Irish Chemical News

The Journal of the Institute of Chemistry of Ireland

Feature Articles:-

Chemical Sensing with Autonomous Devices in Remote Locations: Why is it so difficult and how do we deliver revolutionary improvements in performance?

Sensitizing Polyoxometalate Photochemistry for Photoelectrochemical Applications

Paris Agreement: Developing clean technologies for a better future.

Protecting Endangered Elements Report

DCU's New "Water Institute"

Dioxin/PCB Analysis by High Resolution Gas Chromatography Mass Spectrometry (HRGCMS).

Knowledge Transfer Ireland KTI

Optimizing Processes with Design of Experiments

Irish
Chemical
News

The Institute of Chemistry of Ireland

PO Box 9322, Cardiff Lane, Dublin 2

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A Message from the President

Dear Fellows, Members, Graduates and Associates,

It is hard to believe that the first year of my term of office as President is already nearing its end. The past year has flown and has been marked by a number of significant events. On the day of last year's AGM, The Boyle-Higgins Award Medal was presented to Professor Dermot Diamond of DCU. The text of his award lecture is published in this issue of 'Irish Chemical news' (ICN). We had a most successful Annual Congress, hosted by UCD with the theme 'Asymmetric Synthesis' and an equally successful Research Colloquium, hosted by NUI Maynooth. Reports of both of these events have already been published in ICN. In November, UCD hosted our awards seminar, during which two prestigious awards were made. The inaugural Industrial Chemistry award, Sponsored by Henkel, was presented to Donal Coveney of TopChem, while the Eva Philbin Annual Award for Chemistry went to Professor Michael Zaworotko of UL.

The year 2016 ended on a sad note, as we learned of the sudden and untimely passing of former President of the Institute, Paraic James of DCU. His Obituary appears in this issue of ICN. He will be sadly missed. Early this year, we were saddened to hear of the death of another former President of the Institute, Professor Dick Butler of NUI Galway, who died on February 10th. His Obituary will be published in a later issue. May they rest in peace.

Looking forward to the year ahead, the first major event coming up is the 2016 Boyle-Higgins Award lecture, which will be given by Professor Kieran Hodnett of UL. He will give his lecture at the FOCAS Institute at DIT on April 14th at 5.00 p.m., after which he will be presented with the Boyle-Higgins gold medal. There is a notice of this event in the current issue of this journal and I encourage as many members as possible members to attend this event. Please pass on the word to your colleagues, as this lecture is open to all who are interested, members and non-members alike. Following the lecture and presentation, there will be a wine and finger food reception and this will be immediately followed by the AGM. I appeal to all members to please make an effort to attend the AGM, as this is your opportunity to become actively involved with the work of the Institute and to make your voice heard. I look forward to meeting you there.

Margaret Franklin, FICI, President.

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Editorial

With the arrival of 2016 I am delighted to say ICN is starting to establish itself and I'm now being offered papers for publication. This is very encouraging and I will be endeavoring to increase publication frequency with more predictable publication dates. This year I expect to publish four issues and maybe a fifth if I get a sufficient number of papers.

Premier Publishing & Events who have organized a number of scientific conference and seminars have invited and facilitated the Institute to attend a number of these and provided space and opportunities to us to exhibit and promote the Institute. Such events provide great opportunities to source papers for publication and I expect to provide these in the Issues of ICN throughout the rest of the year. The next event is Research & Innovation at Croke Park Stadium on Thursday 3rd March with a full agenda of topics many of interest to chemists.

This edition brings two feature articles from DCU, a Eurachem Ireland/State Lab paper, an article on the Paris Agreement courtesy of French Ambassador to Ireland Jean-Pierre Thébault followed by an article by our European representative Patrick Martin on Endangered Elements based on EuCheMS workshop in Brussels last September. Also featured is an article on the new DCU Water Institute which was recently launched. Knowledge Transfer Ireland have provided an article explaining the framework for the way in which companies and research performing organisations can work together. The finally paper is on Optimizing Processes with Design of Experiments provided by SAS/JMP.

Sadly this Issues carries an Obituary for our Registrar and Past President Dr Paraic James, DCU who passed away suddenly last December, provided by his colleagues at DCU. Both DCU papers are dedicated to him and Professor Diamond has added a short Eulogy to Paraic. He will be very much missed by Council members.

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.

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.

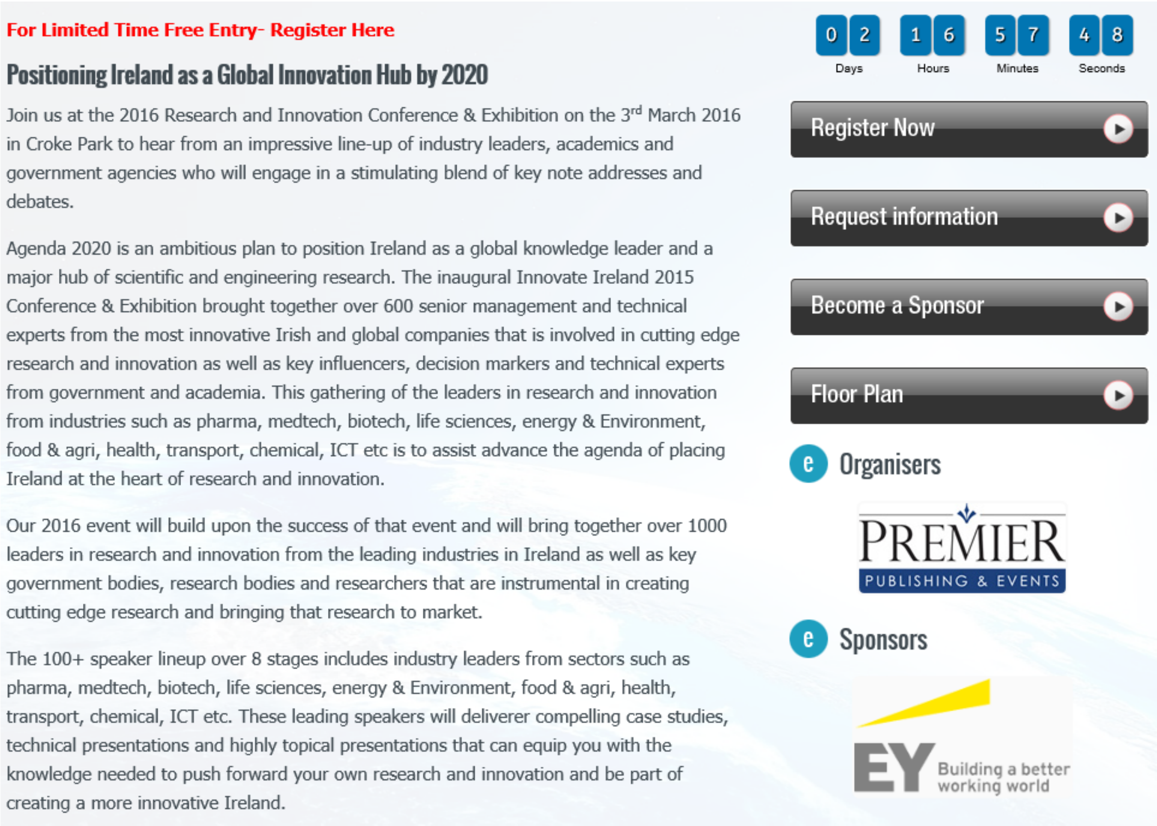
You can sent these to The Editor at:-

mailto:info@instituteofchemistry.org

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

Editor ICN,

Immediate Past President.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Our 2016 event will build upon the success of that event and will bring together over 1000 leaders in research and innovation from the leading industries in Ireland as well as key government bodies, research bodies and researchers that are instrumental in creating cutting edge research and bringing that research to market.

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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).

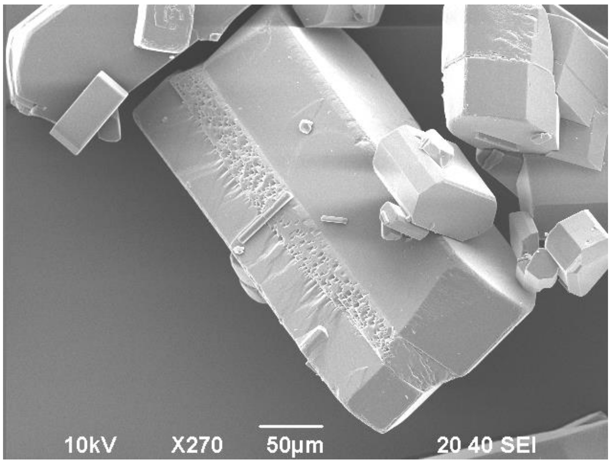

Figure 2. FIV Sulphathiazole dissolving and roughening while it is epitaxially sandwiched between two layers of FII.

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.

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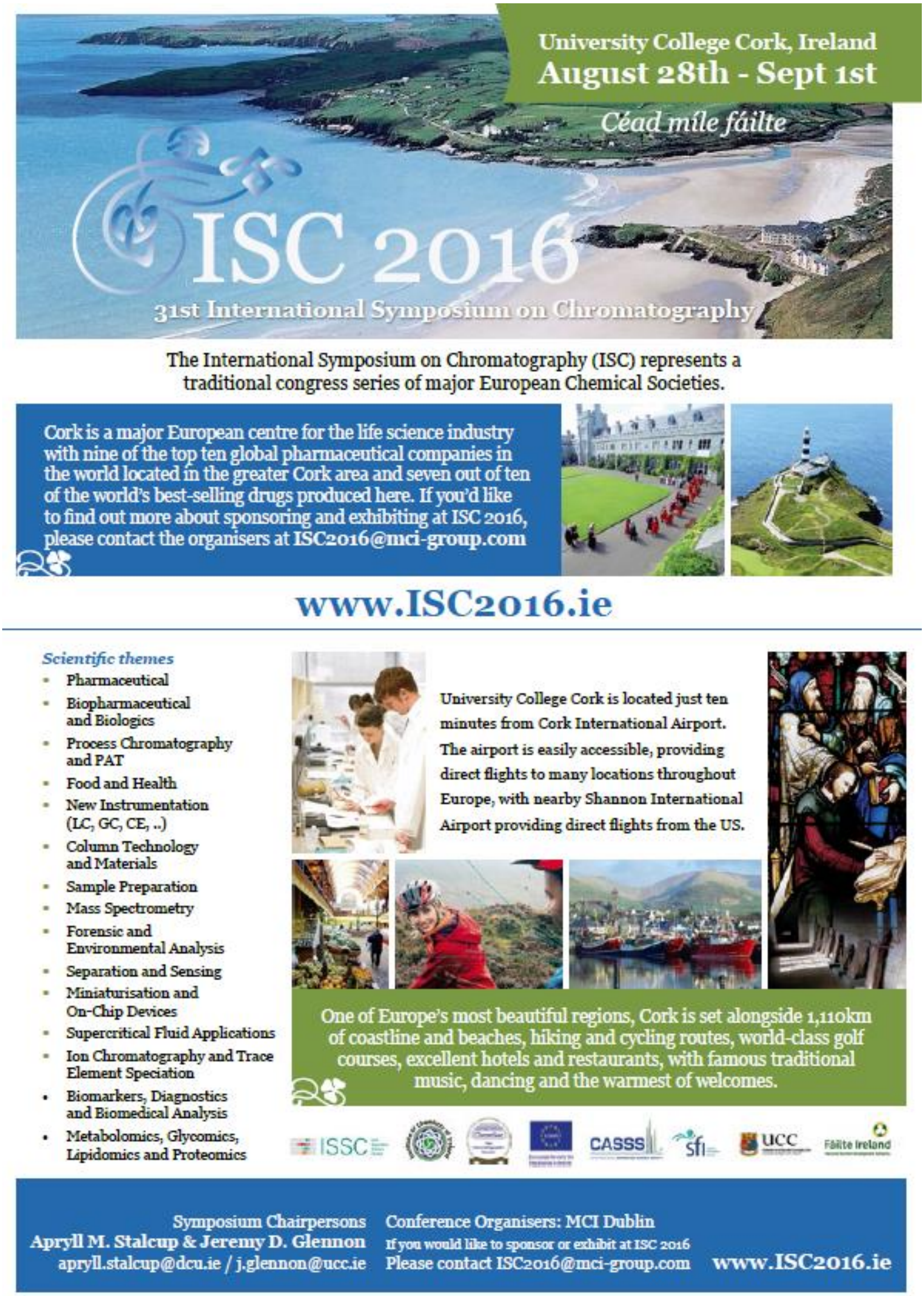

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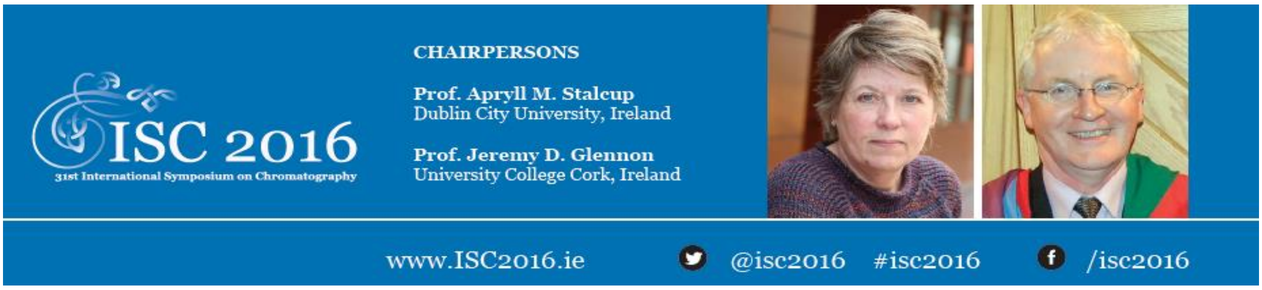

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Paraic James

(1959 – 2015)

Paraic James died suddenly on 4 December 2015 aged 56. Paraic was a committed teacher, researcher, and promoter of chemistry. He served as Vice President and President of the Institute of Chemistry of Ireland and most recently as the Institute's Registrar.

A native of Cloonakeemogue, Beltra, Co. Sligo, he was born on 8 March 1959, the second of three sons of Mary (née Donegan) and Hughie James. Christened John Patrick he was always known as Paraic. Educated at Ballinlig National School, St. Mary's College Ballisodare, and University College Galway, he graduated with a B.Sc. (First Class Honours) in Chemistry in 1980. His post-graduate research on the chemistry of nitrogen heterocycles was undertaken under the supervision of Professor R. N. Butler in Galway. He was awarded a Ph.D. by the National University of Ireland in 1983 for this research and earned the 1851 Exhibition Scholarship to work at the University of Oxford with Professor Jack Baldwin. This work focussed on the chemistry of penicillin.

In 1986, Paraic was appointed Lecturer in Chemistry at NIHE Dublin (now Dublin City University), being promoted to Senior Lecturer in the year 2000. He served as Head of the School of Chemical Sciences for a number of years during which his great management and organisational skills became evident. He maintained strong interests in heterocyclic chemistry and Nuclear Magnetic Resonance spectroscopy. This work led to many publications in international peer reviewed academic journals. Paraic supervised 16 graduate students to Ph.D. and M.Sc. degrees.

He made major contributions to the development of the B.Sc. programme in Analytical Science and was instrumental in establishing the B.Sc. programmes in Pure and Applied Chemistry (now simply called Applied Chemistry), Environmental Science with Health, and Chemistry with Language degrees. Paraic lectured across all years of the undergraduate and post-graduate degree programmes, and his approach to teaching was characterised by a deep concern for the welfare of his students. He was always careful to identify those students who were struggling with the course content and to ensure they received the extra supports necessary for them to succeed. Indeed the outpouring of affection from the student body at DCU following the news of his passing was evidence of this.

Paraic's interest in chemical education was not confined to the third level. He was heavily involved with the Science Olympiads. Starting in 1995, Paraic organised the Irish team's participation in the International Chemistry Olympiad (IChO) aimed at second level students. This competition had been running since 1968 and Paraic conducted the training in organic chemistry and spectroscopy. Several of his former Olympians went on to make a career in chemistry and they happily acknowledge the influence Paraic had on their career choice.

Paraic was central to the development of two science Olympiads for younger second level students and served as Scientific Co-ordinator at the first and third European Union Science Olympiads (EUSO) competitions. The International Junior Science Olympiad (IJSO), for students under 16, commenced in 2004 and Paraic served as European Vice-President from 2004 to 2012 and assumed the role as Treasurer more recently. All of this involved a significant commitment in time and energy, liaising with schools, team selection and training, and accompanying the teams to the competitions as a mentor and jury member.

His involvement in the various science Olympiads also allowed him to indulge his passions for international travel and photography. Among his most treasured possessions was his collection of more than twenty volumes of carefully catalogued photographs from all over the world. He had little interest in sporting matters with one exception, horseracing. For a time, he was part-owner with his cousin Hubert of a racehorse "Star Storm". Paraic always claimed to own the hind legs!

Paraic served as Secretary of the Society of the Chemical Industry (Irish Branch) and was a member of the Radiological Protection Board. He served on the Board of Management of Coolmine Community School from 1993 to 2015, acting as chairperson for much of that period. In that role, he was an invaluable support to successive Principals, assisting them in dealing with many difficult issues. He was also a loyal Fine Gael supporter holding a variety of offices in the Dublin West constituency.

Paraic's Funeral Mass took place at Dromard Church, where he had been christened, and he was the first to be laid to rest in the new cemetery adjoining the Church. He is mourned by his parents Hughie and Mary, his brothers Tom and Dermot, his sister-in-law Anne, his nephew Tomás, and Dermot's partner Anne.

Paraic was a modest and unassuming person, who did much to promote Chemistry in Ireland. He will be greatly missed by his many friends and colleagues.

Chemical Sensing with Autonomous Devices in Remote Locations: Why is it so difficult and how do we deliver revolutionary improvements in performance?

Institute of Chemistry Boyle Higgins Medal Lecture 2015

Simon Coleman, Larisa Florea and Dermot Diamond*

Insight Centre for Data Analytics, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University

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Introduction and Background

The early 1980's was a period of great excitement in the field of biochemical sensing. The theoretical basis, and practical exploitation of polymer membrane ion-selective electrodes (ISEs) was well established, particularly through the use of valinomycin as a receptor for the selective measurement of K^+. Electrodes had more or less displaced flame photometry in routine clinical blood electrolyte measurements. Most chemical sensors and biosensors follow a generic measurement scheme (Fig. 1), in which a surface presents receptor sites that selectively bind a species of interest (analyte or primary ion for ISEs) in a sample. In ISEs, binding at the sample-membrane boundary creates a potential that can be tracked using a Ag/AgCl electrode in contact with an inner-filling solution of the primary ion. This is due to the mixed conductance mode of the Ag/AgCl electrode, which can convert ionic conductivity (at the ISE membrane and internal filling solution) into electronic conductivity (in the Ag wire and external circuitry) as shown in equation 1;

$$AgCl_{(s)} + e^{-} \leftrightarrow Ag_{(s)} + Cl^{-}_{(aq)} \tag{1}$$

Significant progress in the miniaturisation of ISEs had occurred, which began to open up new clinical applications, particularly those requiring in-vivo, real-time measurements. For example, heart transplant surgical techniques that been initiated in the 1960s and refined during the 1970s depended critically on a precise concentration window of K+ in blood within the patient for the transplanted heart to be successfully 'restarted'. This need led to the development of catheter electrodes (Fig. 2) that were typically 1 mm in diameter and could be inserted into the femoral artery and manipulated into the patient's heart to track the K^+ blood concentration in real time [1]. Miniaturisation also overcame another issue with conventional ISEs – they could only be used upright as the internal electrolyte would fall away from the membrane if the sensor was turned upside down or horizontal. With the miniaturised electrodes this did not occur due to the capillary effect, unless the electrode was shaken vigorously. Consequently, there was great interest in the

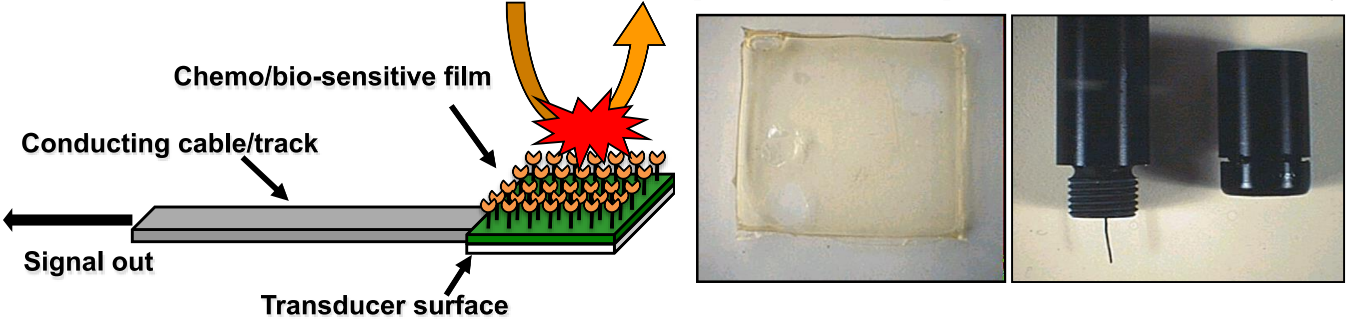

Fig. 1: In a typical biochemical sensor (left), a chemo/bio-sensitive surface presents binding sites to a sample that are designed to selectively bind a target analyte species. Binding events at this tailored surface are converted into a signal (usually electrochemical or optical) by a transducer (e.g. Ag/AgCl electrode) and the resulting signal transferred to external circuitry by a conducting cable or track. In polymer membrane ISEs, the receptors (ionophores) are dispersed in a highly plasticised PVC film (centre). Discs are cut from the membrane and clipped on the end of a an electrode tip (right), that can be screwed onto the electrode body. For metal cation selective electrodes, the body is typically filled with a 0.1 M Cl^- solution of the primary metal ion e.g. KCl for a K^+- selective electrode. A Ag/AgCl electrode (seen protruding from the electrode on the right) enables changes in the outer membrane boundary potential to be observed.

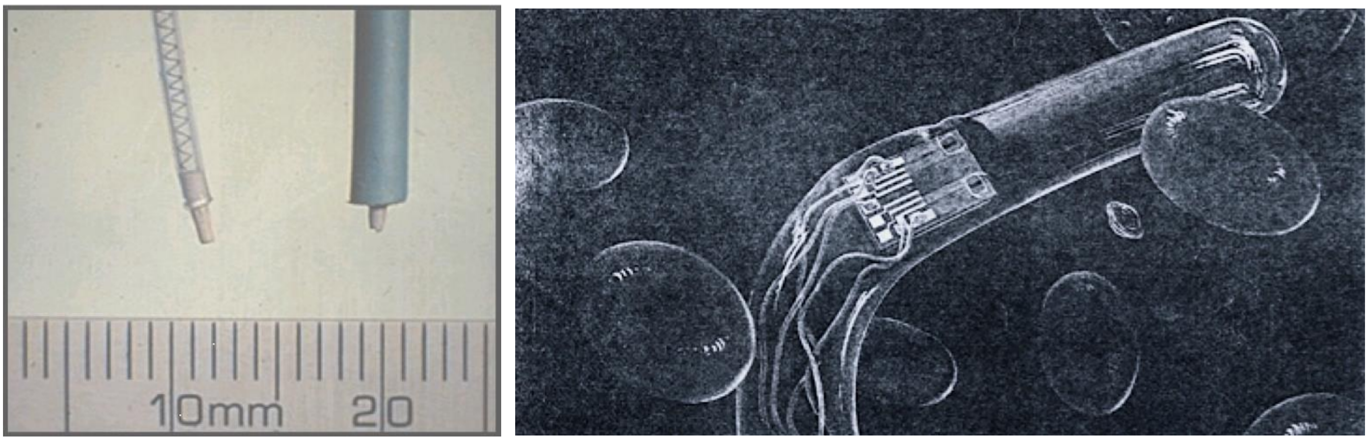

Fig. 2: Catheter electrode (left) shown outside and inside an 8-gauge catheter. The ca. 1 mm diameter sensor is based on a conventional design, with internal filling solution and a Ag/AgCl electrode (in a spiral). The ion-selective membrane is formed by dip casting from a solution of the PVC-ion-receptor/plasticiser formulation in THF [PhD thesis, D Diamond, Queen's University Belfast, 1987]. Representation of a glucose sensing ISFET in blood (right) [3].

development of solid-state versions of these devices. The emergence of the 'Ion-Selective Field-Effect-Transistor' or ISFET therefore created great excitement, as it appeared to be the perfect solution to many issues associated with conventional ISEs [2]. These devices were solid-state, with no need for a filling solution, inherently miniature, low signal impedance sources, and compatible with mass production technologies employed in the microelectronics industry. As this concept gained traction, the popular media began to speculate on the potential impact of these miniature biochemical sensing devices (Fig. 2), speculating that these could form the basis of artificial organs that could sense and regulate critical body functions, such as the controlled dosing of insulin to maintain glucose blood levels for diabetics [3]. Of course, the implication was that, as implants are long-term interventions, these devices would function reliably inside the body for many years.

If we now fast forward, some 35 years or so, from then to today, we see that the current use model for glucose maintenance by diabetics is overwhelmingly dominated by finger-prick measurements made with single use, disposable biosensors. The latest trends, typified by the Abbott Libre platform (Fig. 3), are towards patch-type devices that are attached to the skin using a customised applicator [4]. Application of the patch also punctures the skin and places a 0.5 cm fibre wick so that interstitial fluid can be sampled and monitored for glucose in real time, for up to 2 weeks, at which point it is replaced. Data can be accessed wirelessly using a mobile phone-like base station [5]. The use model is therefore to measure outside the body, and replace the sensors at relatively short intervals - the concept of the long-term implantable 'artificial pancreas' that created so much excitement in the 1980s has been abandoned as a practical solution.

Fig. 3: The Abbott Libre applicator (left, [4]) showing the sampling fibre and (right,[5]) the glucose sensing patch on the upper arm after attachment.

What's the Problem with Biochemical Sensors?

Let's consider how these devices function. In contrast to physical transducers like thermistors, photodetectors and movement sensors, biochemical sensors rely on an intimate contact with the sample, like blood. In order to ensure that the resulting signal can be confidently ascribed to a particular species in the sample, receptors of exquisite selectivity are required, as described above.

