The University of Nottingham

Commercialisation – not really an activity for a gentleman?

Martyn Poliakoff

www.nottingham.ac.uk/supercritical

Conclusions!

- Commercialisation cannot be planned beforehand
- Seize opportunities as they arise
- **Disappointments are not failure**

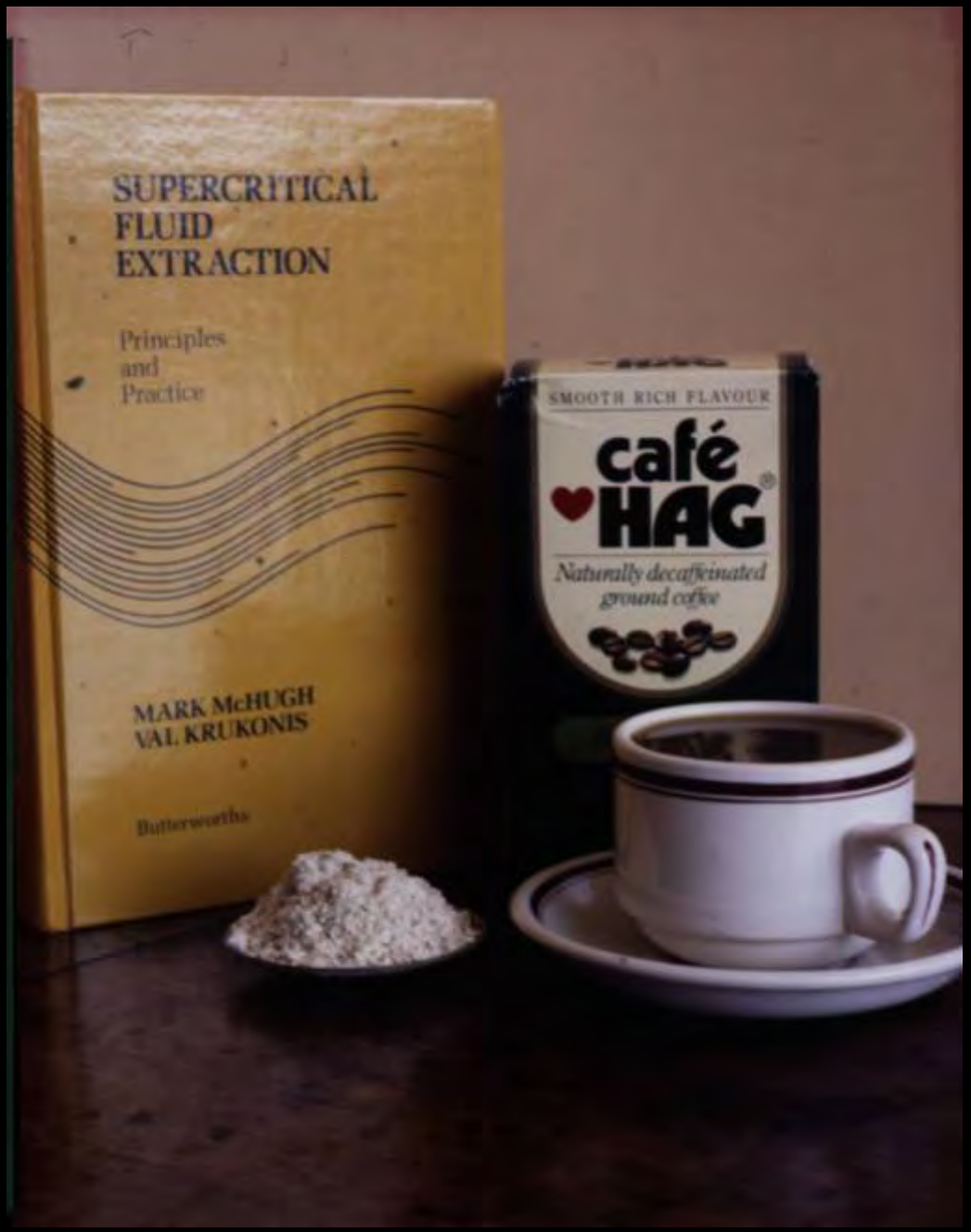
Matrix Isolation: reactive molecules immobilized in a solid at low temperature

