training (NIBRT) in Dublin to establish a process science and technology laboratory that will strengthen productivity of manufacturing processes for biologicals. The lab will house a team of 12 Bristol-Myers Squibb scientists who will advance complex bioprocesses used to produce BMS's biologics products and benefit from close collaboration with the scientific staff at the NIBRT. The laboratory is expected to be operational by June 2016.

The collaboration comes ahead of Bristol-Myers Squibb's plans to open a new €900 million state-of-the-art, large-scale biologics manufacturing facility in Cruiserath, County Dublin, near Blanchardstown that will produce multiple therapies for the company's growing Immuno-Oncology portfolio. The manufacturing facility is estimated to be operational in 2019.

In addition to establishing a laboratory, the Bristol-Myers Squibb-NIBRT collaboration includes:

- Customised NIBRT experiential training programmes for Bristol-Myers Squibb employees across all areas of the biopharma manufacturing process
- Careers Day for prospective candidates
- Four-month training programme with NIBRT, followed by a paid three-month internship with Bristol-Myers Squibb for 20 skilled professionals through an association with Skillnet and the Department of Social Protection

"Bristol-Myers Squibb has a robust and growing portfolio of approved and investigational biologic medicines across multiple therapeutic areas, and NIBRT's facilities and training capabilities will provide innovative and state-of-the-art support for our Cruiserath facility," said Lou Schmukler, President, Global Manufacturing & Supply, Bristol-Myers Squibb. "Our people and operations in Ireland are integral to helping Bristol-Myers Squibb deliver innovative medicines to our patients around the world."

The Cruiserath facility, which will employ up to 400 skilled science, professional and technical staff, will produce multiple therapies for the company's growing biologics and diversified specialty medicines portfolio. Bristol-Myers Squibb employs 25,000 people worldwide, including 550 in Ireland.

"We are delighted to expand our partnership with Bristol-Myers Squibb," said Dominic Carolan, chief executive officer, NIBRT. "As the national bioprocessing training and research facility, NIBRT is committed to supporting international and domestic biologics investment to Ireland. Working with companies to develop innovative, tailored programmes to complement recruitment, training and research needs is core to our mission. Our collaboration with Bristol-Myers Squibb has thus far seen us facilitate a very successful BMS Careers Day last November and delivering customised training programmes to BMS employees and Skillnet students. We're delighted to be welcoming the BMS scientific team to NIBRT."

Martin Shanahan, CEO, IDA Ireland said "This is a welcome collaboration following the announcement by BMS to establish a new large-scale biologics manufacturing facility in Cruiserath employing 400 people by 2019. IDA is committed to supporting continued growth in the biopharma sector. As the pipeline of new biologic drugs continues to improve, it is clear that there is more potential in this industry for job creation and investment. The availability of such excellent research and training facilities as the IDA Ireland supported National Institute of Bioprocessing Research and Training (NIBRT) assists us as we seek to attract further biopharma companies to establish operations here."

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The machine offers good sensitivity and the high resolution allows spectra to be measured quickly. The data can be processed directly (even while wearing safety gloves) through the built-in resistive touchscreen without connecting an external computer.

Contact Information:

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Website: <http://www.gpescientific.co.uk/products/chemistry/nanalysis-nmready-benchtop-spectrometer>

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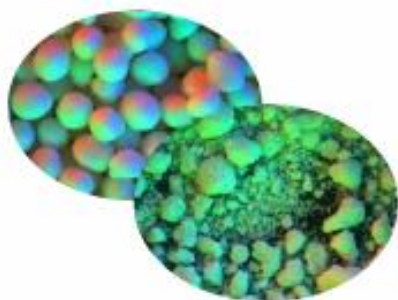


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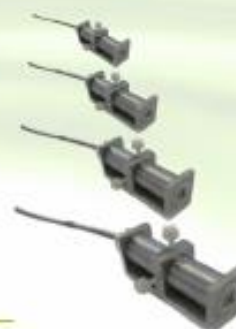
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