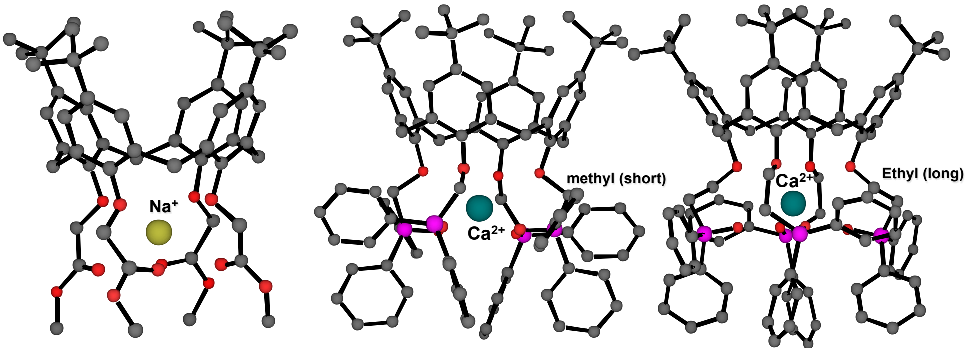

Fig. 4: Examples of calix[4]arene synthetic ion-receptors. All are based around a tetrameric structure that has four t-butyl-phenol moieties linked via methylene spacers into a lipophilic macrocyclic arrangement. Attached to the phenols are four pendent groups that define a strongly polar cavity in which ions can be bound. The tetramethyl ester (left) is very selective for Na+ due to its optimum 3D arrangement of negatively polar carbonyl and phenol oxygen atoms. This relatively rigid cavity does not interact so strongly with smaller cations like Li+ or Mg2+, while larger cations like K+ are too big to occupy the polar cavity. In contrast, the tetraphosphine oxide derivative (right) displays striking selectivity for Ca2+, whereas its close cousin (middle), also a tetraphosphine oxide derivative has no Ca2+ selectivity. The two phosphine oxide derivatives differ only through a single methylene group – the methyl (short) derivative (centre) has only a single methylene linker between the phenyl oxygen at the base of the macrocycle annulus and the phosphine oxide groups, whereas the ethyl (long) derivative (right) has two linkers. Atom Colour Code: grey – carbon; red – oxygen; pink – phosphorus; hydrogen atoms not shown for clarity [8].

Fig. 4 shows examples of ion-selective calix[4]arene cation receptors Na$^+$ or Ca^{2+}. PVC membranes incorporating the tetraester (left) are Na$^+$ selective [6] whereas electrodes based on the tetraphosphine oxide derivative (middle) are Ca^{2+} selective (Fig. 5) [7]. Both derivatives have exactly the same upper-structure from the phenoxy oxygen atoms, including the phenyl rings and tert-butyl groups that convey significant hydrophobic character to the structures. The selectivity comes from the pendant polar groups that define a negatively polarised cavity into which the cations fit, releasing energy and making the overall process thermodynamically favourable. The 'long' phosphine oxide derivative (right) differs from that on the right by having an additional methylene spacer between the phenoxy oxygen atoms and the phosphine oxide groups [8]. This apparently minor difference leads to a total loss of selectivity in electrodes based on this receptor. Therefore it is clear that the overall process of selective molecular recognition is extremely subtle, and in bioreceptors such as the glucose oxidase enzyme) this is even more pronounced, as recognition involves much larger entities and more complex interactions.

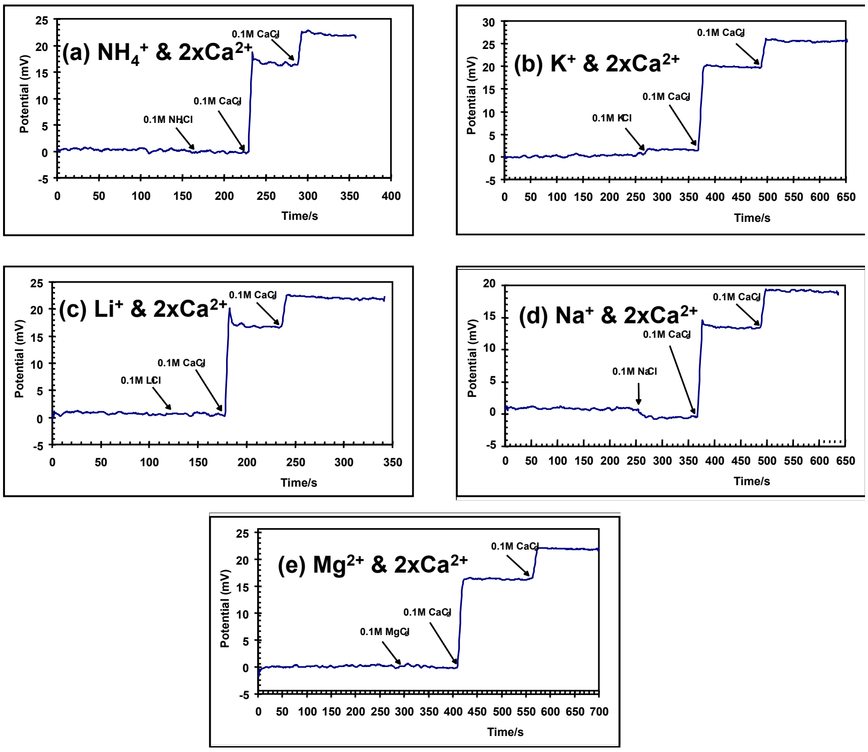

Fig. 5: Response of ISEs based on the 'short' calix[4]arene phosphine oxide (middle, Fig. 4). In each case, the signal shows minimal response to injection of an interfering ion, followed by two injections of equivalent amounts of Ca^{2+}*, that produce almost theoretical Nernstian responses in the presence of the interfering ion [7].*

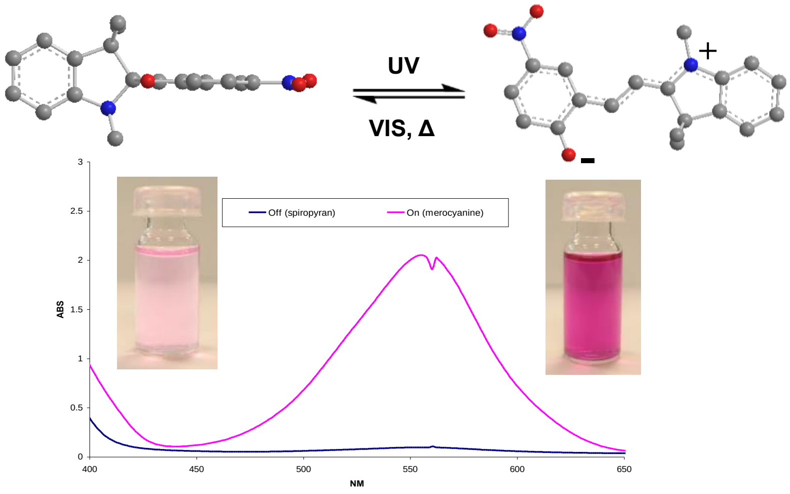

Fig. 6: Colourless, hydrophobic spiropyran (left, top) can be converted to the zwitterionic, hydrophilic merocyanine form by exposure to UV light at ca. 360 nm. The merocyanine can be converted back to the spiropyran using white of green light. The planar merocyanine isomer is highly conjugated and absorbs strongly in the visible region around 560 nm [10]

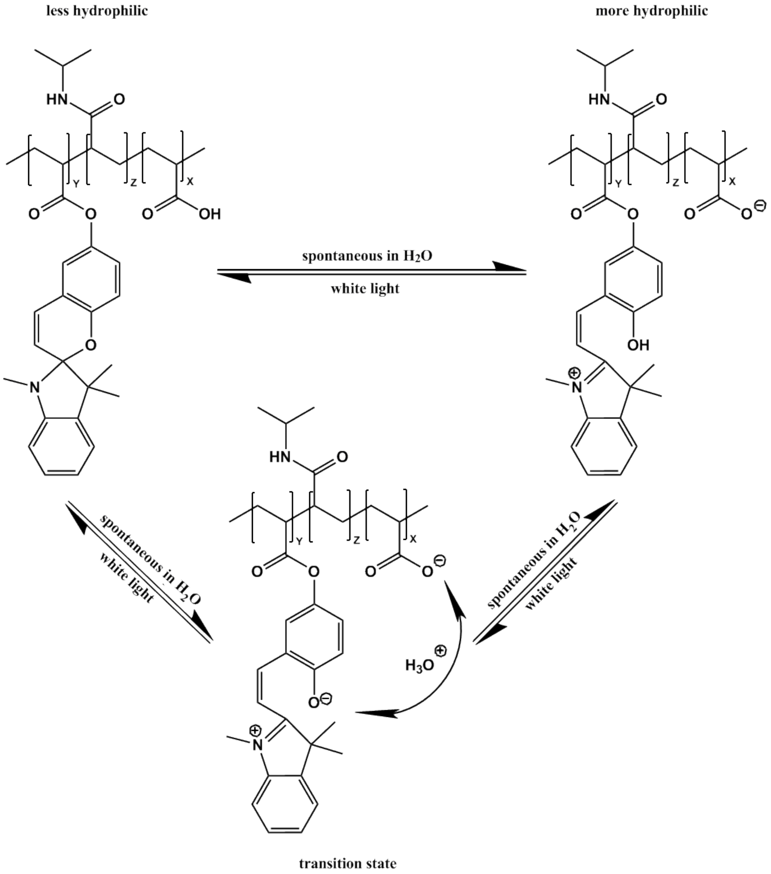

Fig. 7: Spiropyran modified pNIPAM swells spontaneously when protonated, and contracts under exposure to white light. Inclusion of acrylic acid provides an internal source of protons that extend the useful pH range of the gels to around pH7.5 [11].

When one considers the intricacies of these selective binding events, it is not surprising that they are difficult to maintain within calibration, are prone to changes in baseline and sensitivity, and loss of selectivity over time, and their mode of use is inherently much more challenging than equivalent physical transducers. This is why they are either single use, disposable sensors (e.g. for diagnostics), or, for continuous operation they are integrated into operational modes that enable calibration parameters to be checked on a regular basis. In turn, this usually means incorporation of pumps and valves, and a flow system through which samples and standards are transported to the sensor. The arrival of microfluidics and the lab-on-a-chip concept in the late 1980s was also heralded as the solution to many of these issues, but after years of research, George Whitesides could only lament that '*....microfluidics, to date, has been largely focused on the development of science and technology, and on scientific papers, rather than on the solution of problems*' [9].

Future Perspectives: Can Research Deliver Revolutionary Advances in the Field of Biochemical Sensing?

Part of the difficulty with microfluidics and Lab-on-a-chip is that the early concepts and fabrication technologies were taken from the microelectronics industry. Microelectronics had revolutionised the electronics industry through the 1970s, and microfluidics was expected to do the same for analytical chemistry including biochemical sensing. Problems associated with the high cost and slow turnaround microfluidics prototyping slowed progress. And while biochemical sensors could be more stable

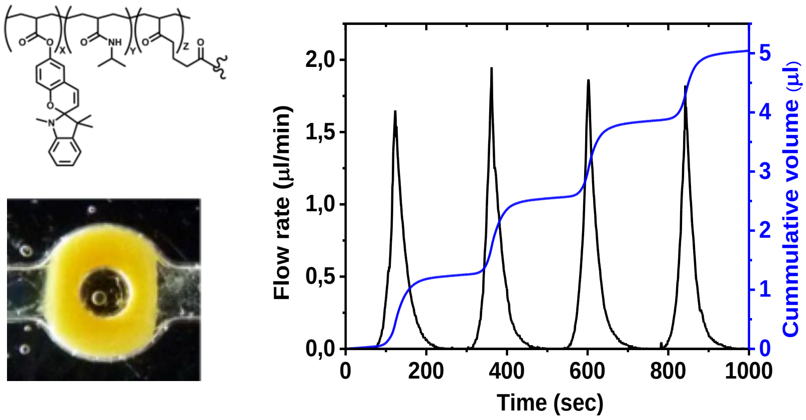

Fig. 8: Performance of pNIPAM gel valve structures in a microfluidic channel. The gel (top left) is photopolymerised using a mask to forma doughnut shape around a central pillar (bottom left). The pillar provides a local anchoring function so the polymer is retained in position. Note the yellowish colour of the protonated merocyanine in the swollen gel. Four valve opening/closing cycles (right) showing increase in flow upon exposure to white light followed by rapid closing of the valve when the light is turned off. Each event is reasonably reproducible releasing ca. 1.25 µl of liquid [13].

within the relatively benign environment of the microfluidic platform, they still suffered from drift and change of characteristics, and regular recalibration was still required. In addition, reliable pumps and valves were macro-dimensioned, and these components tended to be located off-chip, requiring sampling loops from/to the chip, complicating the flow system in the process. Coupled with expense and power demand, this approach was unscalable and restricted to mainly relatively simple microfluidic designs within expensive instruments (i.e. costing >€10K). At the other end of the analytical spectrum, simple capillary fill, single use, disposable microfluidic chips that required no pumping found applications in biodiagnostics, particularly for sample preparation and delivery to a disposable sensor.

So is there a pathway towards the realisation of biochemical sensing platforms with dramatically enhanced specifications compared to current approaches? Biology already has solved these challenges, and perhaps we now need to create bioinspired platforms based on biomimetic principles. For example, a key challenge is to create effective fluidic control using constructs that are fully integrated within the fluidic system, and based on soft, polymer gel-type materials that are much more reminiscent of biological valves than silicon micromachined microvalves. For example, pNIPAM absorbs large quantities of water and forms an expanded hydrated polymer that reversibly switches back to a much more globular, compact, lipophilic form. Switching between the two forms results in dramatic expansion and contraction behaviour, triggered normally by crossing a temperature threshold, often in the range 30-40^{o}C depending on the derivative used and content of the liquid phase. Incorporating the molecular photoswitch spiropyran into the polymer structure enables this *lower critical solution temperature* (LCST) behaviour to be triggered using light. Spiropyran is an uncharged, colourless, hydrophobic molecule that switches to the zwitterionic, strongly coloured, hydrophilic isomer merocyanine when exposed to UV-light. The reverse process can be triggered using white or green light, thus enabling the isomer of choice to be remotely selected using light (Fig. 6) [10].

The spiropyran modified gels swell spontaneously under acidic conditions (ca. pH 3), due to the formation of the protonated merocyanine. Exposure to white or green light (e.g. from an LED) causes rapid contraction of the gel, by more than 50% by volume in some cases. However, inclusion of acrylic acid into the polymer matrix provides an internal proton source, and this expends the useful range of up to ca. pH7.5 (i.e. acidified external conditions are not necessary), see Fig. 7 [11]. Effectively the protons hop between the merocyanine phenoxy site and the acrylate anion, and this also increases the switching rate. These gels can be easily photopolymerised in-situ within microfluidic channels so that, when swollen, the gel blocks the channel [12]. Under exposure to white light, the gel rapidly contracts as protons migrate from the protonated merocyanine to the acrylate anion, opening the channel. When the light is turned off, the gel spontaneously expands as the protons return to the merocyanine, blocking the channel again (Fig 8) [13]. This is an important development as it provides a route to implementing multiple valves within a microfluidic system that can be controlled externally through light, which is non-contact, i.e. no need for electronic connections to the valves.

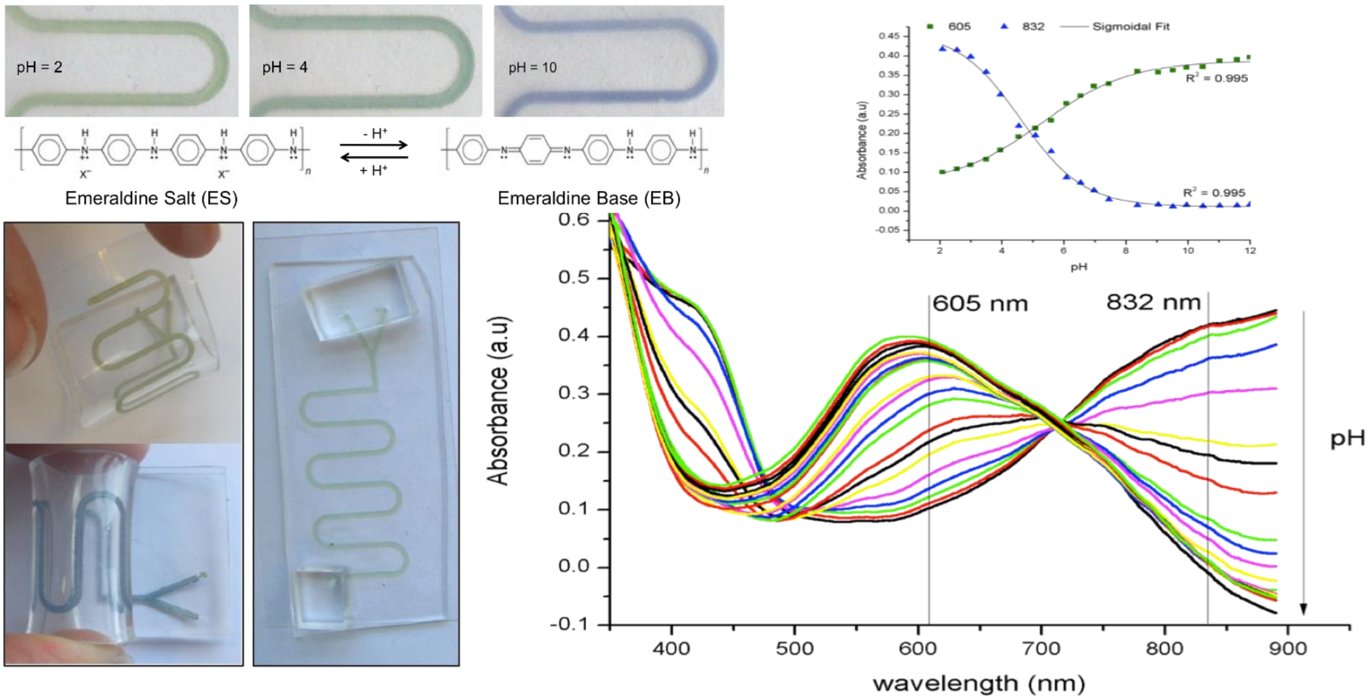

Figure 9. *Images (left, top) of a polyaniline functionalised PDMS microchannel loop when solutions of different pHs are flushed through the channel together with the equation showing the pH induced switching between the green emeraldine salt form (predominant under acidic conditions below about pH 5) and the blue emeraldine base form (predominant at pH> ~5.0. The flexible nature of these microfluidic platforms is apparent (left, bottom). The changes in the absorbance spectra of the PAni coatings in response to different pH solutions flushed inside the microchannel were recorded using two fiber-optic light guides connected to a Miniature Fiber Optic Spectrometer and aligned using an in-house made cell. Absorbance spectra of the polyaniline coatings in the channel when solutions at different pH are passed through (pH 2-12). (right, bottom) Inset (right, top) – Slices through the spectra showing the absorbance change of the polyaniline coatings vs. pH at 605 nm and 832 nm [13].*

Towards Biomimetic Microfluidics

The soft gel valves described above can be categorised as biomimetic, in that their form and function mimics bio-valves rather than conventional engineered structures.

Building on this strategy, other characteristics of biological systems can be transferred into microfluidics to provide dramatic enhancements in performance.

For example, moving from the micromachined channels produced from etched silicon that dominated the early years of microfluidics, much greater emphasis is now being placed on channels created in soft polymeric materials like PDMS. These fluidic systems are flexible and conformable, and can adapt to the surrounding environment, for example, by conforming to changes in topography of an underlying substrate, or flexing due to movements. This opens the way to new applications in, for example, wearable fluidic systems and functional patch-type devices with sophisticated functionalities made possible through integrated soft fluidics. Fig. 9 shows a flexible microfluidic system fabricated in PDMS [14]. The channel walls are functionalised with pH colour responsive polyaniline, enabling pH to be monitored along the entire length of the channel, rather than at a single detector point, as is the norm in microfluidics. The concept of giving the channel walls an active role, rather than just defining the pathway along which fluids can move, represents move towards the creation of fluidic systems that have distributed functionality, and in which the channel walls play a key role in providing this distributed functionality. In living systems, the fluidics system (e.g. blood circulation system) performs multiple complex functions besides transport of fluids and other components. The combination of soft, conformable fluidics with the distributed sensing role along the channel could therefore be regarded as the beginnings of an evolution (albeit in a very simplistic manner) towards more bio-inspired fluidic systems.

Building on this idea, Fig. 10 illustrates photo-controlled binding and release behaviour of spiropyran modified surfaces. In this case, UV light is used to convert the modified surface to the charged merocyanine form, which can bind metal ions electrostatically through the phenoxy oxygen anion (see Fig. 6) [15]. The micro-fluidic device consists of five independent 94 µm depth, 150 µm width channels fabricated in polydimethylsiloxane. The spiropyran 1′-(3-carboxypropyl)-3,3′-dimethyl-6-nitrospiro-1-benzopyran-2,2′-indoline is immobilised by physical adsorption into a polydimethylsiloxane matrix and covalently on the ozone plasma activated polydimethylsiloxane micro-channel walls. When the colourless, inactive, spiropyran coating absorbs UV light it switches to the highly coloured merocyanine form, which also has an active binding site for certain metal ions. Therefore metal ion uptake can be triggered using UV light and subsequently reversed on demand by shining white light on the coloured complex, which regenerates the

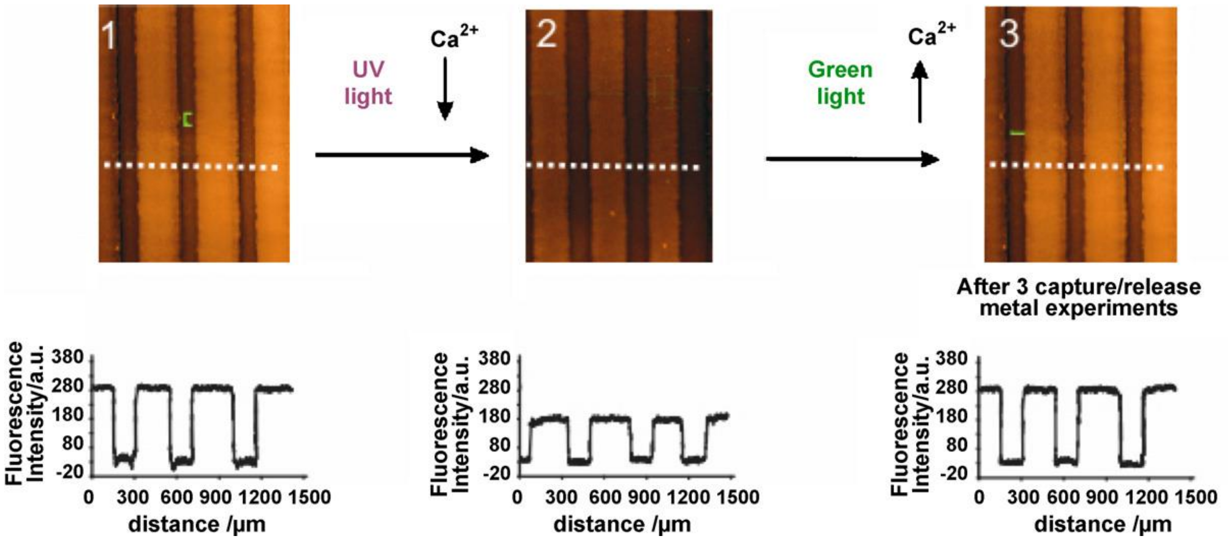

Fig. 10. Fluorescence intensity images (4× microscope magnification) of the merocyanine carboxylic acid derivative adsorbed in the PDMS channel walls before (photo-1) and after (photo-3) three consecutive capture/release metal ion experiments (Ca^{2+}) in ethanol. A dotted line across the chip in photos-1, 2 and 3 shows were the fluorescence emission intensity values were taken [16].

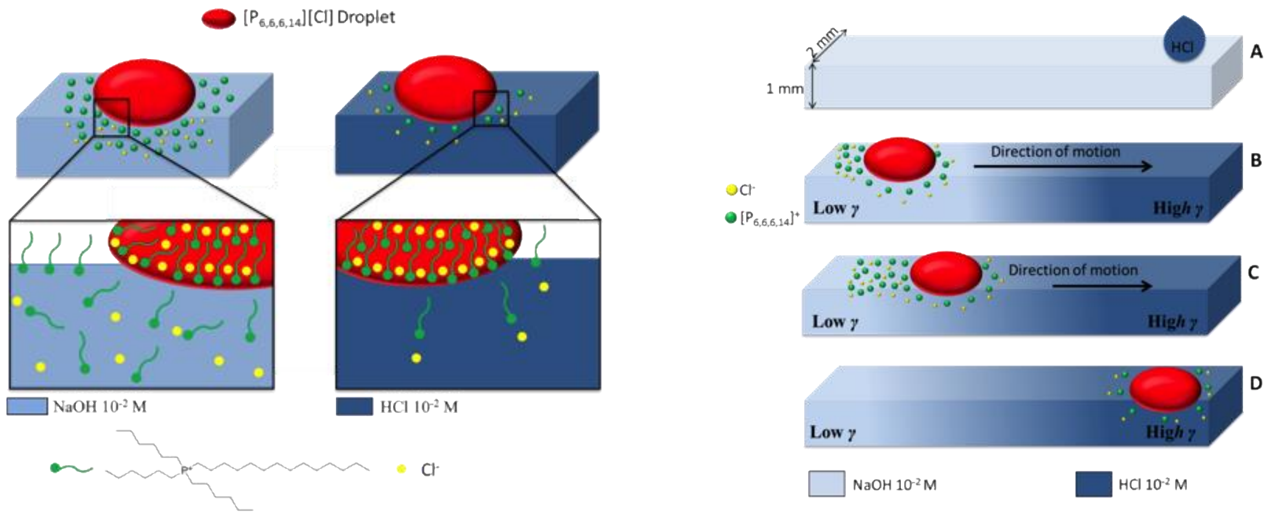

Fig. 11. Left: Diagram illustrating the much greater release of $[P_{6,6,6,14}]^+$ and Cl^- ions from the droplet 10^{-2} M NaOH (left) compared to 10^{-2} HCl (right). Right: Schematic representation showing the movement of droplet in open fluidic channels. A – Depicts the creation of the Cl^- gradient by adding a droplet of HCl to the channel, which was initially filled with 10^{-2} M NaOH solution. B –The IL droplet is placed at the alkaline end of the channel and in the $[Cl^-]$ gradient, surfactant $[P_{6,6,6,14}]^+$ ions diffuse into the solution preferentially from the droplet where the $[Cl^-]$ is lower (i.e. furthest away from the HCl). C – The local imbalance in the surfactant concentration leads to a corresponding imbalance in the local surface tension and the droplet is propelled towards areas of higher surface tension (towards the HCl source). D – Droplet arrives at the desired destination [17].

inactive spiropyran form, and releases the metal ion. When stock solutions of several metal ions (Ca^{2+}, Zn^{2+}, Hg^{2+} , Cu^{2+} , Co^{2+}) are pumped independently through the five channels, different optical responses were observed for each metal, and the platform can therefore be regarded as a micro-structured device for photo-controlled self-indicating metal ion complexation, accumulation and release [16]. In this particular experiment, Ca^{2+} ions accumulate only at locations that are in the merocyanine form. The dark vertical lines (1, left) define the spiropyran functionalised channels, which are easily distinguished by an enhanced fluorescence signature as illustrated by the horizontal cut marked by the white dashed line. When exposed to UV light, and Ca^{2+} ions, the active merocyanine form is created, and Ca^{2+} ion binding is signalled by a decrease in the fluorescence (2, middle). Exposure to green light restores the non-binding spiropyran with simultaneous release of the accumulated Ca^{2+} ions (3, right). This cycle of uptake and release of bound ions can be repeated multiple times. This shows again that the channels in microfluidic systems can play a much more active role, in this case through stimuli-responsive surfaces that can be switched between binding and non-binding forms using light.