Supercritical Fluids

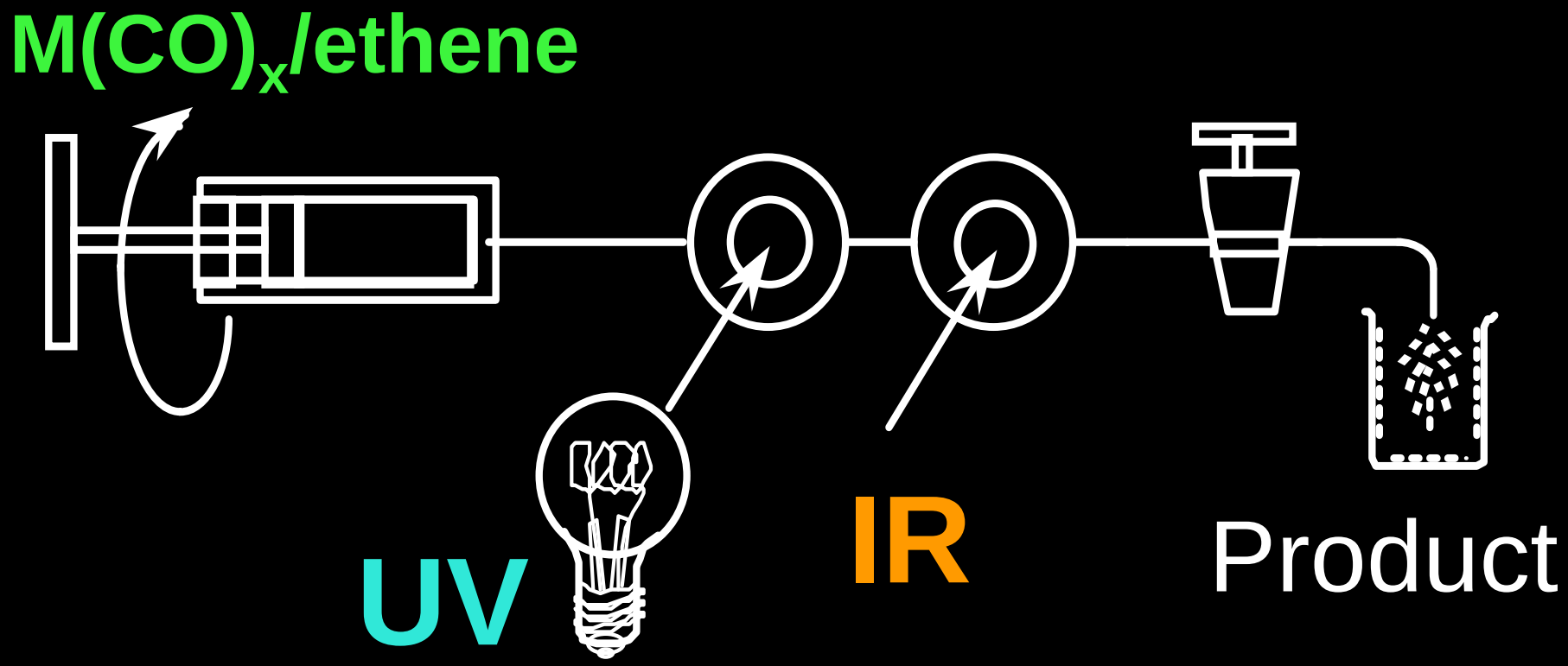
- Gases e.g. CO_2, C_2H_4, H_2O compressed until they are nearly as dense as liquids
- **SCFs can dissolve solids** solubility increases with density (applied pressure)