Another interesting property of biological systems is chemotaxis, or the ability for an entity to move spontaneously along a chemical gradient to a particular location (usually the source of the molecular stimulant or signalling moiety). This behaviour can be mimicked using droplets that move spontaneously in response to a chemical stimulus. Movement is usually generated through asymmetric release of a surfactant, which results in an imbalance in the local surface tension, and the droplet moves spontaneously towards regions of lower surface tension. This interesting behaviour is of great interest, as it provides a simple mechanism for programmed movement to a specific location, without the need to pump or move the bulk fluid, and it points the way towards fluidic systems that can, to an extent, monitor its own condition using the chemistry of the local environment to provide a driving force and propel the droplet. The mechanism is illustrated in Fig. 11.

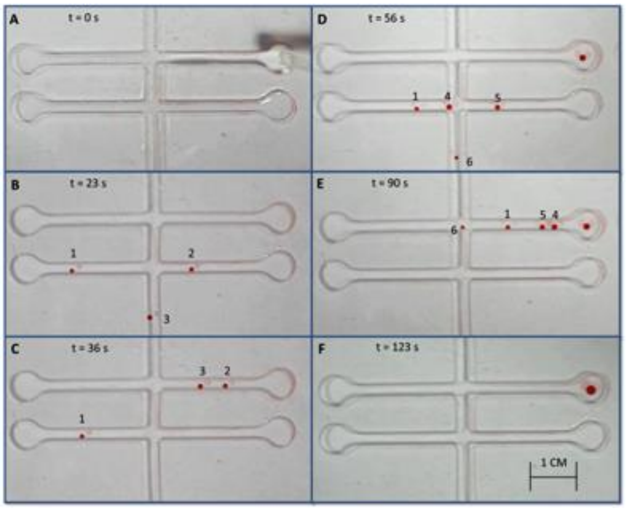

Fig. 12. Sequence of video frames showing multiple droplets travelling towards source of chemoattractant. A – Placement of chemoattractant. B – Place of first three droplets. C – First two droplets moving towards source. D – Place of final three droplets. E – Movement of all droplets toward source. F – All droplets arrive at destination and merge [17].

In this particular example [17], the droplet is formed from an ionic liquid ($[P_{6,6,6,14}][Cl]$. The sparingly soluble $[P_{6,6,6,14}]^+$ cation is a surfactant, which in the ionic liquid is strongly ion-paired with the Cl^- ion, in the form of a stable, lipophilic droplet that sits at the air-water interface. The $[P_{6,6,6,14}]^+$ cation solubility is mediated by the Cl^- ion solubility (due to charge balance in the droplet phase), which in turn is controlled by the local Cl^- concentration in the bulk aqueous phase. Therefore, when a local Cl^- ion concentration gradient is formed, for example, by diffusion of HCl or NaCl added at one end of the microfluidic channel, an unbalanced release of the surfactant $[P_{6,6,6,14}]^+$ cation occurs across the droplet/water boundary. The droplet begins to move and travels along the Cl^- concentration gradient to the point at which the HCl was added. It is envisioned that these droplets could be used for dynamic sensing (*e.g.* in this case they indicate the direction of increasing Cl^- concentration in the channels through their movement). In addition, they could provide energy-free molecular-cargo transport to specific destinations where they perform advanced functions. For example, through fusion of droplets that contain reaction precursors, they could cause localised polymerisation to block channels that may have become damaged. Damage may be detected through the introduction of chemical species that are not present in the normal fluidic system. Droplets programmed to respond to these species in principle should be able to find the location of the source of the species (the point of damage where the concentration is highest) where they automatically react to close off the damaged area. Fig. 12 shows an experiment in which a number of droplets (red) move to a location spontaneously, where they merge. Although this approach is limited (for example, the fluidic channels are open to provide the air-water-droplet interface that facilitates rapid droplet movement through surface tension effects) it does offer an intriguing insight into how microvessels might be able to perform autonomous damage detection and repair. The challenge is to demonstrate this behaviour in enclosed channels using perhaps channel surface/liquid boundary effects or other mechanisms to create spontaneous movement. Chemical gradients can also be created photonically [18] or electrochemically [19] within channels, enabling droplets to be directed or steered to particular locations.

Conclusions

Today, I believe that we are on the cusp of great advances that will lead to the realisation of devices with very advanced functionality, capable of performing tasks at a level far beyond what is currently possible. I have illustrated some of the functions that may illustrate the way ahead, which I am certain lies in the creation of devices that are bio-inspired in nature. Underpinning these advances will be the incredibly creative advances in materials chemistry and the emergence of hybrid materials based on synthetic biology. An increasing focus on stimuli-responsive materials and constructs (like beads, micro-swimmers and walkers, or other motile entities) will enable multifunctional fluidic systems to be realised. Fluidic channel walls will play a very active role, rather than just passively facilitate the movement of fluidics from one location to another. Fluidic systems will incorporate advanced functions such as autonomic detection and repair of damage, self-management and healing, which in turn will lead to longer functional lifetimes. Ultimately, perhaps we will be able to create platforms that can self-assemble to perform a function, and thereafter, dissociate back into the materials whence they came [20]. Perhaps through these exciting developments in stimuli-responsive materials, and creation of futuristic bioinspired microfluidic platforms, Richard Feynman’s ‘nanobots’ will finally become a practical reality [21]!

Acknowledgements

I wish to acknowledge the kind support of funding sources, Science Foundation Ireland, Enterprise Ireland, the Irish Research Council, The European Union, The EPA and Marine Institute, and the Australian Research Council. I particularly want to highlight the privilege I have had of working with the talented members of my research group over many years, and the numerous academic colleagues and friends who have so generously shared their ideas and knowledge with me. I also must mention the forbearance and support of my family (Tara, Helen, Danny and Anna) and of DCU in providing me with the facilities and environment to undertake my research. Finally, I wish to acknowledge the great honour of having received the Boyle Higgins medal from the Institute of Chemistry for 2015.

Biographies

Dr. Simon Coleman

Dr. Simon Coleman received his BSc in Analytical Science in 2006 at Dublin City University and subsequently his PhD in 2010 under the supervision of Prof. Dermot Diamond investigating the physicochemical properties of ionic liquids. His research interests encompass ionic liquids, polymer synthesis and stimuli responsive materials for sensor applications within the medical and environmental sectors. He is currently a Research Fellow in the INSIGHT Centre and coordinator of the EU project NAPES, which is a trans-European research effort involving industry and academic partners focused on the development of next generation analytical instruments incorporating advanced microfluidics functionalities for remote monitoring of key biological and chemical targets in water.

Dr. Larisa Florea

Larisa Florea studied organic chemistry and chemical engineering at University "Politehnica" from Timisoara, Romania (B.Sc. Hons 2009). In 2009 she joined the Adaptive Sensors Group at Dublin City University where she earned her Ph.D. under the supervision of Prof. Dermot Diamond and Dr. Fernando Benito-Lopez. Since 2013 she has carried out her postdoctoral research with Prof. Dermot Diamond in the INSIGHT Centre at Dublin City University, where she is currently Team Leader in smart materials and microfluidics. Her research interests include the design, synthesis and applications of stimuli-responsive polymers as novel sensing and actuating materials in microfluidic devices.

Prof. Dermot Diamond

Dermot Diamond received his Ph.D. and D.Sc. from Queen's University Belfast and joined DCU in 1987. He was Vice-President for Research at Dublin City University (2002-2004) and was director (2007-2015) and founding member of the National Centre for Sensor Research (www.ncsr.ie) at DCU. In 2002, he was awarded the inaugural silver medal for Sensor Research by the Royal Society of Chemistry, London. He was awarded the DCU President's Award for Research Excellence (2006) and the DCU President's Award for Innovation (2015). In May 2014, in recognition of his academic contributions and achievements, he was admitted to Membership of the Royal Irish Academy. In April 2015 he was awarded the Boyle Higgins Gold Medal by the Institute of Chemistry of Ireland in recognition of his research achievements. He is currently a principal investigator in the SFI INSIGHT Centre (http://www.insight-centre.org) and a member of the EU Future and Emerging Technologies programme advisory group (FETAG). His research is focused on the fundamental science of stimuli responsive polymers, the development of futuristic autonomous chemical sensing platforms, and the use of analytical devices and sensors as information providers for wireless networked systems i.e. building a continuum between the digital and molecular worlds. Further details of his research can be found at www.dcu.ie/chemistry/asg.

Eulogy to Dr. Paraic James

In 1987, I joined the faculty staff in the School of Chemical Sciences, of the then NIHE Dublin, now Dublin City University. On my first day, I was brought to an office I was to share with Paraic, who had been recruited the previous year. When I entered the office, Paraic greeted me and immediately made me welcome, dispelling the nervousness that always accompanies a move to new job. Over the years, Paraic played a major role in organising and managing many aspects of the School, ensuring that exam boards ran like clockwork, with any potential issues identified well in advance and solutions ready for proposal. Invariably, these solutions focused on the students involved, ensuring that their cases were dealt with fairly and humanely. His knowledge of organic chemistry was broad and deep, and he was always ready to assist me and other researchers with interpretations of characterisation data for new compounds. We are still trying to deal with the scale of his loss, which will be deeply felt in the years to come. In some small way I wish to acknowledge him as a person, and a colleague, through the dedication of this paper to his memory.

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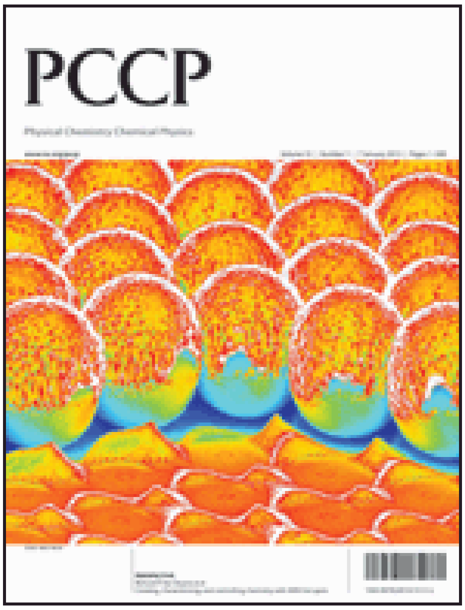

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Sensitizing Polyoxometalate Photochemistry for Photoelectrochemical Applications

Hugo Nolan & Tia E Keyes

School of Chemical Sciences, Dublin City University, Dublin 9.

This contribution is written in fond memory of Dr Paraic James, DCU.

Introduction

Photocatalytic materials are important across a range of applications from energy conversion and storage through environmental applications such as water purification to chemical synthesis. The most widely studied photoelectrocatalytic materials, where application of light and potential promotes the rate of photochemical reactions, are the semiconducting metal oxides including TiO_2, WO_3 and ZnO. However, a class of materials that is of growing relevance in this field is that of The Polyoxometalates (POMs). Research into catalytic applications of these metal clusters has been driven by their range of very attractive chemical properties including well defined redox behaviour, simplicity and low cost of synthesis and their low environmental impact. Indeed, POMs have been investigated across a very wide range of application fields outside of catalysis, including in sensing and medicine.[1–7]

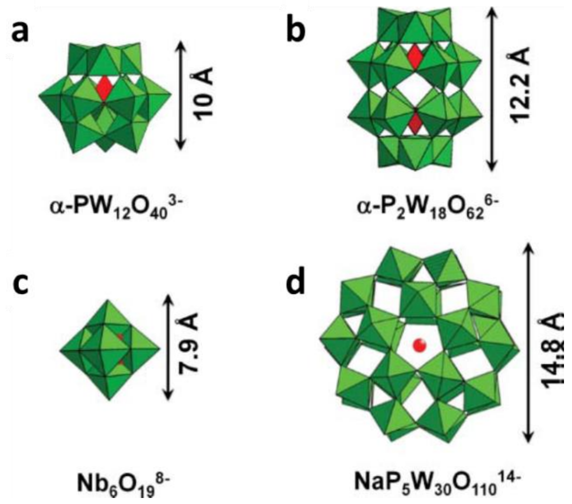

Figure 1: Schematics of various well-known POM structures: (a) Keggin, (b) Dawsom, (c) Lindqvist and (d) Preyssler. Reproduced from Wang and Weinstock[9] with permission from the Royal Society of Chemistry.

Polyoxometalates are anionic clusters comprised of high oxidation state transition metals (Mo, W, V and Nb, for example) linked *via* shared oxygen atoms. The polyoxometalates have diverse structural topographies, some examples are shown in fig.1. Here, we chiefly focus on Dawson and Keggin-type structures, which are counted amongst the earliest discovered and most widely studied POM-types.[8] Many POM structures (including those discussed herein) feature co-ordinated heteroatoms encapsulated within the cluster, sulfur in the form of SO_4^{2-} being an example. There is even structural diversity amongst single classes of POMs. Different structural isomers of a Dawson-type molybdate POM, for example are shown in fig.2, with the conventional structure shown in fig.2 (c). Non-conventional sulphite containing analogues of this structure are illustrated in fig.2 (a) and (b), representing the β and α phases, respectively. In the case of the α isomer the sulfite groups are staggered whilst in the β case they are eclipsed, with the α isomer being more stable owing to the thermodynamic favourability of this isomer.

Dawson-type POMs exhibit very well behaved electrochemistry; capable of undergoing multiple reversible proton coupled electron transfers under potential control, they also show resilience in various chemical, thermal and electrical environments.[9]

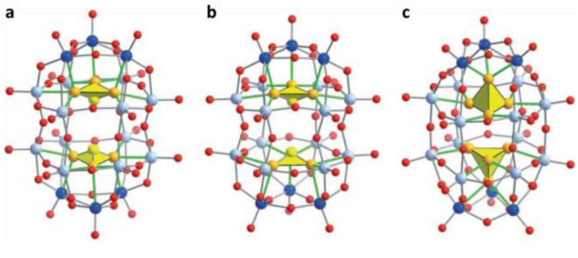

Figure 2: Structural isomers of the Dawson molybdate POM; (a) β-$[Mo_{18}O_{54}(SO_3)_2]^{4-}$, (b) α-$[Mo_{18}O_{60}(SO_3)_2]^{4-}$ and (c) α-$[Mo_{18}O_{60}(SO_4)_2]^{4-}$. Red=oxygen, light blue=belt Mo, dark blue=capping Mo, yellow=sulphite or sulfate anions. Reproduced from Baffert et al.[10] with permission from John Wiley and Sons.

In their oxidized state Dawson and Keggin POMs display Ligand to Metal Charge Transfer (LMCT) transitions with maxima in the near UV spectral region (typically between 250 and 380 nm), although in some cases absorption can extend into the visible.

The resulting excited state comprises a reduced metal centre and cation radical at the oxygen donor. The reactivity of this radical is considered to be the origin of the photocatalytic ability of POMs. POM LMCT excited states can lead to photocatalytic oxidation of a wide range of organic substrates through direct electron or electron coupled atom transfer, leading to reduction of the POM. Photochemically induced oxidation of the substrate is believed to occur *via* pre-association of the POM and substrate by H-bonding with water or a labile proton in an organic substrate.[11] In aqueous systems, excitation of the POM-H_2O complex leads to the formation of a hydroxyl radical.[12] This OH radical is itself a powerful oxidant capable of reacting with most organic compounds. In non-aqueous systems, pre-associated POM-substrate complexes form which can lead to direct electron or atom (H or O) transfer.[13]

Owing to the fact that POMs based on Mo and W exhibit little or no absorbance at visible wavelengths, exploiting their photocatalytic ability using solar irradiation is impractical under most conditions. Whilst extensive research has been carried out into sensitizing photocurrent generation on semiconductor-based systems (particularly TiO_2) under solar irradiation using visible absorbers such as ruthenium polypyridyl complexes, analogous work on POM photoelectrochemical systems is still in its infancy. Inspired by the sensitisation of TiO_2-based Dye Sensitised Solar Cells (DSSCs) visible region by red absorbing dyes,[14] we and others have been investigating the possibility extending the performance of POM-based photocatalysts to visible wavelengths by combining them with visible absorbing dyes.

Success here relies on understanding the photophysics of the sensitized system. Also of paramount importance to the development of industrially feasible POM photocatalysts are the stability of materials under photocatalytic conditions, fast interfacial Charge Transfer (CT) kinetics and an efficient closed photocatalytic cycle. The latter concerns the re-oxidation of the POM catalyst and is often rate-determining.

Photophysics of polyoxometalate charge-transfer salts

The formation of CT salts present one avenue by which sensitisers can be built into the POM structure. First explored by Balzani *et al*. using tungstate POMs and $[Ru(bpy)_3]^{2+}$,[15] it was found that changing the nature of the POM and Ru complex allowed the electron transfer between both to be tuned in solution based systems. Subsequent studies, such as those by Anson *et al*.,[16] examined electrostatically formed layered structures of POM/metal polypridyl complexes on electrode surfaces.

Whereas POMs such as the Dawson ions; $[S_2Mo_{18}O_{62}]^{4-}$ and -$[S_2W_{18}O_{62}]^{4-}$ have been shown to produce photocurrent in solution through oxidation of organic donors such as an alcohol under direct UV irradiation,[17–20] This photocatalytic ability is limited to excitation wavelengths shorter than 380 nm as the oxidized polyoxometalates do not absorb in the visible region.

However, photocurrent generation has been demonstrated in solution for Dawson-type POMs ion paired with a range of Ru(II) complexes under visible light irradiation, using both benzyl alcohol and DMF as electron donors.[21]. Our group have[22] shown that the Dawson POM Ru ion pair; $[Ru(bpy)_3]_2\alpha$-$[S_2Mo_{18}O_{62}]$ exhibits a new optical absorption centred around 480 nm. It was confirmed from resonance Raman spectroscopy that this feature is a CT transition between the ruthenium and POM. [21] Subsequent work indicated that this CT transition is nessecary to enable visible sensitization of POM photochemistry.[22–24] From analysis of a wide variety of POM/polypyridyl complexes, it is clear that a correlation exists between the generated sensitised photocurrent and strong inter-ion electronic communication. Even relatively small changes to the POM or ruthenium sensitizer structure can cause significant changes in CT behaviour in the ion pair switching on or off sensitization. Current data suggests that sensitization and CT are facilitated through H-bonding or through anion-π interactions between terminal POM oxygen atoms and the polypyridyl ligands on the ruthenium complex. Most notably, to date, we have only observed sensitization in ruthenium (II) complexes that contain a bipyridyl ligand.[22–24]

Chromophoric cations other than Ru-complexes have also been associated with POMs. Veya *et al*.[25] reported the Lindqvist POM $[Mo_6O_{19}]^{2-}$ forms a CT salt with a ferrocene derivative, $CpFeCpCH_2N^+(CH_3)_3$, resulting in a new absorption band at approximately 550 nm. Electrostatic composites of POMs and cationic porphyrins have also been reported; with these salts exhibiting high association constants, luminescence quenching and becoming dissociated in high ionic strength solutions. Further CT complexes have been reported in a wide range of salts formed between POMs and anthracene, perylene, quinolones, Co(III) macrocycles, single-wall carbon nanotubes (CNTs), spiropyrans and TiO_2 nanoparticles (NPs). However, to date there have been limited investigations into the capacity of these CT compounds to produce visible light sensitized photocatalysis.

Whilst POM CT assemblies can be conveniently formed through electrostatic association of component ions as outlined above, this approach is somewhat limited by lack of stoichiometric control and dissociation of the ion assembly in ionic environments. Reports of POMs covalently bonded to chromophores to form CT complexes are growing as this approach can offer greater control over POM functionalization. However the synthesis of such compounds can be onerous. Proust *et al.*,[26] for example, have described POM/$[Ru(bpy)_3]^{2+}$ complexes which are covalently bound and which exhibit predictable electron transfer kinetics but preparation of the complex requires 7 synthetic steps and multiple purification stages.

Interfacial polyoxometalate photochemical assemblies

Extending sensitized POM photocatalysis to interfacial films is an important step toward their implementation in solar energy or environmental applications. Our group have been focussing on translating Ru(II)polypyridyl-POM ion pairs into thin interfacial films at conducting surfaces. Typically, thin films of Ru(II)polypyridyl complex or metallopolymers containing the Ru(II)bipyridyl unit are deposited by layer-by-layer (LBL) assembly with POMs to form electrostatically associated structures which show good stability in contact with electrolyte.

POM-chromophore photocatalysts formed in this way have shown stable photocurrent generation in the presence of a range of organic substrates under broad spectrum visible illumination. Fig.3 shows as an example of the stable photocurrent which is generated due to oxidation of benzyl alcohol (BnOH) in an aqueous solution (2% v/v) at a single layer of α-$[S_2Mo_{18}O_{62}]$-$[Ru(bpy)_3]^{2+}$ formed on an ITO/glass electrode. An applied potential of 0.4 V vs. Ag/AgCl is maintained to re-oxidise the molybdate POM to ensure regeneration of the photocatalyst. These results have positive implications for the development of solar photocatalysts for organic synthesis and in environmental applications.

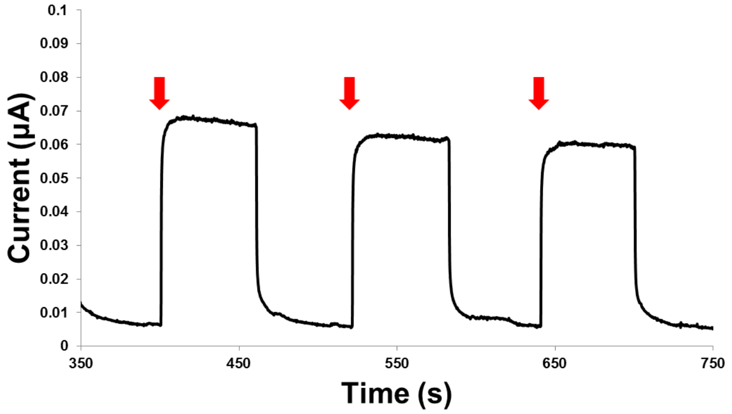

Figure 3: Photocurrent generation due to oxidation of BnOH (2% v/v) dissolved in water at an electrode of 1 layer α-$[S_2Mo_{18}O_{62}]$-$[Ru(bpy)_3]^{2+}$ on ITO under an applied potential of 0.4 V, vs. Ag/AgCl. Red arrows indicate start of illumination.

Metallopolymers are particularly attractive in thin film applications because of their processability, The metallopolymer $[Ru(bpy)_2(PVP)_{10}]^{2+}$ (where PVP = poly(4-vinyl)pyridine), structure illustrated in fig.4 (a), spontaneously forms stable interfacial films at gold and ITO electrodes and has performed positively in applications such as DNA detection and electroluminescence.[27,28]

We compared the photocatalytic performance of $[Ru(bpy)_2(CAIP)co\text{-}poly_7]^{+}$, fig.4 (b), (where (CAIP)co-poly$_7$ is poly(styrene$_6$-co-p-(aminomethyl)styrene) amide linked to 2-(4-carboxyphenyl)imidazo[4,5-*f*][1,10]phenanthroline) with that of $[Ru(bpy)_2(PVP)_{10}]^{2+}$ in multilayer assemblies formed with the Dawson-type POM α-$[S_2Mo_{18}O_{62}]^{4-}$ and found $[Ru(bpy)_2(CAIP)co\text{-}poly_7]^{+}$ did not sensitise the POM photoelectrochemistry under visible excitation whereas $[Ru(bpy)_2(PVP)_{10}]^{2+}$ did. Correspondingly the inter-ion electronic CT in the case of the$[Ru(bpy)_2(CAIP)co\text{-}poly_7]^{+}$-$\alpha$-$[S_2Mo_{18}O_{62}]^{4-}$ material was considerably weaker than the $[Ru(bpy)_2(PVP)_{10}]^{2+}$ as indicated by both UV/Vis and resonance Raman spectroscopy.[29]

Furthermore, it was found that the tungstate Dawson-type POM α-$[P_2W_{18}O_{62}]^{6-}$ exhibited a 7-fold increase in generated photocurrent when compared to the molybdate analogue, α-$[S_2Mo_{18}O_{62}]^{4-}$, when complexed with $[Ru(bpy)_2(PVP)_{10}]^{2+}$. This was attributed to the larger re-oxidation overpotentials of tungstates relative to molybdates.[30] It was also demonstrated that relatively high photocurrents could be generated in these systems without supporting electrolyte;[31] an attractive feature given the propensity for high ionic strength solutions to interfere with the electrostatic stability of POM salts.[32],[33]

Other groups have observed sensitization of POM photocatalysis by CT salts at electrode interfaces. For example hemicyanines have been used sensitisers for photocurrent generation.[34,35]

To date there have been few examples of interfacial photoelectrocatalysis in covalently bonded POM-chromophore systems.[36] Although there is growing interest in visible light sensitisation of POMs in conjunction with semiconductor materials such as TiO_2 nanotubes, TiO_2 nanoparticles, TiO_2 nanorods, CdS NPs, Au NPs and even graphene oxide.

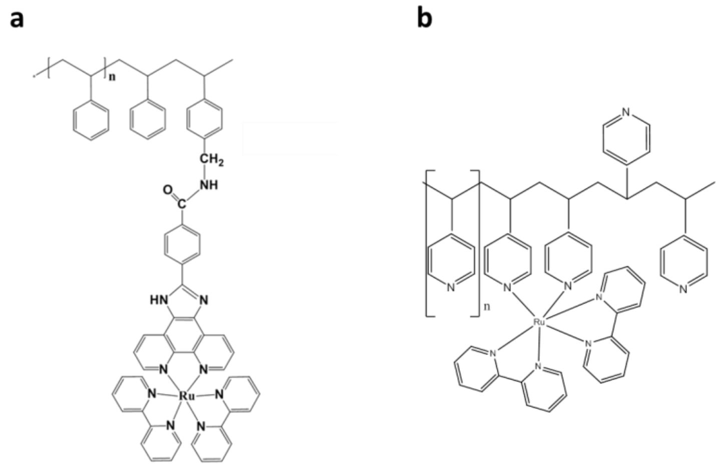

Figure 4: Structures of Ru(II) metallopolymers (a) $[Ru(bpy)_2(CAIP)co\text{-}poly_n]^{+}$ and (b) $[Ru(bpy)_2(PVP)_n]^{2+}$.

A rapidly growing research field in recent years has been that of water oxidation with the intent of generating clean fuels. Photo-oxidation of water aims to convert solar energy to chemical energy in the form of hydrogen gas; a means of energy storage. And, direct water photo-oxidation using POM-based photocatalysts are an attractive approach. Examples reported include catalysts based on sandwich-type.[37] Sensitized water oxidation photocatalysis by the sandwich POM structures has been reported with $[Ru(bpy)_3]^{2+}$;[38,39] $[Ru(bpy)_2(bpy\text{-}PO_3H_2)]^{2+}/TiO_2$[40] and Ru(II) metallodendrimers.[41] In addition, immobilized water oxidation electrocatalysis has been reported in films with polypyrrole[42] and also as the charge-compensated $[Ru(bpy)_3]_5[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]$.[43] Sandwich POMs substituted with metals such as Co[44] and Ni[45] have also been reported as reagents for water oxidation electrocatalysis. Sandwich-type POMs are not as well understood as the better established POM structures thus, future efforts will not doubt focus on fully understanding the catalytic mechanisms and stability of these materials.

Conclusions

Hybrid-POM materials where the POM photocatalysis is sensitized by a visible light initiated charge transfer process is a viable route to overcoming the poor visible absorption by POMS. However, there remain a number of challanges which must be overcome in translation of this approach to interfacial films; (a) Increasing surface area: Although they can be nanostructured, POM and hybrid POM thin films do not typically exhibit the high surface areas observed in nanocrystalline semiconductor materials, leading to small photocurrents in the region of 10^{-5} A cm^{-2}.[46] (b) Film conductivity: The limited conductivity of LBL assembled POM-chromophore films also limits generated photocurrent.[47,48] Incorporation of non-catalytic conductive materials within the POM thin films may improve films conductivity, though the cost/benefit of this approach must be considered. (c) Film crystallinity: LBL deposition of electrostatically formed POM hybrid materials forms amorphous films, which may impact upon film conductivity. Electrochemical cycling in acid has been demonstrated to improve crystallinity, although the impact on charge transport has yet to be established.[49,50] (d) The ruthenium polypyridyl sensitizers have performed well in sensitising POMs to visible light photocurrent generation, but suffer from narrow absorption cross sections. Recent developments in wide spectrum dyes for DSSCs might be applied to POM sensitisation;[14] provided electronic communication between the dye and POM is maintained.

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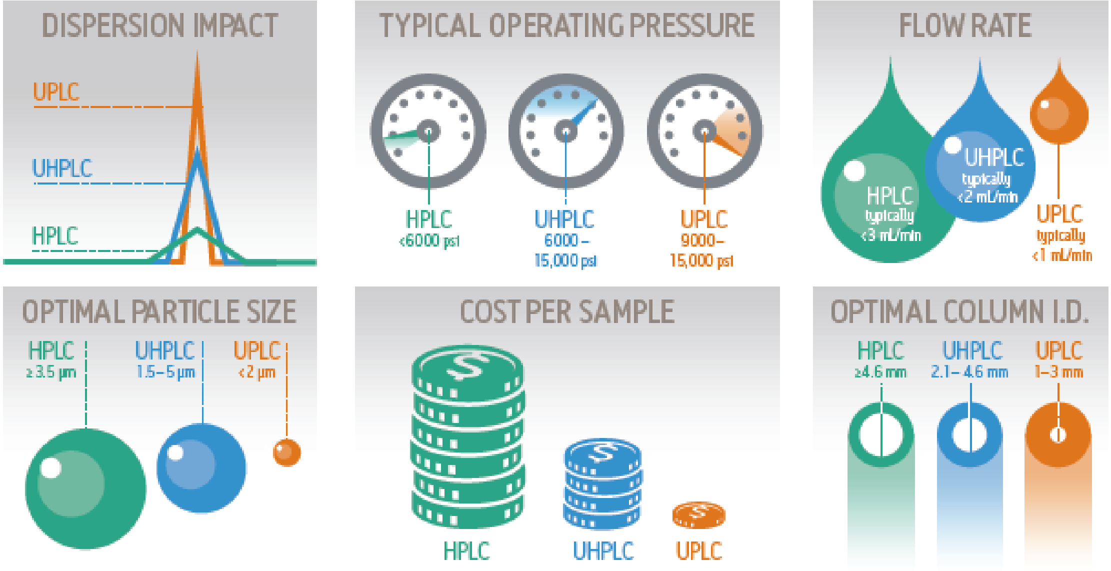
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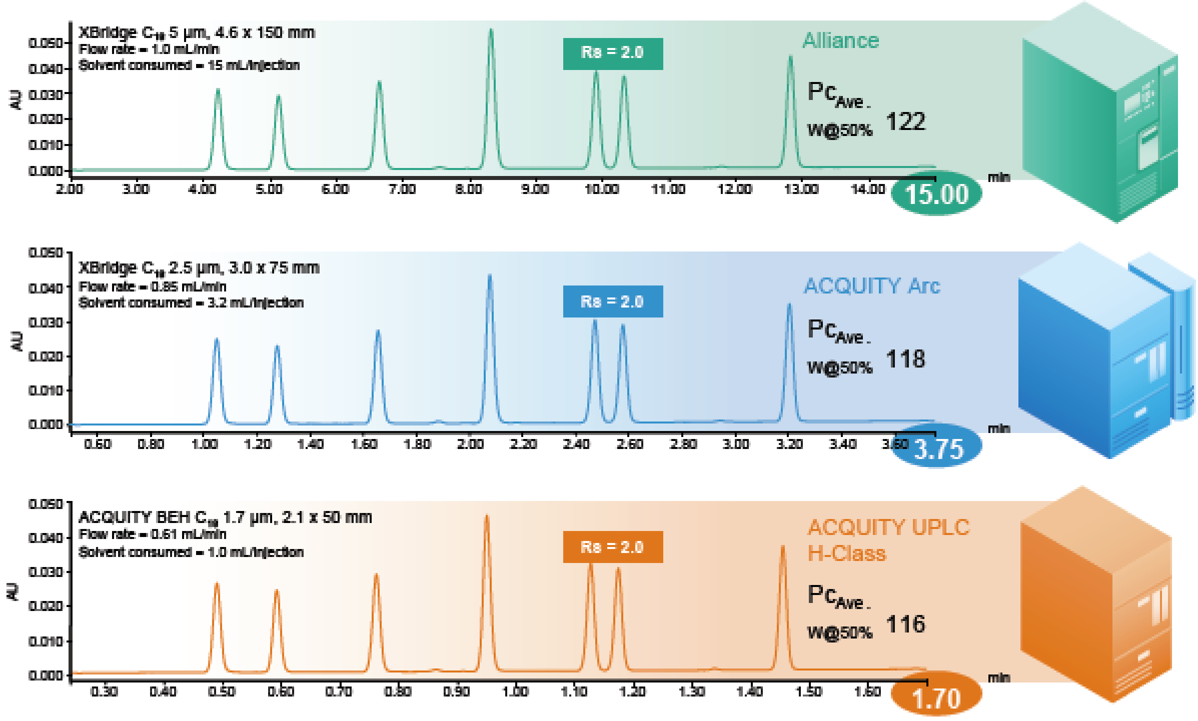

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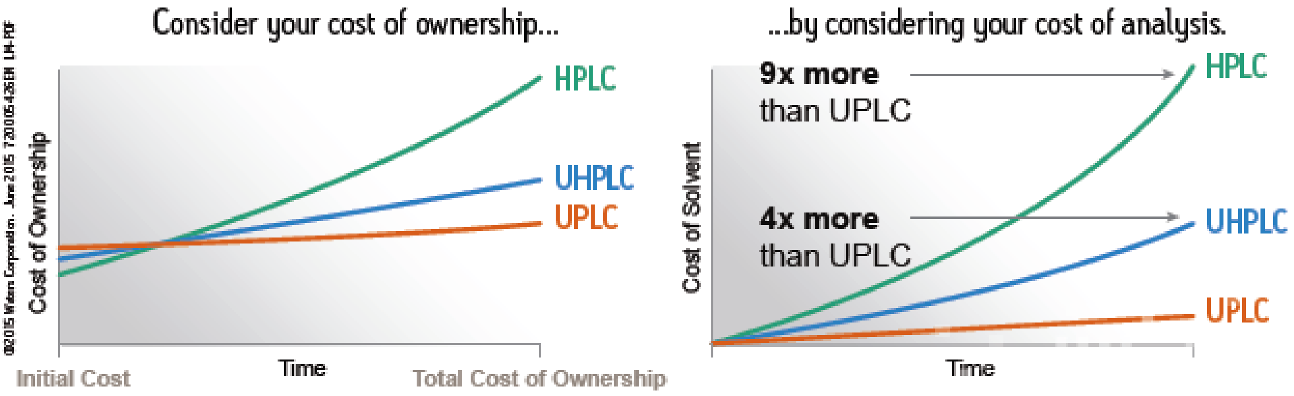

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To enhance the understanding of human interactions and attitudes with water;
To develop and promote improved methodologies for water management and;

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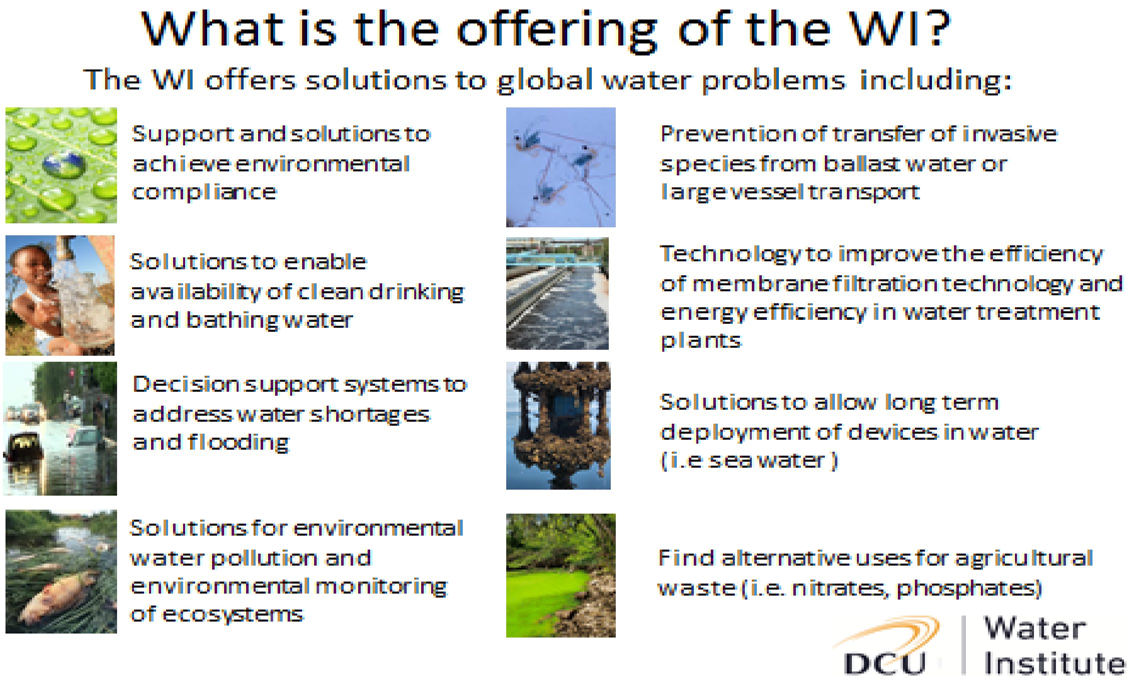

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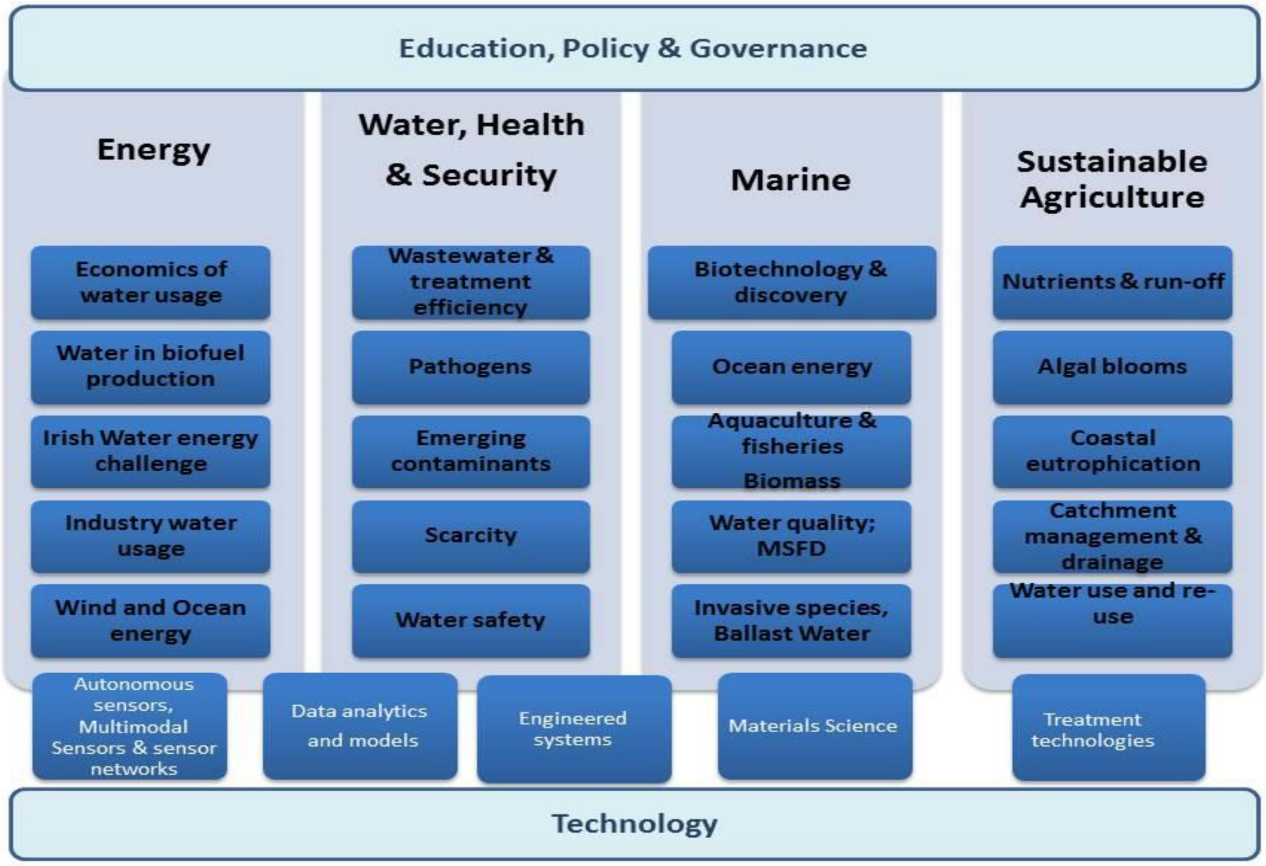

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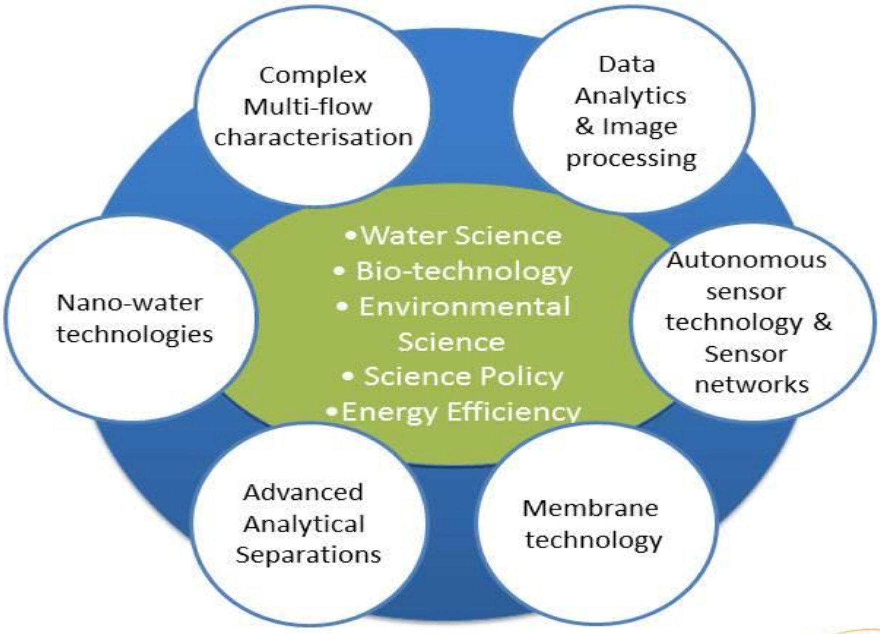

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Paris Agreement: Developing clean technologies for a better future.

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Introduction

The adoption of the Paris Agreement was an unprecedented political victory and represents a turning point towards low-carbon, resilient development. It was a huge event, with 37878 accreditations, 19385 national delegates, 8338 observers, 2825 journalists, 202 side-events and 203 exhibitions.

This victory has been welcomed by the whole world. For President Obama, "*the Paris agreement establishes the enduring framework the world needs to solve the climate crisis*", while Chancellor Angela Merkel said that the Paris Conference will be remembered as the turning point in climate politics and President Xi Jinping declared that the Paris deal, which resulted from concerted efforts by the international community, "*has charted a clear course for global cooperation on coping with climate change.*" Lastly, Prime Minister Narendra Modi considered that "*climate justice has won and we are all working towards a greener future.*"

It has also been welcomed by the scientific community and NGOs, which see it as "*a historic moment, not just for us and our world today, but for our children, our grandchildren and future generations*" (Lord Nicholas Stern), setting "*us on course to 100% clean energy*" which the world wants and the planet needs (Avaaz).

1. The Paris agreement

This text offers the best possible balance.

It prepares for the future and contains solutions for the present. It is universal, ambitious, fair and legally binding. On each of the key points of the negotiations, and particularly on the level of ambition, differentiation between developed and developing countries, and the necessary finance, an approach of receptiveness and determined compromise helped strike the right balance between ambition, universality and solidarity.

It is an ambitious agreement: it establishes the target of limiting the increase in temperatures to well below 2°C, and pursuing efforts to limit it to 1.5°C. In concrete terms, this ambition takes the form of a global emissions pathway: peaking of emissions as soon as possible, and emissions neutrality in the second half of the century.

In order to gradually enhance collective ambition, the agreement provides an enduring mechanism:

- all countries will submit or update a national contribution every five years, which will need to be increasingly ambitious each time;
- a global stocktake will be carried out every five years from 2023 onwards to review countries' commitments and decide on the measures that need to be taken to keep us on track towards meeting our targets;
- all Parties will hold an initial meeting in 2018 to review their progress, with a view to preparing or updating their national contributions.

It is a differentiated agreement: for the first time, all countries are committing to a universal agreement, reflecting the commitments of developed countries to reduce their emissions and acknowledging the gradual convergence of developing countries towards such a reduction, taking into account respective national circumstances and capabilities. The agreement establishes a mechanism to facilitate implementation and promote compliance. It will support States – from a facilitation, rather than a punitive, point of view – to implement and foster fulfilment of national commitments. Its rules of procedure will be established in the next few years, so that it can start operating from 2020.

It is an inclusive agreement: the agreement affirms the obligation to support developing countries in their efforts to reduce emissions and adapt to climate change. The accompanying decision extends until 2025 the commitment of $100 billion per year, which will then serve as a basis for a more ambitious financial target.

For the first time, adaptation to the effects of climate change is treated with equal importance to the reduction of greenhouse gas emissions. The agreement sets an overall objective for adaptation, and affirms the need to rebalance finance, especially public funds and grant-based resources. The issue of loss and damage is formally recognised, with the creation of an appropriate cooperation framework - including, in the decision, regarding to people displaced by climate change effects.

Lastly, the agreement establishes an enhanced transparency framework that is universal and flexible, so as to ensure effectiveness over time and build confidence between countries. It will help track the progress of each Party on mitigation, adaptation and support, while taking into account the respective capabilities of the countries.

The agreement does not simply state these targets. It converts them, in concrete terms, into a global greenhouse gas emissions pathway, and combines them with a dynamic ambition mechanism. It will enable us to gradually reduce the gap between current national contributions (around 3°C) and our targets. In 2018, the IPCC will publish a report on the impacts and emissions pathway linked to 1.5°C.

It is the most ambitious balance possible. It demonstrates the common determination of States to provide a universal response to climate change. That determination has been shown in the 187 national contributions published to date. In the agreement, many points - five-year cycles, long-term objectives, taking into account loss and damage - go far beyond what we could have hoped for just a few months ago.

The States are going to start implementing their contributions. The concrete cooperation projects launched in Paris, on clean technologies, climate warning systems, and renewable energy in Africa, are going to be implemented straight away. Non-state actors are going to take further action, as they are encouraged to do in the Paris decision, which is immediately applicable. They will meet in 2018 to review their progress and prepare or update their respective national contributions.

The Paris decision explicitly mentions carbon pricing as an incentive to reduce emissions. It also underlines the importance of renewable energy, in particular to expand access to sustainable energy in developing countries, notably in Africa. The Paris Agreement, on its part, leaves to States the sovereignty to decide the means they will use to fulfil their goals. In reality, many States, regions and businesses have already chosen to adopt carbon pricing and develop renewable energy: more than two thirds of countries that have submitted a contribution set out new objectives for these energy sources for 2025 or 2030. The momentum generated in Paris will speed this movement up, and the five-year review of the contributions will be an opportunity to unveil energy policies that are more ambitious each time.

After a formal signing ceremony on 22 April 2016, the agreement will be opened for ratification by States. It will enter into force after ratification by 55 countries, representing at least 55% of worldwide greenhouse gas emissions. Implementation of the agreement will lead to the creation of mechanisms for raising ambition, providing financial support, and tracking support and effort.

Regarding finance, the agreement establishes an obligation for developed countries to provide and mobilise finance, based on a principle of progression. It also recognises that public funds should play a “significant” role in climate finance. The agreement reached in Paris sends a strong signal to businesses, investors, local governments and citizens - the signal they were waiting for in order to strengthen their commitment. It will speed up the process of redirecting financial flows from high-emitting sectors, especially the fossil fuel industry, towards the low-carbon economy.

2. The role of science and technology

One important aspect in this process is the role of science and technology, both in the public and private sector.

First, scientists played a great role in the knowledge of climate change. The scientific conference “Our Common Future under Climate Change” (CFCC15), held in Paris in July, covered the full landscape of scientific knowledge on climate change. It was the largest international science conference before COP21, with nearly 2,000 participants from almost 100 countries. It was a great opportunity to explore current understanding of the climate change challenge and mitigation and adaptation options. The conclusions were circulated to all Higher Education Institutions and, within a few weeks, all Irish universities had signed with enthusiasm this declaration. Ireland was among the first countries in the world to achieve this.

Scientists can assess risks and options. They can help for smart decisions. As mentioned in the outcome statement : “*Solving the challenge of climate change requires ambition, dedication, and leadership from governments, the private sector, and civil society, in addition to the scientific community. We in the scientific community are thoroughly committed to understanding all dimensions of the challenge, aligning the research agenda with options for solutions, informing the public, and supporting the policy process*.”

Scientists play a key role in raising awareness and proposing new development models. During COP21 for instance, University College Cork presented a side-event on the “regional perspectives of an equitable decarbonisation of the global energy system” at Le Bourget. This led to explore what the fair decarbonisation of the energy system means from a justice, technology and financial perspective.

The investment in R&D is crucial. Solutions are proposed by companies and public laboratories, sometimes working together. They require investments for tests, development, prototypes, etc. National programmes are funding these projects. In France, the national agencies ANR (Agence Nationale de la Recherche) and ADEME (Agence de l'Environnement et de la Maitrise de l'Energie) are launching regularly calls for proposals with specific targets (marine renewable energies, green chemistry, etc.). In Ireland, similar agencies (Sustainable Energy Authority Ireland, Science Foundation Ireland, Environmental Protection Agency…) are also funding R&D in this sector. Other research programmes in Agriculture also focus on climate change. Recently, a new “ERA-NET” was launched for monitoring and mitigation of greenhouse gases from agriculture and silviculture. The name is ERA-GAS and European partners (including Teagasc in Ireland and INRA in France) are planning to launch a call for transnational research projects on 1st March 2016. Four research themes are proposed : “*Improving national GHG inventories and monitoring, reporting and verification of emissions; Refining and facilitating the implementation of GHG mitigation technologies;*

State of the art production systems that are profitable and improve food and forest biomass production while reducing GHG emissions; Assessment of policy and economic measures to support emissions reductions across the farm-to-fork and forest-to consumer chain."

Other examples exist in different thematic areas (sustainable energies, environment, etc.). Investments in climate-change adaptation and mitigation can provide benefits for everyone, as a "win-win" situation. The public sector will gain a protection from current climate variability, decrease damages from air and water pollution, and advance sustainable development. Private companies will find new opportunities and sell new products with a large demand. Thus, the investment in research, development, and technology transfer is crucial for our economies. It can concerns deforestation, energy efficiency, electricity generation, buildings, cars, aviation, heavy trucks, ocean ships and agriculture. New technologies with huge potential are already ongoing with solar energy, wind, bioenergy, and nuclear, with the possibility of breakthroughs.

Local authorities also played a great role in the development and implementation of initiatives. For instance, the Drive4 zero initiative was launched in October 2014 to promote electric vehicles in Cork City. Electric vehicle users benefit from free parking, free refills through ESB for employees of participating companies, free tolls… Incentives are provided for the purchase of an electric vehicle (€ 5000), including models such as Renault ZOE and Fluence. Today, similar initiatives emerge in both Ireland and France, and all over the world. They are supported by local authorities and at times by national agencies. They complement and answer proposals and recommendations brought forward by citizens and civil society.

Conclusion

On 16 December, more than 800 stakeholders – major cities, regions, companies and investors from around the globe – representing 150 million people and US$11 trillion promised to "quickly and effectively help implement the Paris Pledge for Action and accelerate the transformative changes needed to meet the climate change challenge."

The agreement will provide developing countries with the resources they need to extend access to renewable energy sources, curb deforestation and implement sustainable agriculture. It will also generate the momentum needed to continue the ecological and energy transition in developed countries and create millions of green jobs.

It will enable people everywhere to breathe cleaner air, gain access to a decent quality of life and see their fundamental rights respected. It will help to reduce risks of conflict linked either to competition for non-renewable resources or to climate impacts that have not been prevented or sufficiently well managed.

Jean-Pierre Thébault
Ambassador of France to Ireland

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Protecting Endangered Elements Report

Patrick Martin FICI

I attended this workshop co-hosted by **Ian Duncan MEP** and **David Cole Hamilton EuCheMS President** at the EuCheMS offices in Brussels on 22 September 2015.

Ian Duncan MEP gave the introduction to the workshop. He stressed the need to embrace the "Circular Economy" model, in other words, recycle as much waste as possible. He mentioned that while parliament is progressive with conservation policy, the public, regional politicians and industry are slower to engage in conservation of materials. He suggested that material recycling should be worked into global trade agreements.

At present carbon is by far the most widely talked about element with respect to conservation due to its role in global warming! However, carbon is not an endangered element. See periodic table below (Figure 1) with the endangered elements highlighted:

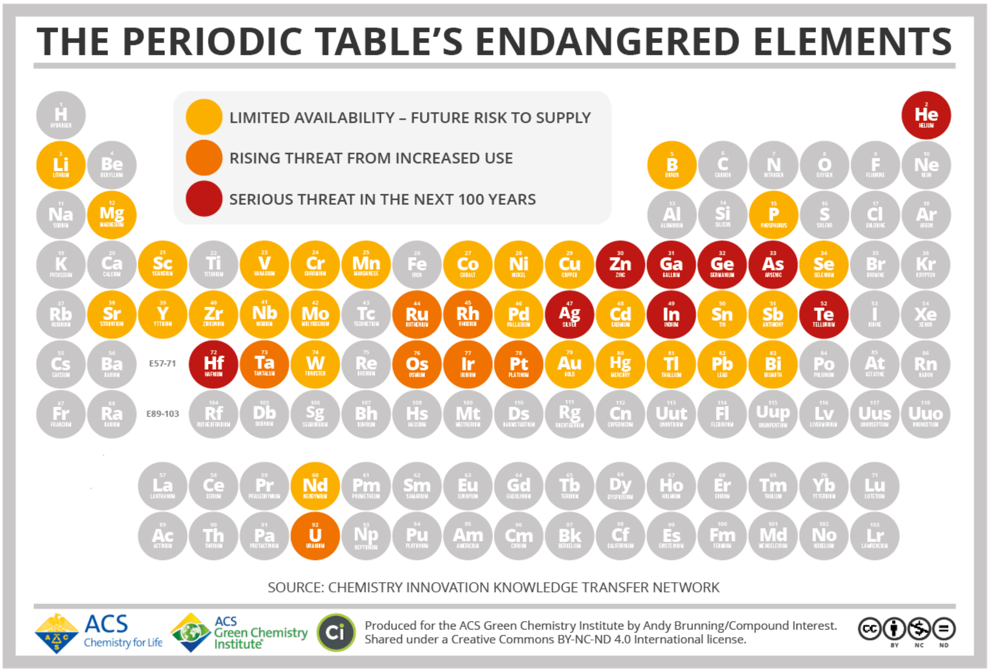


Figure 1. The lanthanides should also be highlighted as "Limited Availability".

Nicola Armaroli, The Institute of Organic Synthesis and Photoreactivity, Bologna gave a presentation entitled:

<u>Hunting the Elements of the Periodic Table on Spaceship Earth</u>.

He discussed how the escalated demand for electronic consumer goods over the past thirty years has led to the dramatically expanded use of several of the endangered elements. Whilst electronic devices have become miniaturised over this period resulting in "demateralisation", the reduction in material per device has been overcompensated by the increased demand of these goods.

There are several elements intensively mined now which were barely sought after thirty years ago. The alkali metal lithium (Li) is one of these and it has limited availability. This light metal has an extremely high electrochemical potential and is thus used in many rechargeable batteries today. Global supply at present is 36,000 tons per year. The largest producers are: Australia, Chile and China, but Bolivia has the largest reserves. If all cars sold today were electric and used lithium batteries, then 700.000 tons of lithium would be required per year. Recycling, which is relatively easy for lithium, needs to be stepped up in order to keep the supply going in the future. To illustrate the poor rates for element recycling see the diagram below (Figure 2):

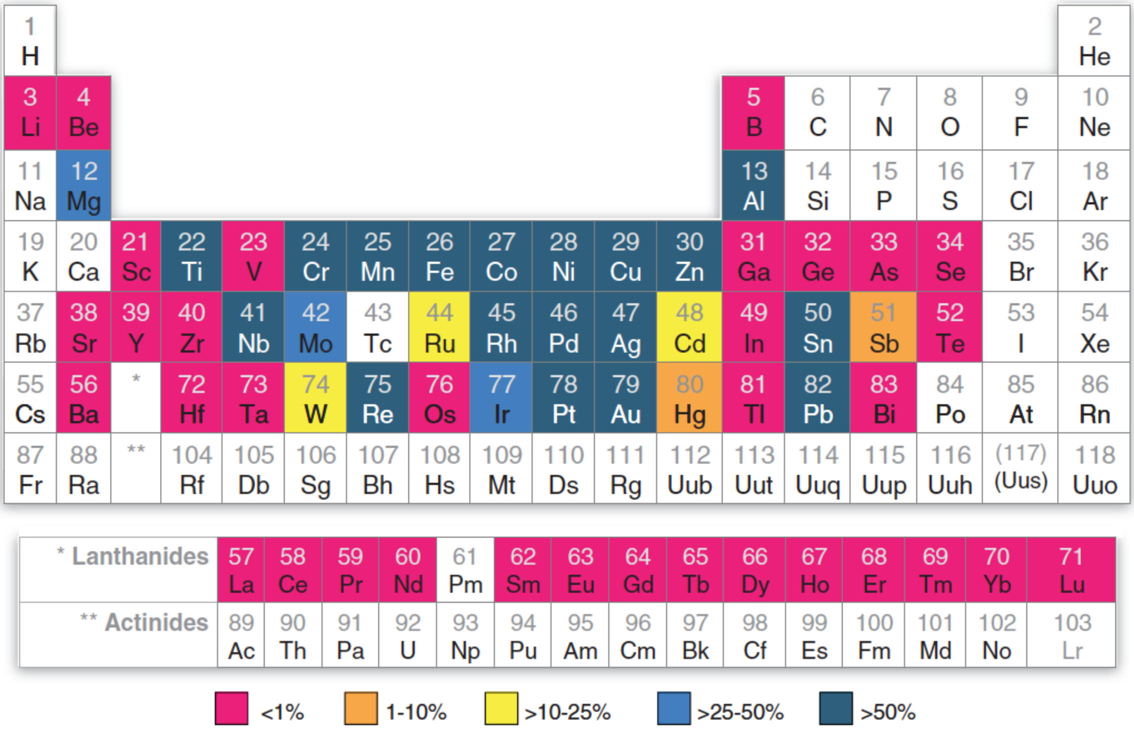


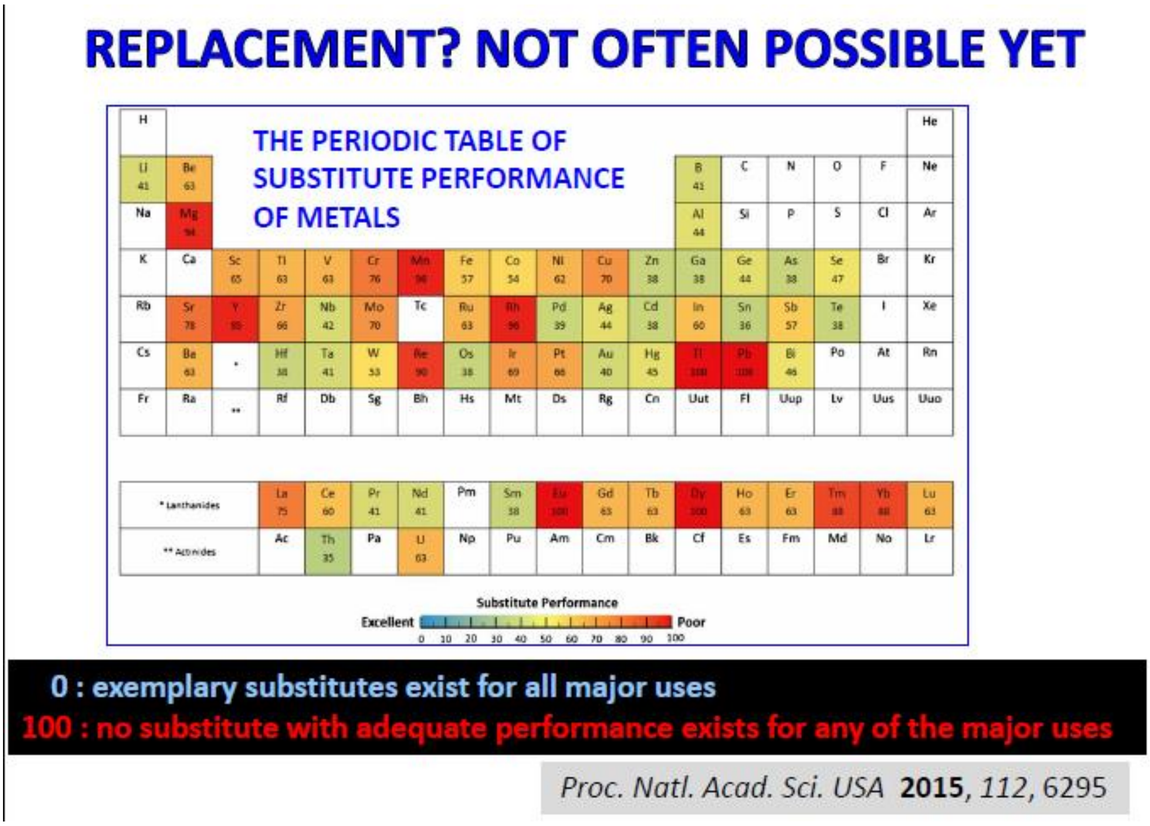
Figure 2. Rates of recycling

Another element the usage of which has increased recently is the metal indium (In). It is used in screens for various devices such as mobile phones due to its transparency and stability in air and water. The major producers are: China, South Korea and Japan, the amount of reserves are presently unknown. As this element is not mined directly but as a by-product of zinc, there is a risk of supply disruptions and price volatility. The rare earth elements, though not particularly rare, are not very economic to recover, as they are not concentrated enough in any one place. The Chinese have a monopoly with 95% of world supply. China sold these metals at low prices and other mines around the world could not compete, now China is exporting much less as its internal consumption has risen and this could lead supply issues. They have good magnetic, phosphorescent, catalytic and optical properties.

They are widely used in smart phones, cars and many other devices. There are now over 40 elements present in an iPhone (8 are rare earths), while in the 90's there were only 20 elements in an entire house http://www.rareelementresources.com. Interestingly Tesla Motors deliberately avoided the use of rare earth metals in their recent all electric Model S car.

Solar radiation (photons) is both extraterrestrial and the most abundant energy source for planet earth, and it must be harnessed more efficiently in the future. Photovoltaic thin film solar panels for renewable energy use these endangered elements: indium (In)**,** gallium (Ga) and tellurium (Te). LEDs are energy efficient lighting devices but use seventeen times more metals than the higher energy consuming CFL bulbs. The platinum group transition metal, iridium (Ir) is endangered due to increased demand and it being one of the least abundant elements. It is used in spark plugs and catalysts as well as electronic devices. Organic complexes of iridium (III) have been developed in Bologna and found to be very stable and tenable. These complexes have found applications in the low energy OLEDs.

Europe relies heavily on imports for most of its metal demands. However, copper (Cu) is recycled in the EU resulting in its import being cut in half. Many endangered elements have no substitutes as shown in the periodic table below (Figure 3):



REPLACEMENT? NOT OFTEN POSSIBLE YET

THE PERIODIC TABLE OF SUBSTITUTE PERFORMANCE OF METALS

H																	He
Li 41	Be 63											B 41	C	N	O	F	Ne
Na	Mg 94											Al 44	Si	P	S	Cl	Ar
K	Ca	Sc 65	Ti 63	V 63	Cr 76	Mn 96	Fe 57	Co 54	Ni 62	Cu 70	Zn 38	Ga 38	Ge 44	As 38	Se 47	Br	Kr
Rb	Sr 78	Y 95	Zr 66	Nb 42	Mo 70	Tc	Ru 63	Rh 96	Pd 39	Ag 44	Cd 38	In 60	Sn 36	Sb 57	Te 38	I	Xe
Cs	Ba 63	*	Hf 38	Ta 41	W 53	Re 90	Os 38	Ir 69	Pt 66	Au 40	Hg 45	Tl 100	Pb 100	Bi 46	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

* Lanthanides	La 75	Ce 60	Pr 41	Nd 41	Pm	Sm 38	Eu 100	Gd 63	Tb 63	Dy 100	Ho 63	Er 63	Tm 88	Yb 88	Lu 63
** Actinides	Ac	Th 35	Pa	U 63	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

0 : exemplary substitutes exist for all major uses

100 : no substitute with adequate performance exists for any of the major uses

Proc. Natl. Acad. Sci. USA **2015**, *112*, 6295

Figure 3. Substitute performance of metals.

Claire Carmalt, University College London, gave a presentation entitled:

Sustainable Manufacturing of Transparent Conducting Oxide (TCO) Thin Films.

Transparent conducting oxide thin films use many of the endangered elements in their oxide forms: In_2O_3, SnO_3, Ga_2O_3, ZnO. These oxides are doped with other elements such as fluorine to provide the desired properties of transparency and conductivity for the thin films. Such thin films are used in photovoltaics, solar panels, touch screen devices etc.

There is a need to replace indium (In) and tin(Sn) due to reduce availability and price rises. 56% of indium usage is in flat panel devices. Titanium oxide (TiO_2), which is much more plentiful has been successfully used as a substitute. Titanium can be doped with fluorine and the transition metal niobium (Nb) for use in TCO thin films.
Methods for manufacture of TCO thin films needed to be optimised to reduce costs. An efficient *aerosol-assisted chemical vapour deposition* process was developed and optimised by Claire Carmalt's team at UCL in collaboration with various faculties at Loughborough University. This has been brought to a commercial scale with significant cost savings over the previous *sputter deposition* process, which had resulted in a lot of waste.

Willem Schipper**,** Schipper Consulting, Netherlands, gave his presentation entitled:

The Story of Phosphorus.

Phosphorus (P) although a ubiquitous element has limited availability. Its largest availability is in the form of phosphoric acid (H_3PO_4). It is essential for life and is endangered due to it going to waste in the ground and not being recovered. Phosphorus is relatively easy to recycle. It was placed on the European Commission Critical Raw Materials list in 2014. Morocco has 77% of phosphorus mine reserves, this could give rise to supply fluctuations if there was to be geopolitical instability.

The use of phosphorus needs to be limited where leaching into water ways is likely. The latter causes over enrichment (eutrophication), resulting in excess growth of algal bloom which has an adverse effect aquatic life. The largest use for phosphorus is in inorganic fertilizers, overuse of which gives rise to leaching. Phosphorus is also lost during slaughtering. There are various directives throughout the EU stating that fertilizers and animal slurry may not be applied to land during the winter months to reduce both phosphate and nitrate leaching. Also there have been soil phosphorus levels determined in order to prevent the over use of phosphorus containing fertilizers. Restriction of phosphorus levels in the soil by some EU member states involve control of livestock density and reduction of phosphorus in animal feedstuffs.

Incineration of phosphorus containing sludge (meat industry, sewage, manure, chemical/metallurgical) has been practised in Europe, however the ash goes to landfill. See www.recophos.org for recovery of phosphorus from sewage sludge by the monoincineration *Thermo-Reductive RecoPhos Process* in Austria. Some of the waste residue is used as a binder for cement and as a high calorific syngas for thermal energy generation. The ash is used by ICL Netherlands to produce fertilizers.

Constantine Ciupagea, European Commission Joint Research Centre (JRC), gave a presentation entitled:

Critical Raw Materials. http://www.criticalrawmaterials.eu

He talked about the Circular Economy based on a life cycle approach. In 2014 the EC produced a list of 20 critical raw materials. These are critical because of their high economic value to the EU and because there could be a supply risk. See global locations diagram below: An EU report on critical raw materials predicts there will be a rapid increase in demand over the next 5 years. Previous research was focused mainly on the energy resources oil and gas. There is a Raw Material Knowledge Base held by the EU. Input to this Knowledge Base comes from international sources: EU-USA-Japan. They have focused on recyclability and substitution in their strategies based on the life cycle approach. Substitution is not only about finding replacement materials but also engaging in activities like reducing reliability on the critical materials. Looking at criticality of a material in the supply chain and how it is managed at end of life is also important.

The research of the Joint Research Centre on critical raw materials also feeds into EU industrial policy. To mitigate against potential supply issues the EU are incentivizing European production of critical raw materials which stimulates the launching of new mining activities within the EU. Europe is the poorest continent in the world when it comes to minerals.

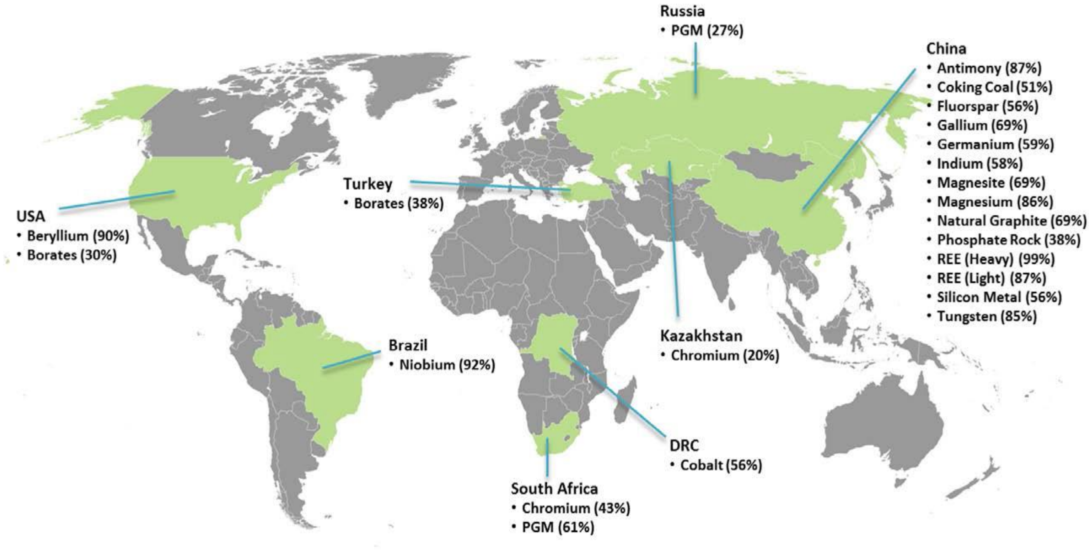


Figure 4. Critical Raw Materials.

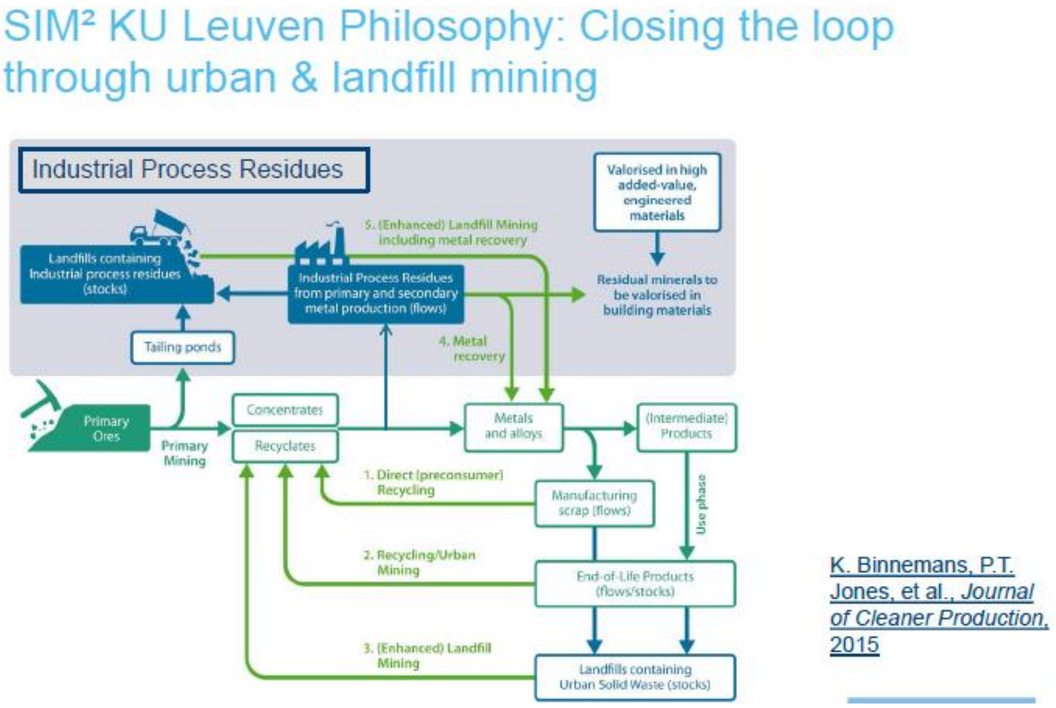
Ecodesign Regulation, which is part of the life cycle approach, will ensure manufactures design goods with ease of disassembly in mind. This makes recycling more efficient, for example components containing critical materials such as circuit boards (platinum group metals - PGM) can be placed in a specific recovery process when recycling.

Amsterdam council in cooperation with numerous other local bodies have established a successful recycling facility based on the “Circular Economy” It is still not complete in all features of recycling such as electricity and heat but it works well so far. The next update of Critical Raw Material list is 2017, the EC is monitoring endangered elements more closely now than at any time before.

Peter Tom Jones, Katholieke Universiteit Leuven, Flanders, gave a presentation entitled:

Towards Zero-waste Valorisation of Fresh Landfilled Wastes and Residues.

He discussed the philosophy behind the recovery of value-added materials from landfill with the aid of flow diagrams, see flowchart below (Figure 5):


SIM² KU Leuven Philosophy: Closing the loop through urban & landfill mining

K. Binnemans, P.T. Jones, et al., *Journal of Cleaner Production*, 2015

Figure 5. Recovery of value-added materials from landfill.

There are many practices where landfill recovery has been successful. For example, in Flanders which has approximately 12000 landfill sites and several metal processing companies which now have the ability to recover high value low concentration metals. Metallo-Chimique and KU Leuven invested in a fumer to clean landfilled fayalite slag which yielded new binders.

A new SUPERMetalEXtractor has been built in Flanders. This facility processes the residue, goethite, produced from zinc smelting by Nyrstar. After extraction of the main element iron (Fe)**,** high value endangered metals such as indium (In), germanium (Ge), thallium (TI), cadmium (Cd), manganese (Mn), copper (Cu) and silver (Ag) are recovered.

CFL bulbs contain expensive rare earth elements which are normally difficult to recover. A new simple three step process was developed at KU Leuven which involves using an ionic liquid to selectively dissolve yttrium and europium (Y_2O_3 :Eu (III)) from the matrix, and recover the expensive Y:Eu phosphor in a purity comparable with that commercially available. Rare earth elements were at their highest price in 2011 but since have dropped, making it less attractive to recycle them.

After extraction of aluminium from bauxite there remains the bauxite residue known as red mud. This residue contains several metals including iron (Fe) and endangered rare earth elements. It has been mainly used in the construction industry after the extraction of iron. However, there exists 2.7 billion tonnes of red mud in holding ponds worldwide thus providing further opportunity to recover rare earths such as scandium (Sc) which is in a relatively high concentration. The first zero-waste valorisation process on bauxite residue has been achieved by KU Leuven. This process yields: aluminium (Al), iron (Fe), titanium (Ti), scandium (Sc) and some other rare earth elements.

The outcome of this workshop is summarised as follows:

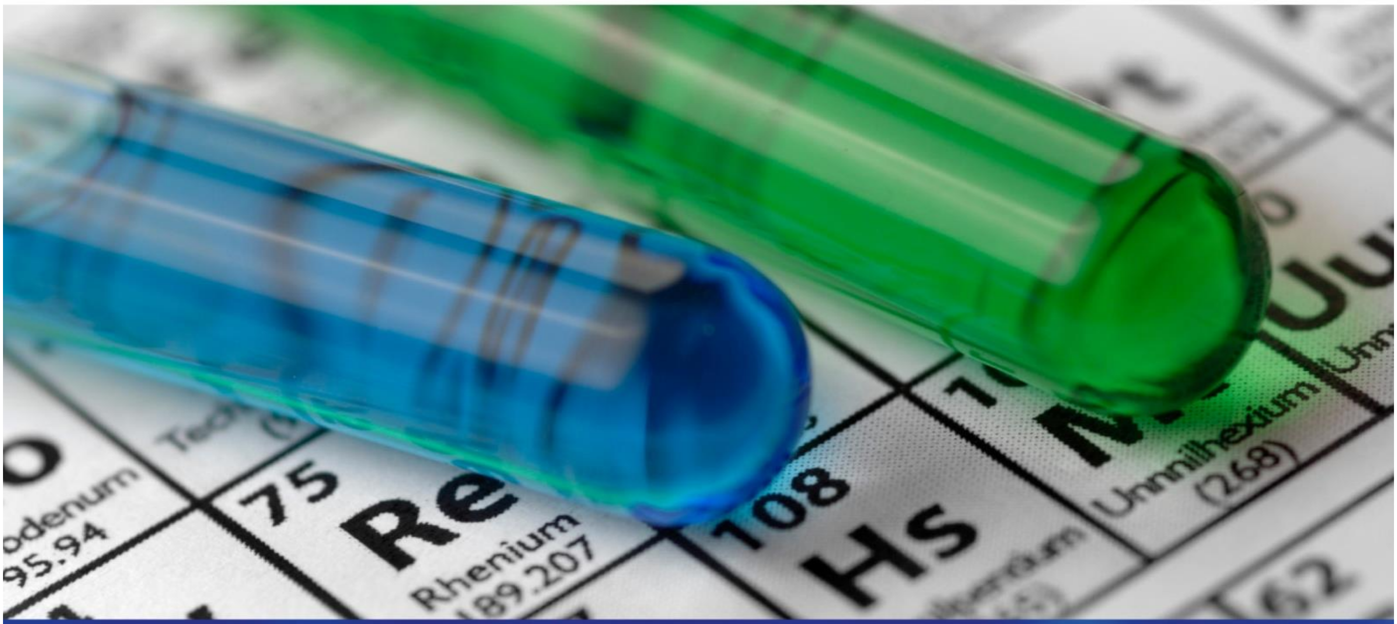
The amount of recycling of endangered elements must be greatly stimulated as it is very poor at present. It remains as an opportunity for technological innovation.

Substitution of components which use rare elements with components that use more plentiful elements is just in its infancy. Collaboration of public and private bodies and higher education research institutes must become more widespread in order to come up with solutions to conserve rare materials. EU directives need to focus more on gathering information on the landfill sites in Europe in order to have a good estimate of reserves for reworking into useful materials. It is estimated that 70% of toxic pollution in landfill comes from electronic waste. This leaves huge opportunity for recovery of rare metals.

Patrick Martin FICI

Institute of Chemistry of Ireland.

European Representative.


75
Re
Rhenium
189.207
108
Hs
Unnilhexium
(268)

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TrainMiC
Training in Metrology in Chemistry

Provided by Barbara O'Leary, Chair Eurachem Ireland, The State Laboratory

Eurachem Ireland will host a TrainMiC® workshop on Metrology in Chemistry on 20 April 2016 at the State Laboratory. The workshop will be delivered by TrainMiC trainers and 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.

TrainMiC® is a European programme for life-long learning about how to interpret the metrological requirements of ISO/IEC-17025 for chemical and bio-analytical measurements in many different sectors (environment, food, consumer protection, etc.). It is co-ordinated by the JRC-IRMM, an institute of the European Commission.

The vision of TrainMiC® is to improve the quality of analytical results by promoting and providing a European-wide, harmonised training in Metrology in Chemistry via a network of national providers sharing resources.

The purpose of TrainMiC® is to facilitate the training of metrology in chemistry to laboratory staff, researchers, educators, decision-makers and accreditation assessors, in order to strengthen the measurement infrastructure.

Details of the workshop including registration details are available at www.statelab.ie/eurachem.html or eurachem@statelab.ie.

Eurachem Ireland Spotlight on Analytical Chemistry

DIOXIN/PCB ANALYSIS BY HIGH RESOLUTION GAS CHROMATOGRAPHY MASS SPECTROMETRY (HRGCMS).

The Contaminants Section. The State Laboratory.

Introduction

Dioxins (PCDD/Fs) and dioxin-like PCBs are persistent organic pollutants (POPs) and have been the main contaminants in food and feed related incidents in the past decade. In December 2008, there was a major recall of Irish pork products following contamination with dioxins **[1]**. It was found that dioxins had entered the food chain through the contamination of animal feed in one location. The incident highlighted the necessity for increased routine monitoring of both animal feed and human food for dioxins and related substances. The State Laboratory is Ireland's National Reference Laboratory (NRL) for dioxin analysis and since January 2009 has developed the expertise and technical capacity to carry out the required testing. This article describes the facility's main analytical method for dioxin determination in samples.

PCDD/Fs and PCBs

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are chemically classified as polyhalogenated aromatic hydrocarbons (PHAHs) and consist of two halogenated phenyl rings with 75, 135 and 209 possible congeners respectively, depending on the degree and location of chlorine substitution **(Fig. 1)**.

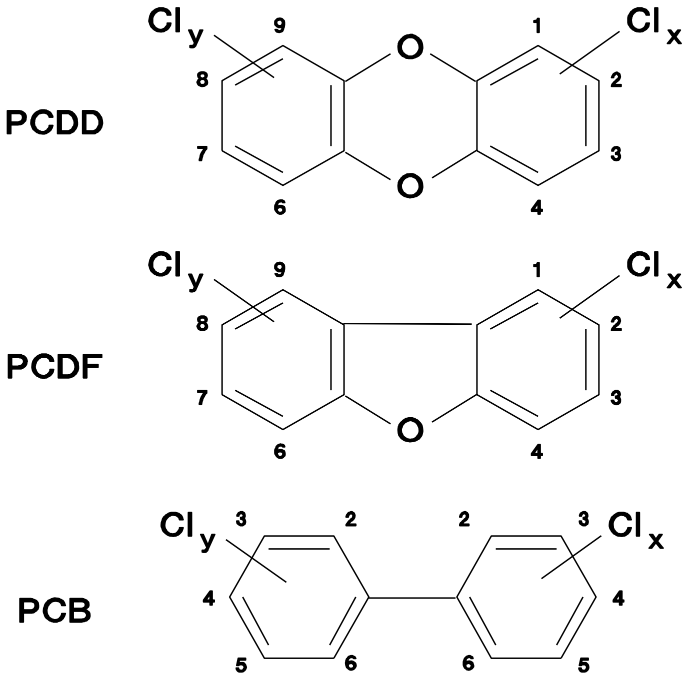


Fig. 1 - Molecular structure and ring position of PHAHs

Toxicity of PHAHs

The toxicity of PCDDs, PCDFs and PCBs depends on the degree and position of the chlorine substituents and only 7, 10 and 13 respectively are thought to have dioxin-like activity. All of the latter 13 PCB congeners have 4 or more chlorines with one or zero substitutions in the ortho position. These congeners are sometimes called co-planar (i.e. they assume a flat configuration with the benzenoid rings in the same plane).

Dioxins build up primarily in fatty tissues over time (bioaccumulate) so even small exposures may reach dangerous levels. Effects on humans may include thyroid/immune disorders, damage to central/peripheral nervous system and the development of a severe form of persistent acne know as chloracne.

FAT Extraction

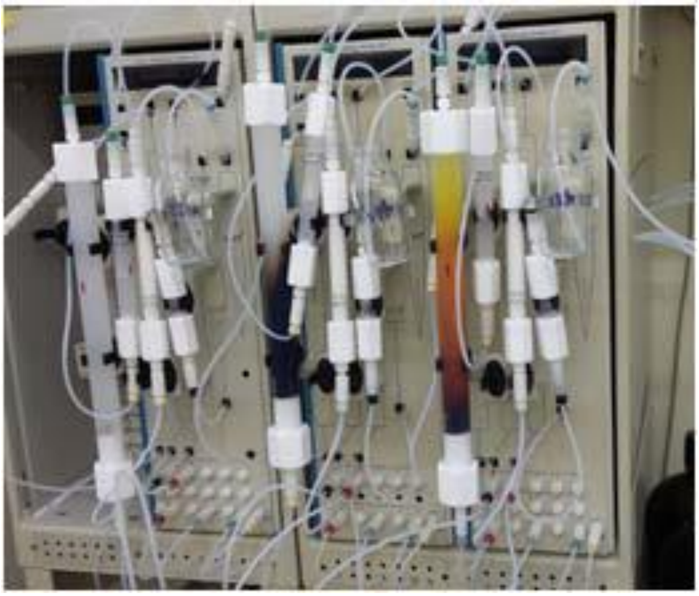
The fat content in a sample is the target matrix as dioxins & PCBs accumulate in this tissue after exposure, and the analytical profile of the congeners gives an indication of the degree of exposure over a period of time. The fat is extracted from the initial sample using a process called Accelerated Solvent Extraction, which is a patented technique for the extraction of solid and semisolid sample matrices using common solvents at elevated temperatures and pressures.

The solvents employed are Toluene and Ethanol for animal feed samples and Hexane, Dichloromethane and Methanol for Dairy/Milk Powder samples. The volumes of the resulting extract are reduced to ~5mls by evaporation prior to clean-up

Power Prep Clean-up

The Power-Prep™ is an automated and Integrated Sample Extraction and Cleanup System with disposable columns through which the sample extracts are pumped. The first column contains acidified silica which digests the fat and renders the extract more amenable to clean-up, which is carried out on the subsequent columns containing Silica ABN, Alumina and Carbon/Celite. The system yields two different fractions per sample by using different solvent combinations which minimise the presence of co-extracting interferences in each one. Fraction A contains the Mono-ortho PCBs and indicator PCBs; Fraction B contains the dioxins and non-ortho PCB congeners.

Each fraction is evaporated to near dryness and the final volume prior to HRGCMS analysis is 500ul. This concentration step enables the required sensitivity to be achieved on the instrument as the levels required by EU legislation are in the parts per billion order of magnitude. Each fraction is injected and processed separately and the results are combined for calculation of TEQ levels for each sample.



Power-Prep™ Sample Extraction and Cleanup System

HRGCMS Confirmatory Analysis

HRGCMS using the isotope dilution method for PCDD/Fs and PCBs can reliably provide quantitative results for the most toxic 35 congeners. This is a highly accurate, sensitive and selective method of determination, requiring a more rigorous extraction and clean up **[2-3]**.

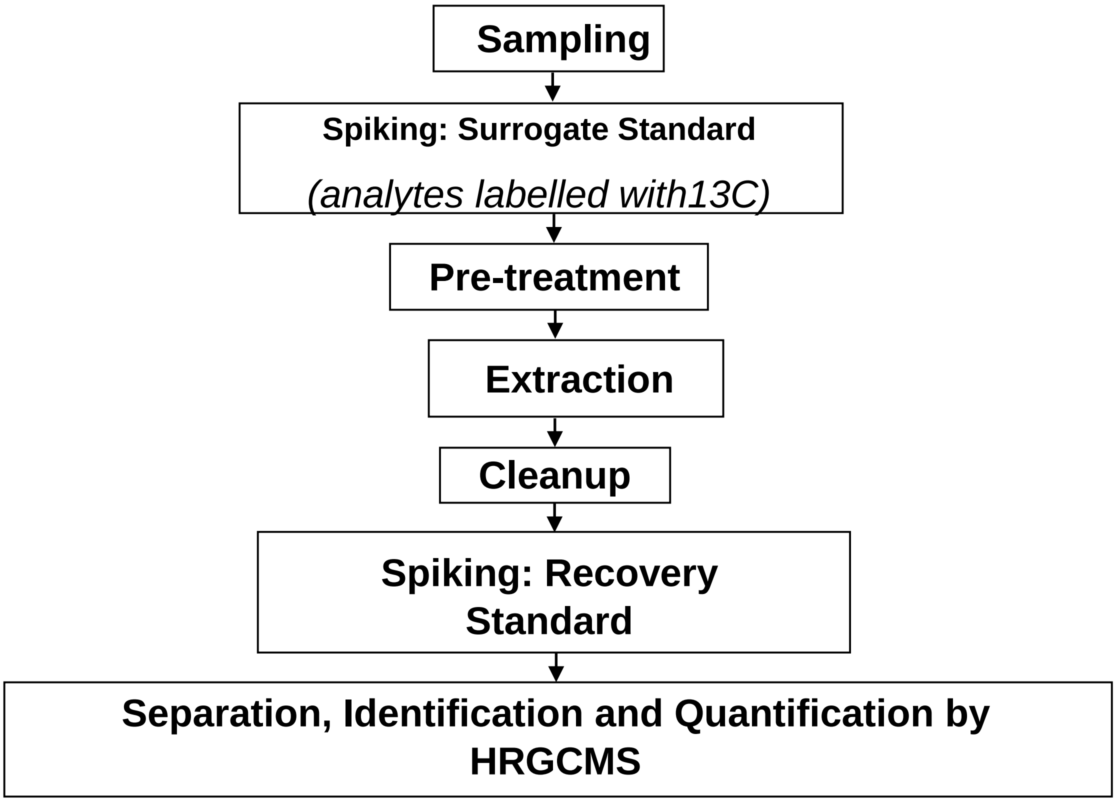


Fig. 2 – Overview of Principal Steps in Dioxin Confirmatory Analysis

The process outlined in Figure 2 allows for a complete forensic profile of the PCDD/Fs and/or PCBs which is very useful in determining sources of contamination.

The TEF concept

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) is considered the most toxic of the congeners. Other dioxin congeners (or mixtures thereof) are given a toxicity rating from 0 to 1, where TCDD = 1. This toxicity rating is called the Toxic Equivalence Factor, or TEF **[4]**.

$$\mathrm{TEQ} = \sum_{i=}^{N} C_i \times \mathrm{TEF}_i$$

The observed concentrations for the congeners analysed are then used to obtain a total TEQ which is compared to the relevant limits laid down in EU legislation **[5-6]**.

Summary

The use of the HRGCMS procedure gives a high level of confidence that the analytical results provide a full and true picture of the dioxin content of the materials supplied. Results can be reported rapidly and in a cost effective manner to clients.

References

1. *Report on contamination of Irish Pork Products. First report of the Joint Oireachtas Committee on Agriculture, Fisheries and Food 2009.*
2. *S. Sporring. et al., 2004. Journal of Chromatography A, 1040, 155-161.*
3. *E.Abad. et al., 2000. Journal of Chromatography A, 893, 383-391.*
4. *Van den Berg . et al., 1998. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife. Environmental Health Perspectives 106, 775-792.*
5. *Official Journal of the European Union. Commission Directive 2006/13 EC from 3 February 2006.*
6. *Official Journal of the European Union. Commission Directive 2009/152 from 27 January 2009.*

EuCheMS is considering responding to a call of the European Commission on open science policy experts, for details please see http://ec.europa.eu/research/openscience/index.cfm?pg=open-science-policy-platform. In view of this, you are kindly invited to send me your proposals for possible applications by no later than **7 March 2016**.

Thank you in advance for your help.
With my best regards

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European Commission

RESEARCH & INNOVATION

Open Science

European Open Science Policy Platform

The Directorate-General for Research and Innovation intends to establish a Commission Expert Group to provide advice about the development and implementation of open science policy in Europe.

It is therefore calling for expressions of interest with a view to selecting members of the **High-Level Advisory Group 'Open Science Policy Platform'** (OSPP)**.** The group will consist of 20-30 high-level representatives of the broad constituency of European (open) science stakeholders.

The mandate of the Open Science Policy Platform is to:

1. advise the Commission on how to further develop and practically implement open science policy, in line with the priority of Commissioner Moedas to radically improve the quality and impact of European science;
2. function as a dynamic, stakeholder-driven mechanism for bringing up and addressing issues of concern for the European science and research community and its representative organisations, following five broad lines for actions which are presented in the **draft European Open Science Agenda** **124 KB** ;
3. support policy formulation by helping to identify the issues to be addressed and providing recommendations on the policy actions required;
4. support policy implementation, contributing to reviewing best practices, drawing policy guidelines and encouraging their active uptake by stakeholders;
5. provide advice and recommendations on any cross-cutting issue affecting Open Science.

DG Research & Innovation is hereby calling for applications with the view of selecting stakeholders as members of the Open Science Policy Platform according to the criteria detailed in the Call for expression of interest.

To ensure that the panel is representative of stakeholders, applicants should clearly demonstrate that they can represent a shared interest by stakeholders or an organisation.

Before sending in an application, please read the Call for expression of interest 110 KB carefully.

Please forward any queries on the Open Science Policy Platform by email to: RTD-Open-Science@ec.europa.eu

KTI
Knowledge Transfer Ireland
Where Research & Business Connect

The National IP Protocol provides a framework for the way in which companies and research performing organisations can work together and how companies can benefit from access to new ideas, technology and inventions (intellectual property or "IP"). The latest version of this Protocol was published in January of this year, setting the stage for increased numbers of partnerships between research and business communities.

The new Protocol entitled ***"Inspiring Partnership - national IP Protocol 2016"*** is an update to the Protocol published in 2012 and as such, it continues the State's aim of making the process of engagement between business and the research base in Ireland more straightforward.

Produced by Knowledge Transfer Ireland for the Department of Jobs, Enterprise and Innovation, the new Protocol is consistent with existing policy and introduces some practical additions to speed up negotiation between industry and research performing organisations – that is, the process of knowledge transfer.

Ireland already performs well within the knowledge transfer space and is set to continue to do so. Latest figures show that the number of companies working with Irish research performing organisations increased by 46% in 2014 - a figure that is expected to continue to grow, not least with the advent of the new Protocol which further simplifies the processes involved. In addition, almost 2,000 new collaborative agreements were signed between industry and research organisations in 2014 and in the same year there was a 21% increase in the number of licences/options/assignments known collectively as LOAs.

The National IP Protocol 2016 comprises two volumes:

1) the policy document which sets out the framework underpinning research collaboration and access to intellectual property from state-funded research.

2) the resource guide which provides an overview of the national IP management guidelines and links to a wealth of resources and template documents that support these guidelines. It also provides an overview of the knowledge transfer structures in Ireland and the kinds of agreements that can be used to formalise research-industry engagements.

Alison Campbell, Director of Knowledge Transfer Ireland welcomed the publication of the updated Protocol saying, "*In working with the Department to produce the IP Protocol, Knowledge Transfer Ireland sought to deliver a simpler and very practical guide for anyone engaging in the process of knowledge or technology transfer. We are very pleased that the IP Protocol 2016 and the associated resource guide does just that.*"

Knowledge Transfer Ireland's function is to make it simpler for business and research performing organisations to work together and Alison Campbell considers the Protocol supports this "*The IP Protocol offers valuable support that will help increase the number of companies and research performing organisations working together and the number of businesses benefitting from innovation.*"

"Minister Damien English and Alison Campbell Director of KTI launch Ireland's National IP Protocol 2016"

In addition to having produced this latest version of the national IP Protocol, KTI offers information and advice across the areas of research collaboration, consultancy, licensing and spin-out opportunities among others. KTI helps companies and investors access expertise and intellectual property and guides them to the right contacts and information on funding supports available to assist innovation.

Through its web portal Knowledge Transfer Ireland provides a range of tools to support the engagement process between industry and research performing organisations in Ireland. As such, KTI has produced a short supplementary document to the Protocol. *"We are also very pleased to have recently produced a short summary guide to the Protocol which is available on our website and which we are certain will further simplify the process of knowledge transfer in Ireland. We invite anyone who is engaged in research or is partnering on a research project to visit our website where they can access a whole range of support, information and advice,"* continued Alison.

Tools such as the *KTI Research Map of Ireland*, *Research Centre Directory* and *KTI Directory of Researchers* are offered by Knowledge Transfer Ireland and can help businesses find and connect with the right research partner in Ireland. The series of *KTI Practical Guides* will support businesses and research organisations through the practical process of engagement and the suite of *KTI Model Agreements* presents a number of functional templates devised to act as the foundation of any negotiating process between researchers and industry.

Knowledge Transfer Ireland – also known as KTI – is a national body whose aim is to drive innovation by maximising the extent to which State-funded technology, ideas and expertise gets into the hands of business. KTI is located in Enterprise Ireland and funded by Enterprise Ireland with co-financing from the Irish Universities Association. For more information, please visit www.knowledgetransferireland.com

Optimizing Processes with Design of Experiments

By Malcolm Moore, Robert Anderson, and Phil Kay, SAS

TECHNICAL PRIMER

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About SAS and JMP

JMP is a software solution from SAS that was first launched in 1989. John Sall, SAS co-founder and Executive Vice President, is the chief architect of JMP. SAS is the leader in business analytics software and services, and the largest independent vendor in the business intelligence market. Through innovative solutions, SAS helps customers at more than 75,000 sites improve performance and deliver value by making better decisions faster. Since 1976 SAS has been giving customers around the world THE POWER TO KNOW®.

SAS Institute Inc. World Headquarters +1 919 677 8000
JMP is a software solution from SAS. To learn more about SAS, visit **sas.com**
For JMP sales in the US and Canada, call 877 594 6567 or go to **jmp.com**

Introduction

Do you need an efficient way to determine which process changes will yield the greatest gains?

Has your organization outgrown one-factor-at-a-time experimentation?

In the rush to get answers, are you forced to cut corners, limiting your understanding of the real drivers of process robustness, effectiveness and efficiency?

Is the time devoted to attempts at problem-solving curtailing opportunities for innovation and process improvement?

If you answered yes to any of these questions and you have insufficient data to address your questions, then read on to see how world-class design of experiment (DOE) capabilities in JMP are helping users gain insights to fix such issues quickly and permanently, giving their organization a competitive edge now, and the bandwidth to innovate for future growth. If you already have sufficient existing data, you might also want to read the companion technical primer, ***Improving Processes with Statistical Models***.

DOE is helpful when you may not have the appropriate data to solve a problem – you may have collected data for a different purpose so it is not directly relevant, or key variables may have been varied in the same way at the same time. Sometimes the processes you are investigating are so new that there is limited prior data available. In these situations, JMP for DOE helps users define the most cost-effective plan to collect new, relevant data and analyse it simply and quickly.

Through real-world case studies, you can discover best practices for defining new, cost-effective data collection plans using recent advances in DOE, statistically model the important patterns of variation in the resulting data, and visually interact with these models to identify optimum and robust operating conditions.

How can design of experiments help my business?

Companies gain value from JMP for DOE in a number of ways. One company couldn't predictably scale up and transfer into production processes for making new products. This resulted in delayed product launches and poor predictability of supply once in production. The organization's engineering practice was to vary one factor at a time (OFAT) to try and fix problems. Employees lacked DOE knowledge and considered the learning overhead too high.

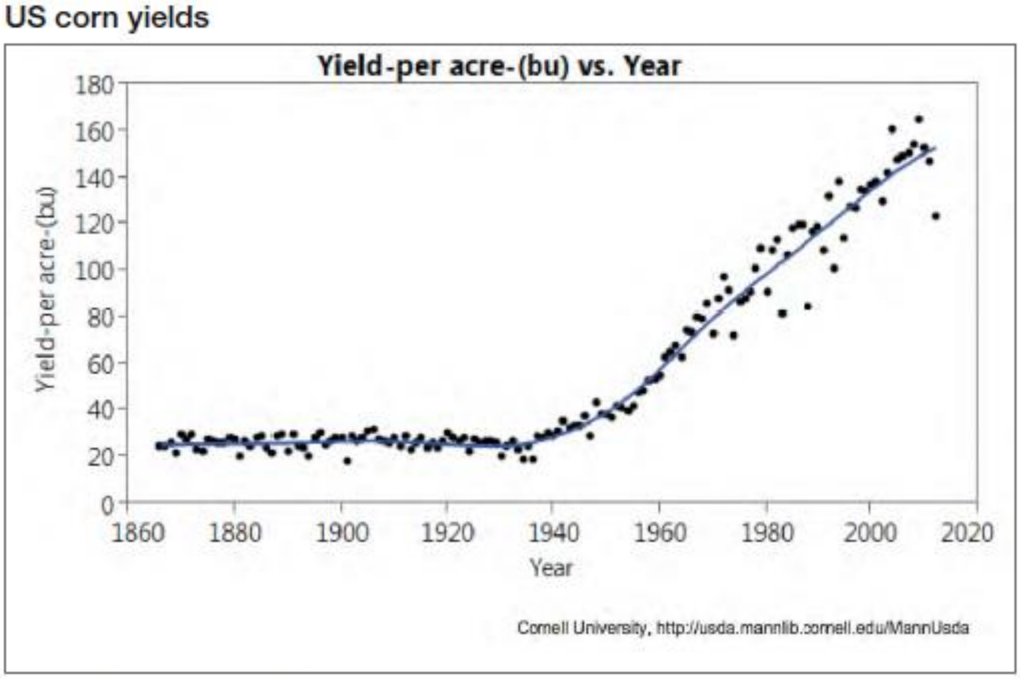
To reduce the learning threshold and perceived complexity of getting started with DOE, an application customized to the company's own terminology and engineering language was developed. This enabled their engineering community to adopt DOE easily, and they are now scaling up and transferring process right the first time. Process scale-up and transfer is now predictable and efficient, and engineers at many production plants worldwide have adopted DOE.

Compared with the old approach of varying one factor at a time, the company is now optimizing and scaling up production processes with fewer individual experimental runs, saving an estimated US$3 million per production site per year in reduced experimental effort alone. There is huge upside from getting to market faster and more predictably.

Another company needed to double the capacity of a product line to meet growing demand. They had limited understanding of the key process steps, a large number of potentially important variables that could be influencing throughput, and limited budget for experimentation. They used a definitive screening design – an innovative new design of experiments – to minimize the experimental outlay. Statistically modeling the resulting data delivered the know-how to help double the production rate with no capital investment. That's right – twice the product, no additional capital outlay! The use of a definitive screening design saved hundreds of thousands of dollars from the development budget, and the development group gained internal credibility.

Background to design of experiments

DOE was pioneered in the 1920s by Sir Ronald A. Fisher at England's Rothamsted Experimental Station. Fisher first applied DOE to increase crop yields in agriculture; ever since, DOE has played a major role in increasing agricultural production (see Figure 1).



Cornell University, http://usda.mannlib.cornell.edu/MannUsda

Figure 1: Increasing agricultural yields since advent of DOE

Fisher introduced four DOE principles:

1. Factorial concept – varying all the factors together using a factorial grid rather than varying one factor at a time.
2. Randomization – randomizing the order of the individual experimental runs in the factorial grid to avoid bias from lurking (unidentified) variables.
3. Blocking – to reduce the noise from nuisance variables.
4. Replication – to reduce the potential masking of experimental factors due to noise (unpredictable) variation.

The DOE method has been improved and enhanced in the ensuing decades:

- Later in the 1930s, Frank Yates simplified the analysis of DOE data by introducing the Yates algorithm, which is the reason why many designs are still coded on a -1 to +1 scale.
- In the 1940s, DJ Finney introduced the fractional factorial design, which allowed many factors to be investigated at half or even a quarter the cost of Fisher's factorial design.
- In the 1950s, George Box and others deployed DOE in chemistry and industrialized its application.
- Each decade since has seen improvements in the DOE method. Within the past few years, the definitive screening design was invented by Brad Jones from SAS and Chris Nachtsheim from the University of Minnesota.

DOE methods are now applied widely in design, development, scale-up, manufacturing and "quality by design" (QbD) areas to ensure that key questions are answered predictably and economically.

When to apply DOE

DOE can potentially help any time you have technical or business problems and insufficient data to answer your questions – particularly if:

- You have more problems than time available.
- The time to solve problems is unpredictable or you find yourself repeating or performing a large number of cycles of learning.
- You feel you are forced to cut corners and make decisions on incomplete information.
- Products and processes are defined or transferred with incomplete understanding of how they work.
- You sometimes get stuck in a reactive, vicious cycle where fixing problems with existing products and processes limits your time for innovation and new process or product development.

Then, providing you have the ability to collect new data through active intervention, DOE will help define the data you need to collect and, by analysing the resulting data, answer your questions efficiently and effectively.

Why apply DOE?

The DOE method will help you optimize products and processes predictably and quickly. It will enable you to make better, more informed decisions, bringing predictability to decision making, thereby reducing risk to your business.

You will be able to transfer products and processes with a better knowledge of how they work. Because of this, there will be less need to improve or "fire fight" products or processes when in production, which makes room for more R&D time to be spent in innovation, new product and process development.

DOE technicalities

The properties of products and processes are usually affected by many factors or inputs. For example, Figure 2 illustrates a chemical process where the chemist believes there are five inputs that may be responsible for causing variation in the two responses or outputs. When determining the set of inputs, statistical analysis of prior data can help identify the factors to investigate. Otherwise, it is better to err on the side of caution and include as many factors as you think might have an effect on one or more of your responses, provided you have sufficient budget.

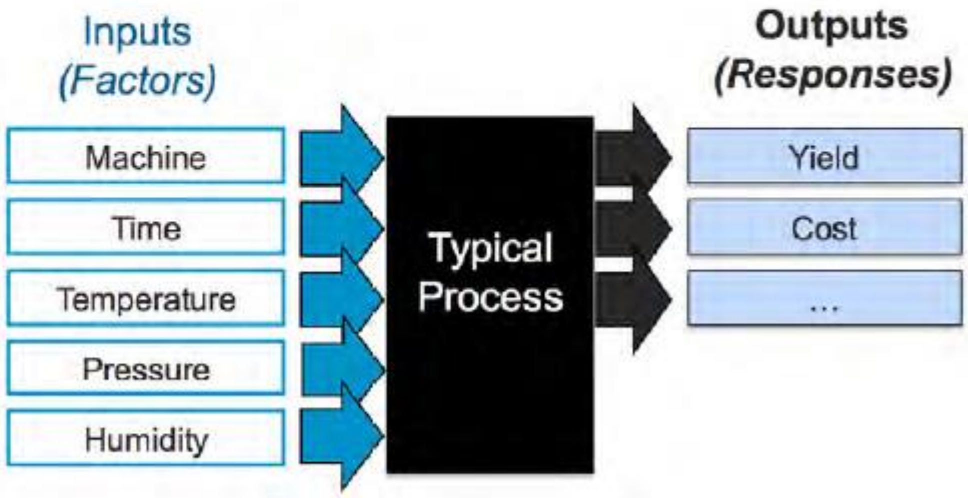


Figure 2: A chemical process

The traditional experimental approach

A common scientific and engineering approach is to experiment by varying one factor at a time (OFAT).The OFAT approach is illustrated using just two of the factors in Figure 2 (temperature and time) to investigate their effect on one of the responses (yield).Prior knowledge indicates that it is best to investigate temperature over the range 500 to 550 degrees C (900 to 1,000 degrees F) and to vary time over the range 500 to 1,300 minutes.

The first sequence of experiments were performed by keeping temperature fixed at 520 degrees C and varying time within the range of 500 to 1,300 minutes in increments of 100 minutes. This resulted in the yield curve in Figure 3; a suggested time of 1,100 to 1,200 minutes is required to maximize yield.

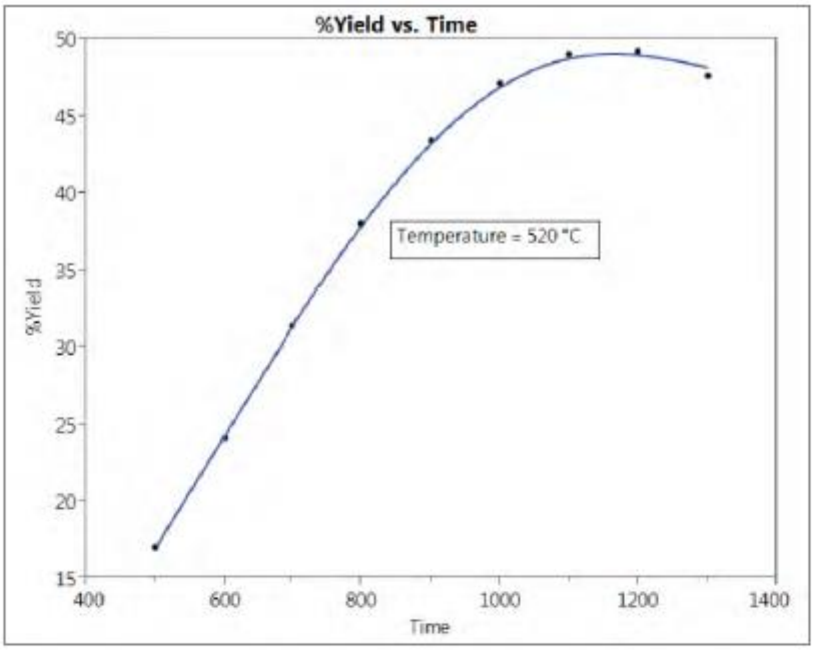


Figure 3: Relationship between yield and time at 520 degrees Celsius

The next set of experiments were performed by varying temperature from 500 to 550 degrees C in increments of 10 C (50 degrees F) while keeping time fixed at 1,100 minutes.(1,100 minutes was favoured to a slightly higher value in order to keep the cost of running the process lower).

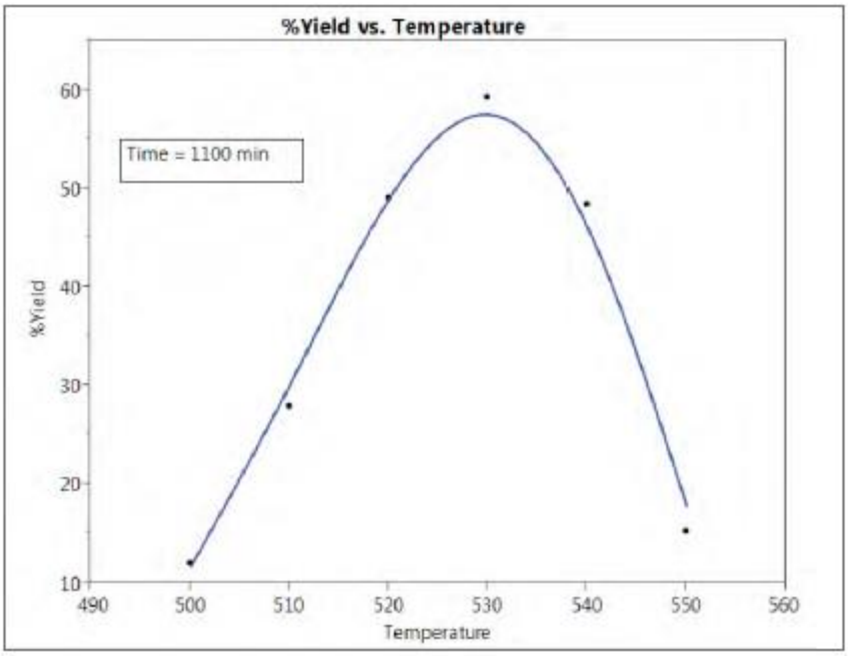


Figure 4: Relationship between yield and temperature at 1,100 minutes

The best setting of temperature at 1,100 minutes is 530 degrees C, which resulted in a yield of just under 60 percent. Figure 5 is a plot of temperature against time using a colouring gradient for the value of yield at each experimental point. It shows highest yield of 59.3 percent at 1,100 minutes and 530 C. It also indicates a lot of white space, which is a concern. This white space indicates we know very little about what yield to expect when:

- Time is less than 1,000 minutes and temperature is greater than 530 degrees C.
- Time is less than 1,000 minutes and temperature is less than 510 degrees C.
- Time is greater than 1,200 minutes and temperature is greater than 530 degrees C.
- Time is greater than 1,200 minutes and temperature is less than 510 degrees C.

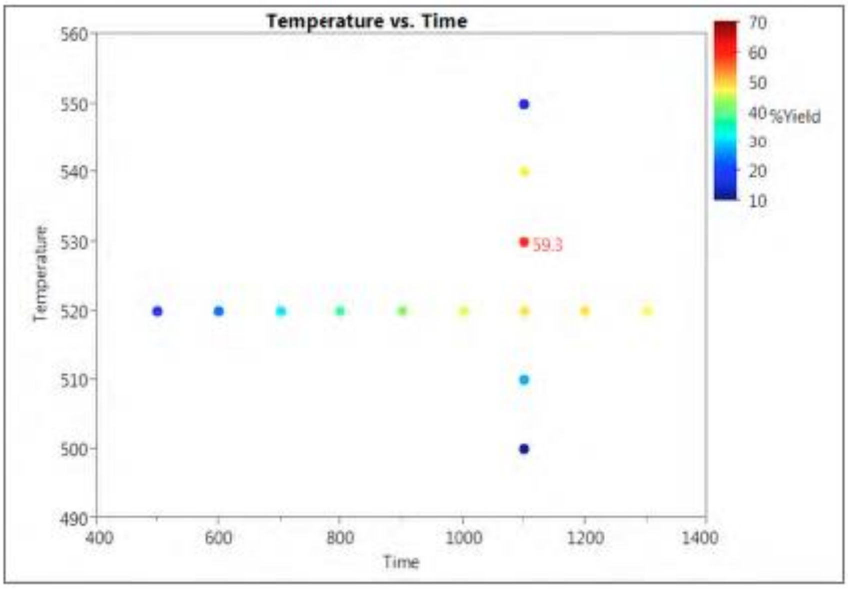


Figure 5: Time vs temperature with experimental points colored by yield

When we learn that a temperature of 550 degrees C and a time of 500 minutes produces a higher yield of 66.5 percent – at significantly lower cost – the risk of experimenting in a series of one-dimensional portions is self-evident.

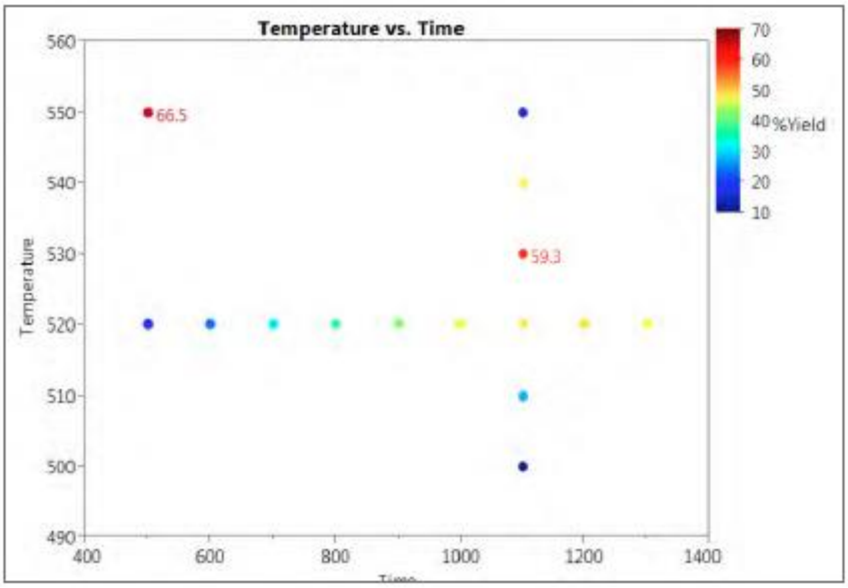


Figure 6: A better yield is obtained at 550 degrees C and 500 minutes

OFAT approaches frequently lead to suboptimal solutions. This is because OFAT assumes the effect of one factor is the same at each level of the other factors, i.e., that factors do not interact. Unfortunately, in practice, factors frequently interact, and the chances of two or more factors interacting increases the greater the number of factors investigated and the wider the range over which factors are varied.

The 3-D plot and contour diagram in Figure 7 illustrate the interactive effect of time and temperature on yield with the ridge effect that runs from time and temperature combinations of 1,200 and 528 with a yield of 56 percent, to 900 and 536 with a yield of 61 percent, to 500 and 550 with a yield of over 65 percent. The effect of this interaction (or ridge) is that the best setting for temperature chosen by OFAT depends upon the value of time.

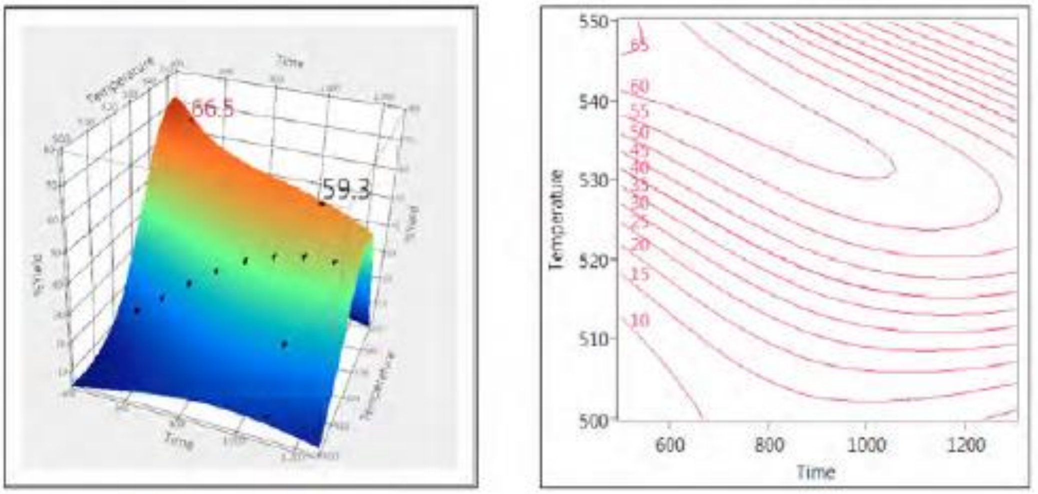
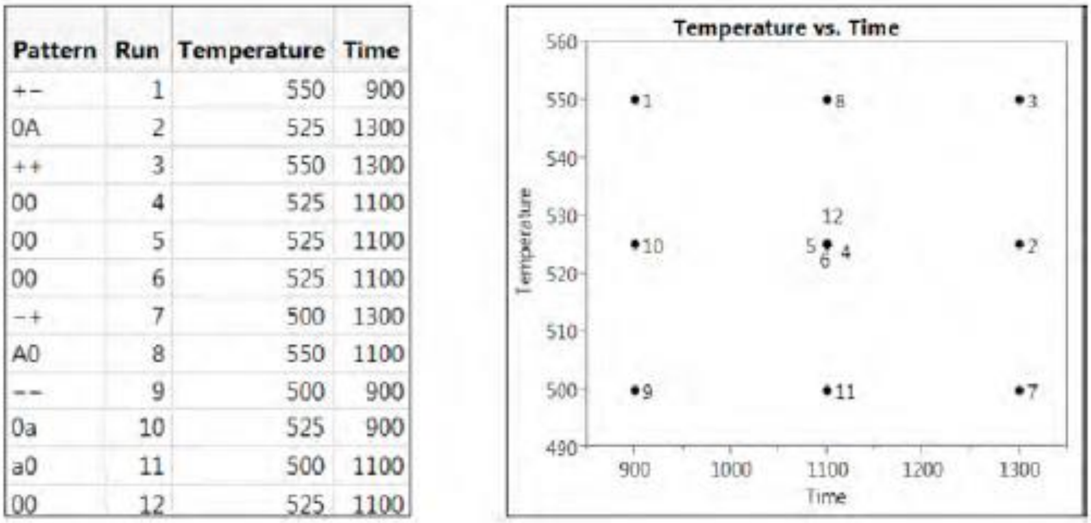


Figure 7: Relationship among yield, time and temperature

For example, if time is fixed at 1,000, the best setting of temperature is 534, resulting in a yield of slightly more than 60 percent. Whereas, as we have already seen, if time is fixed at 500 the best setting of temperature is 550, resulting in a yield of slightly more than 65 percent. In the presence of interactive effect of factors on the response, the solution identified by OFAT depends on your starting point, and it is only by chance that the global optima is determined.

DOE provides the most efficient and effective way of investigating relationships between factors and responses. The efficiency and effectiveness of DOE compared with OFAT increases the greater the number of interactive effects between factors.

The DOE needed to investigate the effects of time and temperature on yield, and to find the global optima, is given in Figure 8.This is a 3x3 grid of points in time and temperature, with three additional replicates of the center point to give a baseline for noise or uncontrolled variation. These 12 rows in the resulting data table indicated in Figure 8 give a balanced distribution of combinations of time and temperature throughout the experimental space indicated in Figure 5.By statistically analysing the resulting data and dependence of yield on time and temperature, we have no gaps in our knowledge. Analysing the resulting data with multiple regression yields the 3-D surface and contour plot depicted in Figure 7, which show that the best place to operate is time of 500 minutes and temperature of 550 degrees C. Further improvement is implied if we go to a lower time and a higher temperature, but an additional cycle of experimentation would be needed to achieve this gain in a reliable manner.

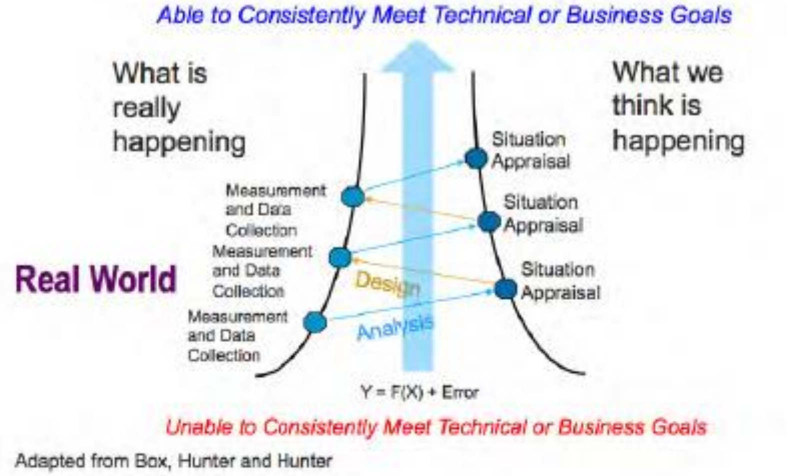


Pattern	Run	Temperature	Time
+−	1	550	900
0A	2	525	1300
++	3	550	1300
00	4	525	1100
00	5	525	1100
00	6	525	1100
−+	7	500	1300
A0	8	550	1100
−−	9	500	900
0a	10	525	900
a0	11	500	1100
00	12	525	1100

Figure 8: DOE in time and temperature

Learning is incremental

Figure 9 illustrates that we typically start with data or a theory that is analysed to help assess our situation or theory, which typically leads to more questions that require collection of new data via DOE to provide answers.



Adapted from Box, Hunter and Hunter

Figure 9: Learning is incremental

If we have a large number of factors and utilize OFAT approaches, we may perform many iterations or cycles of learning, sometimes a product or process may come back to us from production for additional cycles of learning to fix a product or process issue that would not occur if we were able to develop and transfer products and processes with a better understanding. Classical DOE methods – as developed by Fisher, refined by Finney and industrialized by Box – will reduce the total number of learning cycles relative to OFAT, and increase the predictability of R&D. Modern advances in DOE such as definitive screening by Jones and Nachtsheim may further reduce the number of cycles of learning.

By extracting the required information from fewer cycles of learning and doing so predictably, JMP for DOE delivers the information needed to make the correct decisions and increases the predictability of getting to those decisions with a limited budget and time.

Data-driven DOE: Integrating observational data

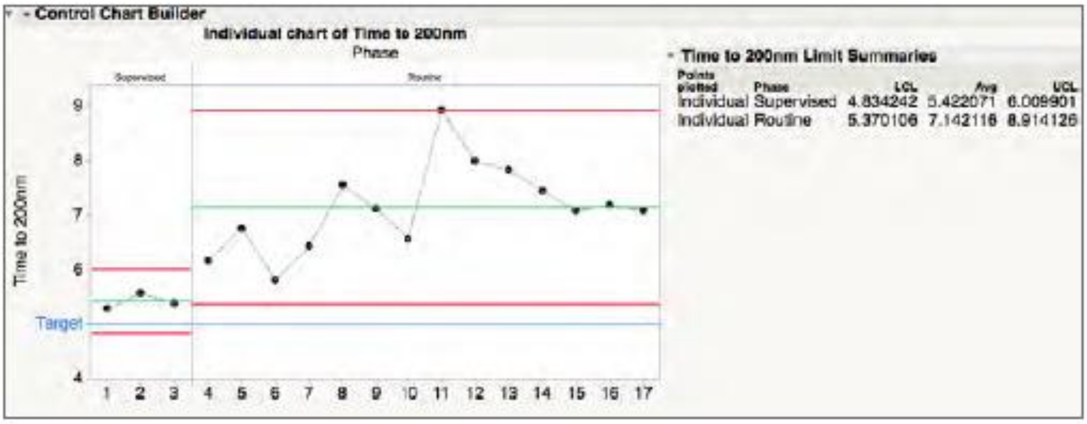
Figure 9 illustrated that learning is incremental. At the start of the DOE learning process, you may have existing data, in which case effective statistical modeling of that data may aid the design of the next DOE. In particular, analysis of prior data may help decide which factors to include in your DOE and the range over which to vary them.

Existing data may be messy, which makes it difficult to correctly extract information on the factors and factor ranges. Messy data issues may include the factors being related (e.g., an increase in one X results in increase or decrease of another X); some of the data cells may be recorded incorrectly; other cells may be empty or missing. JMP statistical discovery ensures that you can extract meaning from your messy data to identify the potential factors and factor ranges. Integrated with modern DOE methods, we reduce total learning time, effort and cost.

Case Study 1: Driving new product introduction by developing robust processes for hard-to-manufacture products

A specialty chemicals supplier of pigments to liquid crystal display (LCD) manufacturers is struggling to manufacture enough pigment to required specifications to meet customer demand. To achieve sharp displays, the pigment particles must be milled down to less than 200 nanometers, and the time taken to do this is extremely variable. The milling stage is energy-intensive and a bottleneck, and the long mill time is incurring excessive energy cost and affecting throughput. The company needs a faster process or additional milling equipment to run in parallel with existing equipment.

Figure 10 shows an upward trend in the time to mill to less than 200 nanometers for recent production batches of pigment. To avoid the capital cost of adding additional milling equipment, we need to get mill time below five hours, which appears to be a challenge; none of the prior batches has achieved this goal.



Time to 200nm Limit Summaries

Points plotted	Phase	LCL	Avg	UCL
Individual	Supervised	4.834242	5.422071	6.009901
Individual	Routine	5.370106	7.142116	8.914126

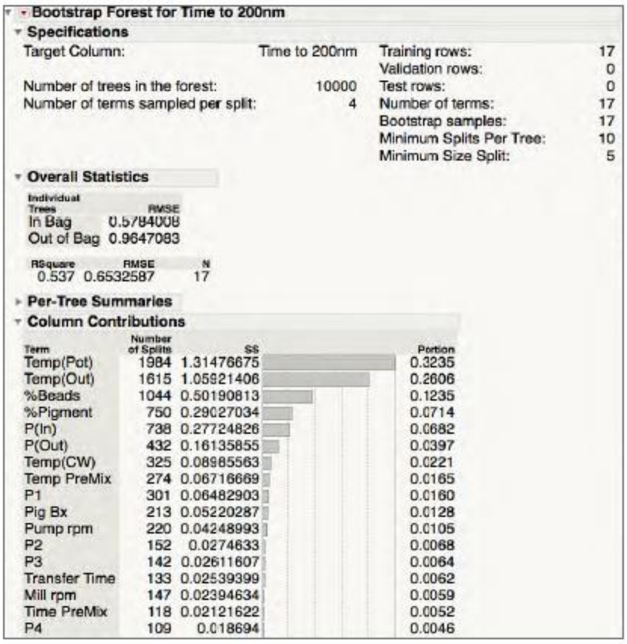
Figure 10: Time to mill of first 17 batches

OFAT was used to develop the process initially, but because the process is taking too long, the company needs to repeat earlier development work to try and learn how to speed the process. In addition to the cost of repeating prior cycles of learning, the current process incurs a high energy cost due to long milling time and does not provide enough material to meet the demands of LCD manufacturers.

If the milling process cannot be operated to the required speed of five hours or less to mill down to 200 nanometers, the company will need to purchase a second milling machine, and still tolerate the ongoing cost of an energy-inefficient process. This will reduce profitability, the availability of capital to invest in other projects, and dividends returned to investors.

Milling is carried out in a horizontal bead mill. This is a chamber filled with beads, through which the dispersion of pigment is passed. The beads in the chamber are agitated at high speeds to grind down the pigment particles.

Analysis of data from the prior 17 production runs using a bootstrap forest identified the top factors to investigate with DOE.



```
Bootstrap Forest for Time to 200nm
Specifications
Target Column:                      Time to 200nm   Training rows:              17
                                                    Validation rows:             0
Number of trees in the forest:              10000   Test rows:                   0
Number of terms sampled per split:              4   Number of terms:            17
                                                    Bootstrap samples:          17
                                                    Minimum Splits Per Tree:    10
                                                    Minimum Size Split:          5
Overall Statistics
Individual
Trees            RMSE
In Bag      0.5784008
Out of Bag  0.9647083

RSquare      RMSE      N
  0.537 0.6532587     17
Per-Tree Summaries
Column Contributions
                 Number
Term          of Splits          SS   Portion
Temp(Pot)          1984  1.31476675    0.3235
Temp(Out)          1615  1.05921406    0.2606
%Beads             1044  0.50190813    0.1235
%Pigment            750  0.29027034    0.0714
P(In)               738  0.27724826    0.0682
P(Out)              432  0.16135855    0.0397
Temp(CW)            325  0.08985563    0.0221
Temp PreMix         274  0.06716669    0.0165
P1                  301  0.06482903    0.0160
Pig Bx              213  0.05220287    0.0128
Pump rpm            220  0.04248993    0.0105
P2                  152   0.0274633    0.0068
P3                  142  0.02611607    0.0064
Transfer Time       133  0.02539399    0.0062
Mill rpm            147  0.02394634    0.0059
Time PreMix         118  0.02121622    0.0052
P4                  109    0.018694    0.0046
```

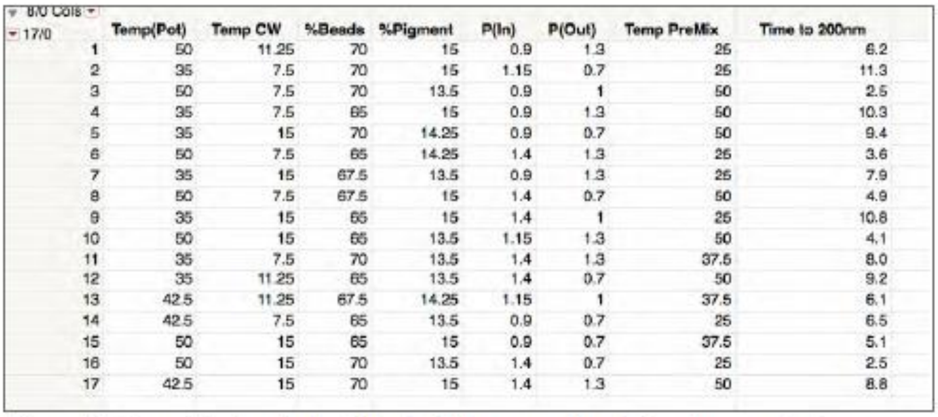
Figure 11: Input variable selection

Engineering judgment indicated that output temperature [Temp (Out)] is correlated with Temp (Pot) and could not be the driver of variation in mill time. Temp (Out) was therefore left out of the DOE.P1 was also excluded, and a cut point at Temp PreMix was used based on the need to limit total cost of experimentation. Inputs from Temp PreMix and above in Figure 11, with the exception of Temp (Out) and P1, were included in the DOE.

A definitive screening design in seven factors was designed, which resulted in 17 DOE combinations. This was deemed the most efficient way of progressing, as it allows screening for the critical factors, and - provided no more than three factors are important – then interactive and nonlinear effects can be modelled to optimize the process without the need for additional experimentation.

Figure 12 contains the completed worksheet for the 17-run definitive screening design in seven factors. Figure 13 shows the profiler and 3-D plot of the statistical model resulting from the DOE. Just three of the seven factors had an important effect on mill time to 200 nm – Temp (Pot), %Beads and %Pigment.

The settings of these three factors needed to minimize mill time to 200 nm are also indicated on Figure 13: Temp (Pot) of 50 C, %Beads of 68.8 and %Pigment of 13.5 with a predicted mill time of 2.6 hours (95 percent confidence interval of 2.2 to 3.0 hours).Three confirmation runs at these settings verified the time to mill to 200 nm was now well below the upper limit of five hours (see Figure 14).



	Temp(Pot)	Temp CW	%Beads	%Pigment	P(In)	P(Out)	Temp PreMix	Time to 200nm
1	50	11.25	70	15	0.9	1.3	25	6.2
2	35	7.5	70	15	1.15	0.7	25	11.3
3	50	7.5	70	13.5	0.9	1	50	2.5
4	35	7.5	65	15	0.9	1.3	50	10.3
5	35	15	70	14.25	0.9	0.7	50	9.4
6	50	7.5	65	14.25	1.4	1.3	25	3.6
7	35	15	67.5	13.5	0.9	1.3	25	7.9
8	50	7.5	67.5	15	1.4	0.7	50	4.9
9	35	15	65	15	1.4	1	25	10.8
10	50	15	65	13.5	1.15	1.3	50	4.1
11	35	7.5	70	13.5	1.4	1.3	37.5	8.0
12	35	11.25	65	13.5	1.4	0.7	50	9.2
13	42.5	11.25	67.5	14.25	1.15	1	37.5	6.1
14	42.5	7.5	65	13.5	0.9	0.7	25	6.5
15	50	15	65	15	0.9	0.7	37.5	5.1
16	50	15	70	13.5	1.4	0.7	25	2.5
17	42.5	15	70	15	1.4	1.3	50	8.8

Figure 12: Completed worksheet for definitive screening design in seven factors

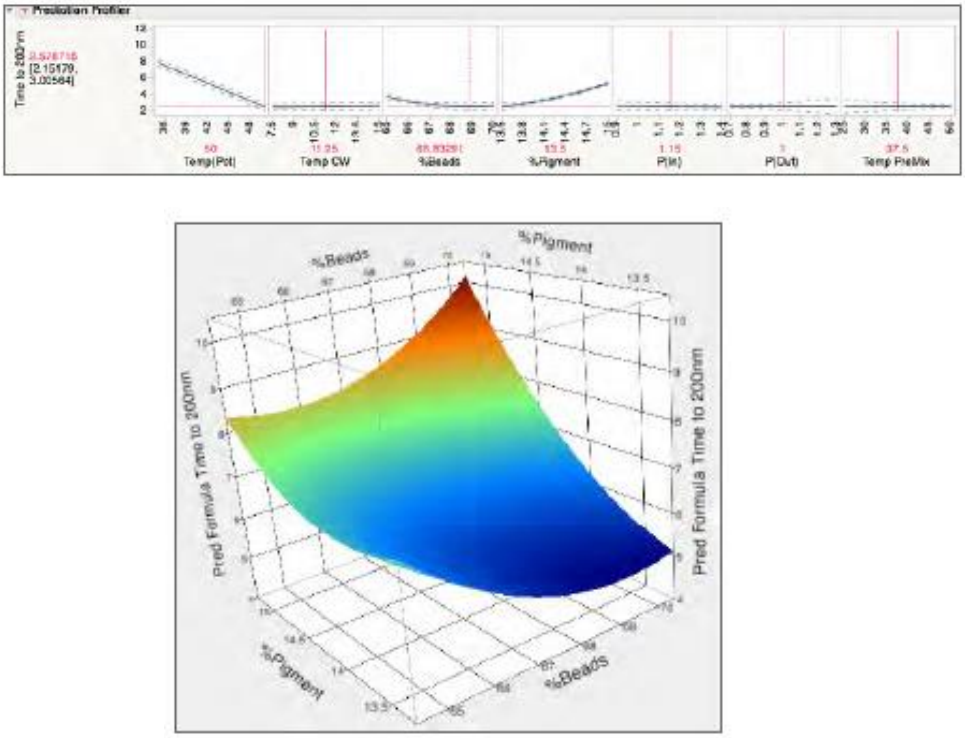
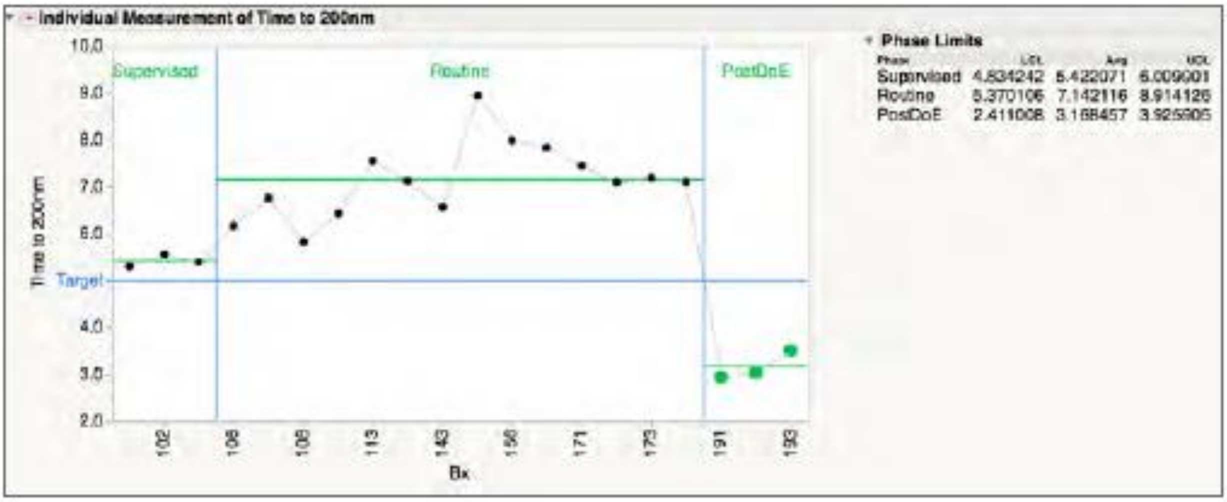


Figure 13: Profiler and 3-D plot of statistical model



Phase Limits

Phase	LCL	Avg	UCL
Supervised	4.834242	5.422071	6.009901
Routine	5.370106	7.142116	8.914126
PostDoE	2.411008	3.168457	3.925906

Figure 14: Three confirmation runs

Summary

Data mining of prior data provided the variables to input to a definitive screening design, which provided an efficient experimental plan. Statistically modeling the resulting data helped identify a permanent solution. The problem was solved quickly, saving hundreds of thousands in the development budget and enhancing the credibility of the site as a location for cost-effective, high-value manufacturing.

Case Study 2: Optimizing a manufacturing process to increase yield and product quality

A semiconductor manufacturer has been experiencing problems in operating a low-pressure chemical vapour deposition (LPCVD) process in a furnace tube to deliver a new product specification. It processes four lots of wafers, each of 24 wafers, each run of the equipment.

During the process, a new layer of silicon nitride is deposited on each wafer, with the goal of each wafer receiving silicon nitride of uniform target thickness and refractive index. The process operates by heating the furnace tube and having gases flow from one end of the tube to the other, passing over and between the wafers. It is run according to a recipe that controls things like the rate of heating, temperature, gas flows and pressures.

The process is monitored with four test wafers, one per lot for each run of the process. Each test wafer has 49 measurement locations within the wafer. Figure 15 shows a plot of film thickness and refractive index for each test wafer. The x-axis identifies the run ID and test wafer ID within run. The y-axis plots the value of film thickness or refractive index for each of the 49 measurement locations within each test wafer. Each graph also shows the specification limits and target.

The primary issue with film thickness is that it is not centred within the specification window, resulting in every wafer being out of specification. There is little wafer-to-wafer variation and moderate (relative to specification range) within-wafer variation. Refractive index is also not centred within the specification window, has wafer-to-wafer variation and low within-wafer variation (relative to specification range).OFAT approaches to improving the situation have failed to deliver any significant improvement.

Continuing with OFAT is resulting in ineffective solutions and repeat work. Inability to solve the furnace tube issue is causing low yield of desired functional devices end of line. The company was unable to produce enough devices of required function with existing equipment. Unless the process could be made to consistently deliver in-specification product, they will need to buy additional equipment. This approach also means we can expect to continue producing many lower-functioning devices that command a lower price. The business impact is reduced profitability and availability of capital to invest in other projects.

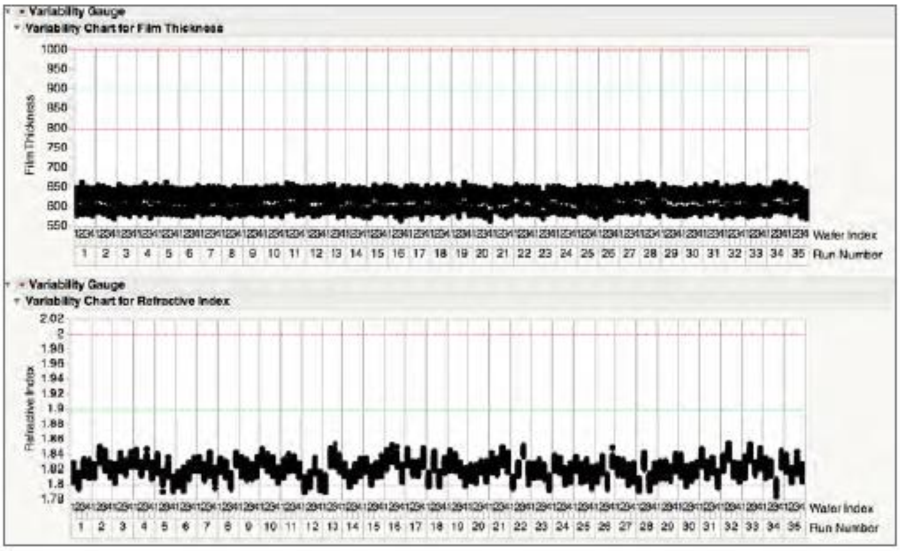
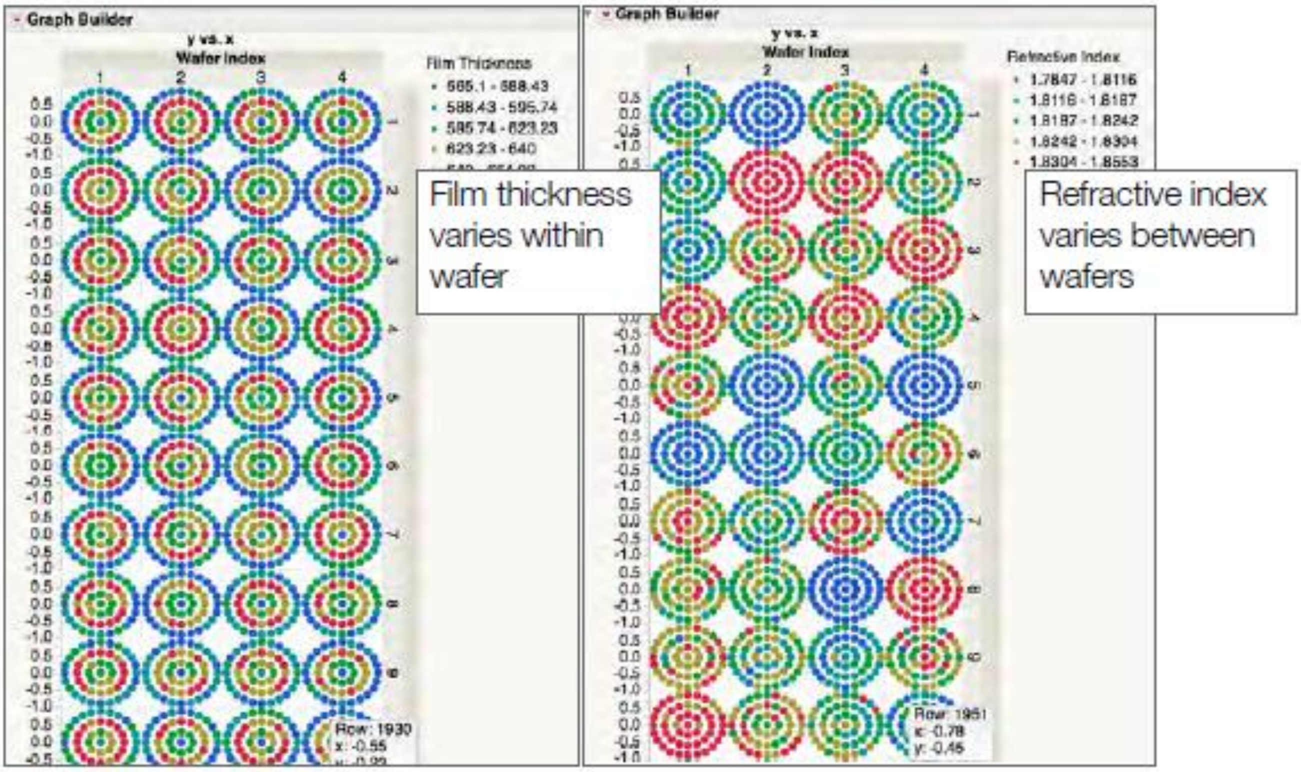


Figure 15: Performance relative to specification

Prior to designing an experiment to understand the drivers of silicon nitride thickness and refractive index, the process engineer wanted to understand the pattern of variation in silicon nitride and refractive index within wafer, between wafers within a lot and between lots. To enable this, he produced a wafer map trellis as illustrated in Figure 16.Each column within the graph trellis represents a test wafer within a production run, and a row within the trellis represents a production run. The intersection of a row and column within the trellis is a wafer, and the value of the test measurement at each of the 49 test locations within a wafer is represented by a coloured circle.

In the case of silicon nitride thickness, there is little between-wafer and between-run variation. The key component of variation is within-wafer, and a radial pattern is illustrated. Thickness measurements are lowest at the outer edge (outer zone) of the wafer, with the highest thickness measurements as we move inward (zone 2).Thickness reduces as we move inward to zone 1, and further reduces at the center. Thickness is being deposited with a radial pattern (similar to a wave pattern emanating from the center of a wafer).



Film thickness varies within wafer

Refractive index varies between wafers

Figure 16: Wafermap trellis

The wafer map trellis of refractive index indicates some between-wafer variation within run and between-run variation, but very consistent measurements within a wafer.

Based on the patterns of within-wafer, between-wafer and between-run variation, the process engineer defined the responses (outputs) to be measured and optimized as mean thickness at the center, zone 1, zone 2, and outer zone along with mean refractive index.

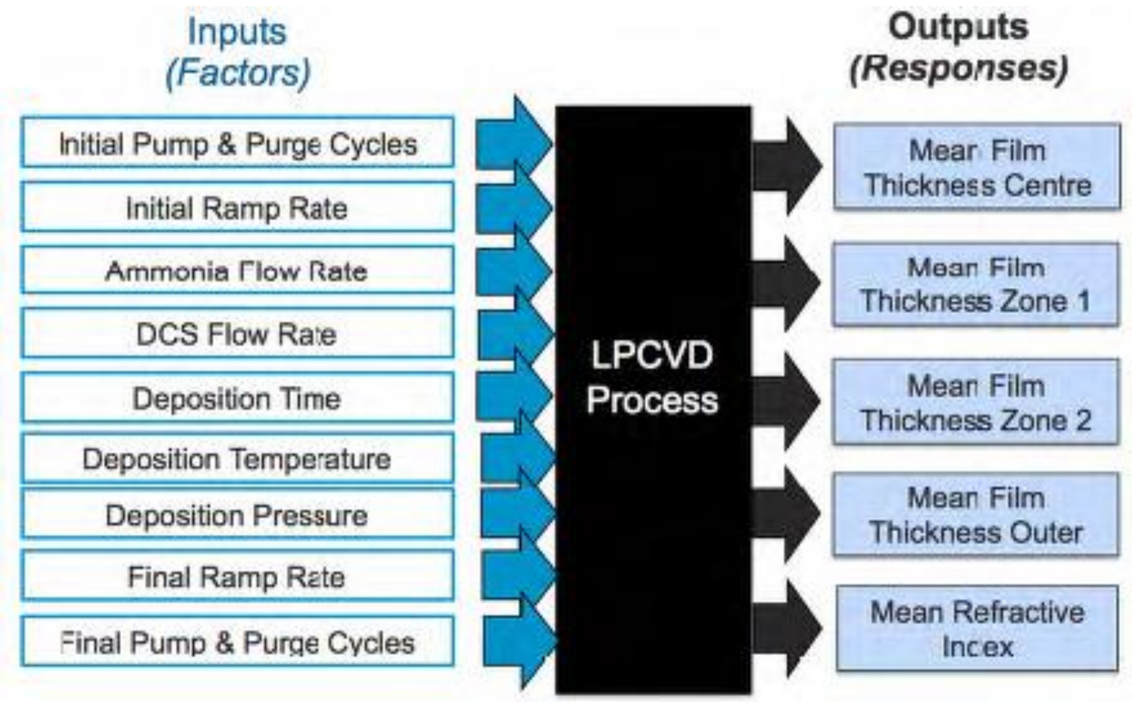
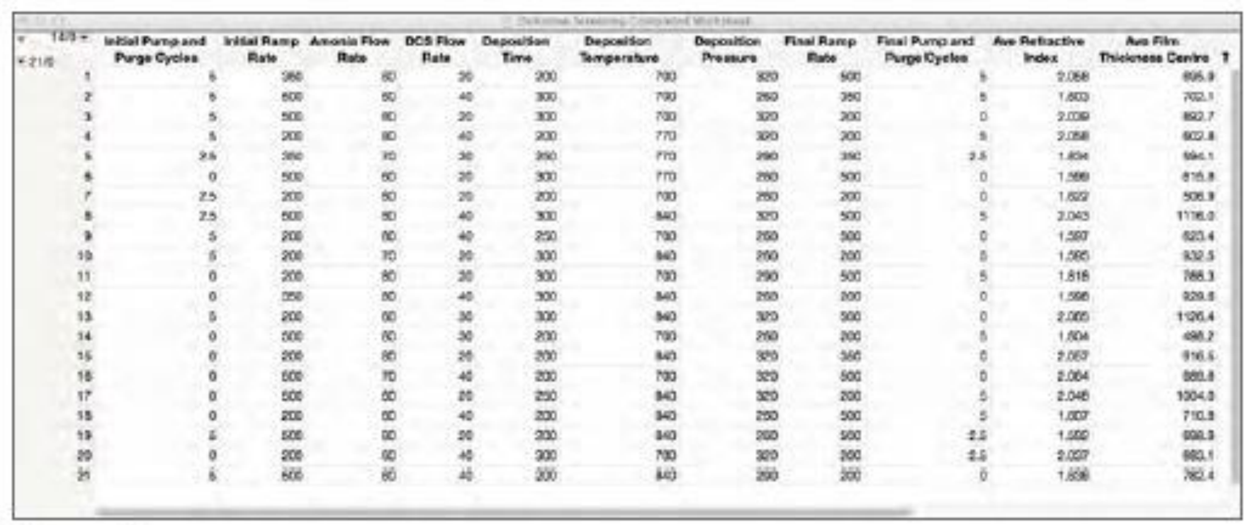


Figure 17: Inputs and outputs

These are summarized in Figure 17 along with the factors (inputs) to be varied in the DOE.

A definitive screening design in nine factors was designed, which resulted in 21 DOE combinations. This was deemed the most efficient way of progressing, as it allows screening for most important factors. If three or fewer factors are important, then interactive and nonlinear effects can be modelled to optimize the process without the need for additional experimentation.

Figure 18 contains the completed worksheet for the 21-run definitive screening design in nine factors. Figure 19 shows the profiler of the statistical model resulting from the DOE. Just three of the nine factors had an important effect on the five responses – deposition time, temperature and pressure.



	Initial Pump and Purge Cycles	Initial Ramp Rate	Amonia Flow Rate	DCS Flow Rate	Deposition Time	Deposition Temperature	Deposition Pressure	Final Ramp Rate	Final Pump and Purge Cycles	Ave Refractive Index	Ave Film Thickness Centre
1	5	350	60	30	200	700	320	500	5	2.058	895.9
2	5	500	60	40	300	700	260	350	5	1.603	702.1
3	5	500	80	20	300	700	320	200	0	2.039	892.7
4	5	200	80	40	200	770	320	200	5	2.058	602.8
5	2.5	350	70	30	350	770	290	350	2.5	1.834	594.1
6	0	500	60	20	300	770	260	500	0	1.588	615.8
7	2.5	200	60	20	200	700	260	200	0	1.622	506.9
8	2.5	500	80	40	300	840	320	500	5	2.043	1116.0
9	5	200	60	40	250	700	260	500	0	1.597	623.4
10	5	200	70	20	300	840	260	200	5	1.585	932.5
11	0	200	80	30	300	700	290	500	5	1.818	788.3
12	0	350	80	40	300	840	260	200	0	1.596	929.8
13	5	200	60	30	300	840	320	500	0	2.065	1126.4
14	0	500	60	30	200	700	260	200	5	1.604	498.2
15	0	200	80	20	200	840	320	350	0	2.057	916.5
16	0	500	70	40	200	700	320	500	0	2.064	880.8
17	0	500	60	20	250	840	320	200	5	2.046	1004.0
18	0	200	60	40	200	840	260	500	5	1.607	710.8
19	5	500	60	20	200	840	260	500	2.5	1.592	898.3
20	0	200	60	40	300	700	320	200	2.5	2.027	860.1
21	5	500	60	40	200	840	290	200	0	1.838	782.4

Figure 18

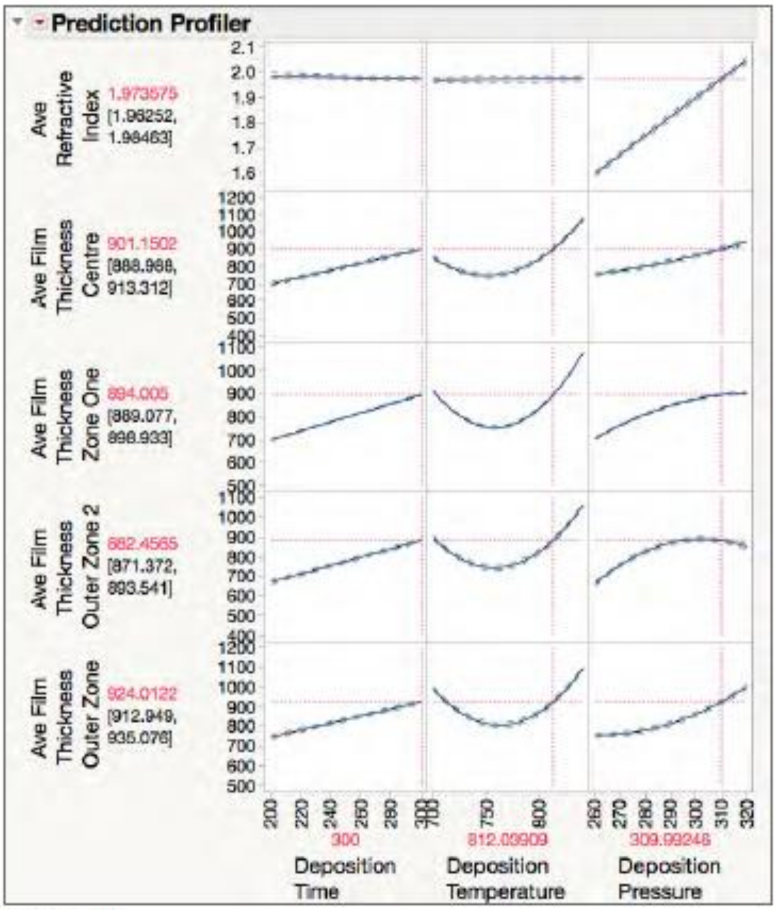


Figure 19

The settings of these three factors needed to center the five responses within their specification range are also indicated in Figure 19:

- Deposition time of 300.
- Deposition temperature of 812.
- Deposition pressure of 310.

These setting produce the following predicted responses:

- Predicted average refractive index of 1.97.
- Average thickness at center of 895.
- Average thickness at zone 1 of 900.
- Average thickness at zone 2 of 880.
- Average thickness at outer zone of 926.

The new process recipe for deposition time, temperature and pressure was implemented cautiously at first and validated after observing that three production runs delivered wafers all within specification. Figure 20 confirms the improvement for the first 20 production runs with the new recipe. Film thickness is centred very close to target, and none of the measurements within a wafer are close to the specification limits.

The process is therefore highly capable of consistently depositing silicon nitride to the required thickness. Refraction index is not quite centred, and wafer-to-wafer variation is evident. However, all refractive index measurements are well within the specification limits, meaning the process is highly capable with regard to refractive index. Although it is possible to improve refractive index further, there is little benefit in doing so.

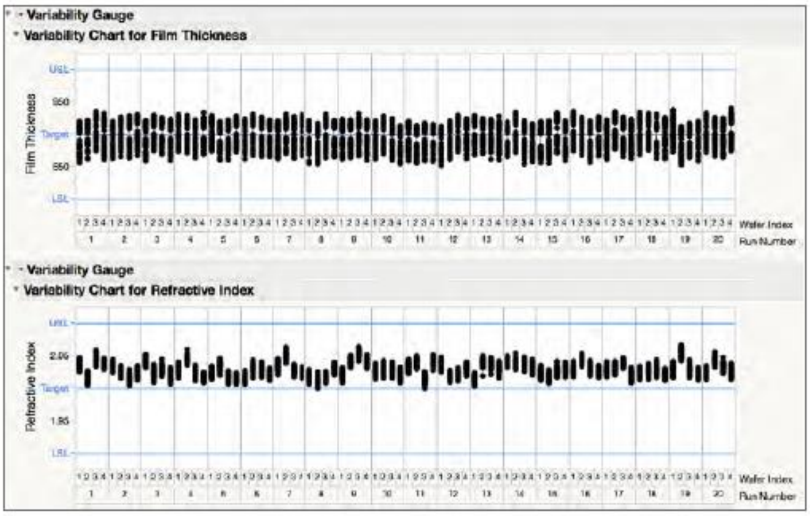


Figure 20: Performance post-improvement

Summary

Exploring prior data helped define the output variables to optimize with DOE.A definitive screening design provided an efficient and effective experimental plan with which to provide the data needed to understand the furnace tube process. Statistically modeling the resulting data provided a solution than ensured future wafers have the desired properties for silicon nitride thickness and refractive index. Further improvements are possible but not necessary.

The problem was solved quickly and permanently, saving hundreds of thousands in development budget by removing the need for now-redundant cycles of learning that are typically required with OFAT. The company assured product supply, enabling sales projections, and saved millions of dollars in additional processing equipment that is no longer needed.

Conclusion

In the interest of brevity, just two examples were presented. If you are able to experiment or actively intervene in your process, you can similarly use DOE to create the data you need to statistically model your process and increase real understanding. This paper has attempted to explain:

- What DOE is.
- The types of problems that benefit from DOE.
- Simple and effective ways to apply DOE.
- How to extract knowledge from DOE.
- How to present and communicate models and resultant knowledge from DOE to other stakeholders.
- How to optimize products and processes better, faster.

DOE might help you or your company to:

- Do more effective work in less time.
- Increase understanding of your products and processes.
- Optimize products and processes more efficiently.
- Increase the predictability of design, development and engineering projects.
- Deliver a competitive edge.
- Increase the availability of money for further innovation and improvement.

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