Decaffeination in $scCO_2$

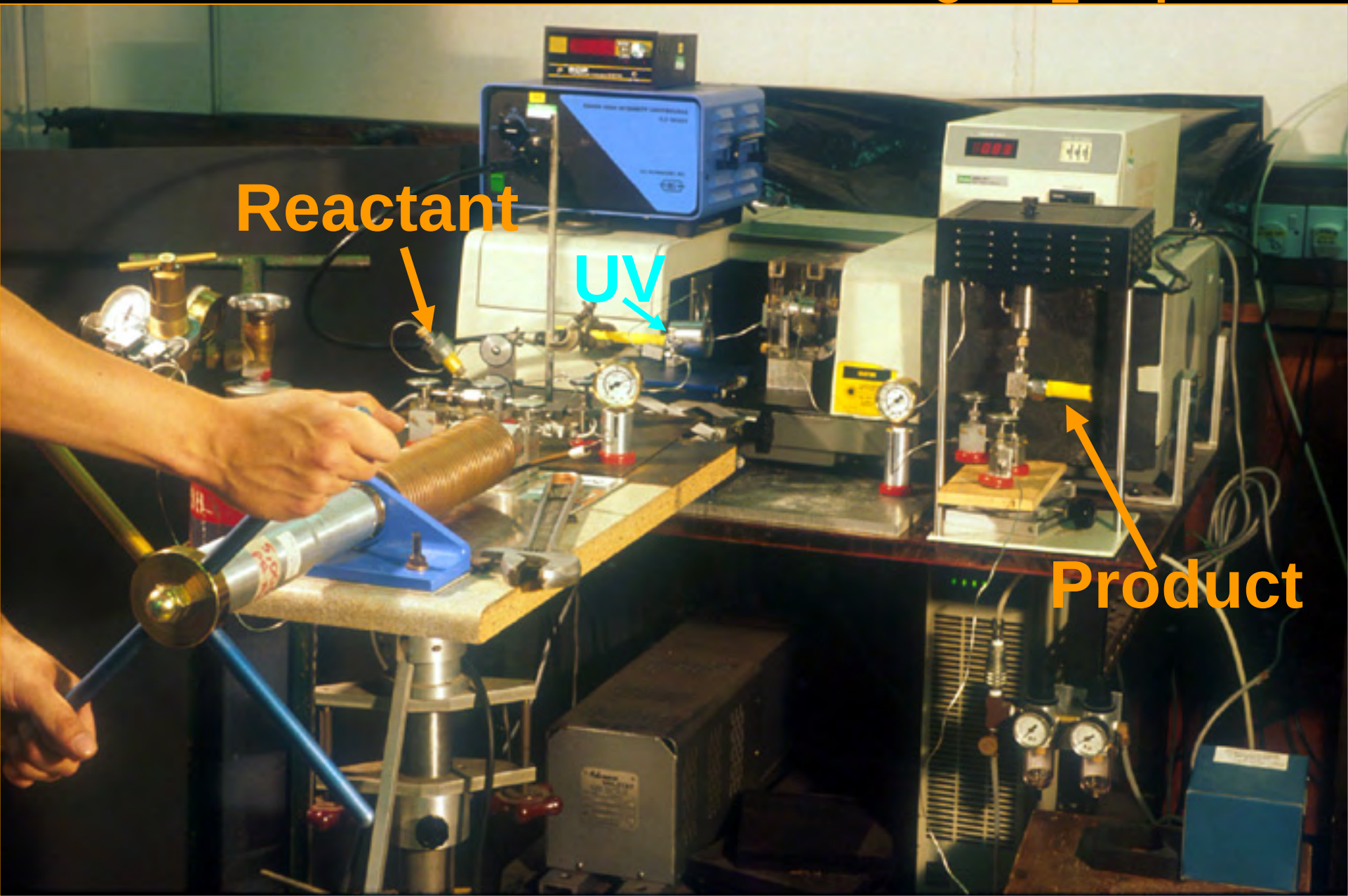
- Well established commercially



Ethene Complexes



Synthesis of $Cr(CO)_5(C_2H_4)$



$Cr(CO)_5(C_2H_4)$

James Banister

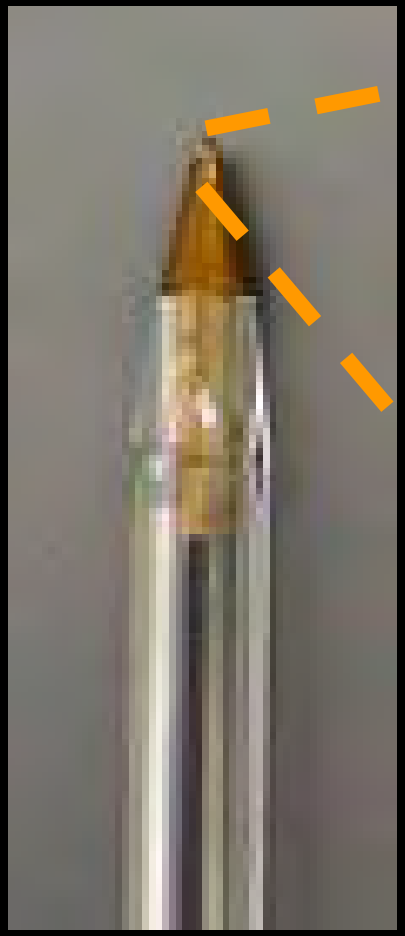
New Scientist, 6 Aug. 1994

SOLVENTS GET THE BIG SQUEEZE

Compress carbon dioxide enough and it will decaffeinate your coffee, improve the flavour of your beer and help chemists find safer ways to make new molecules. David Bradley reports on the strange world of supercritical fluids

Biro Bic

Biro Bic



Making a Biro tip

- Tips are machined out of solid brass
- Machining requires lubricant
- If not degreased, tips don't write
- Current method used $C_2H_3Cl_3$ which might have been banned in 1990s

Could we degrease with scCO_2?

Biro Enquiry – Outcome 1

- Set up a 2 month project
- Hired a finishing PhD, Dr Paul Hamley
- Month 1 degreased 2000 tips
- **Month 2 degreased 100,000 tips, enough for an 8 hour shift on plant**
- Proposed design for commercial use
- **Just then, factory was closed!!**

Biro Enquiry – Outcome 2

- Had 2 boxes of supercritical biros!
- Idea of Technology Transfer Scientist, available for proof of concept
- Visit of Gatsby Foundation
- **2 years funding for Paul Hamley**
- Self funding for next 11 years!
- **BDE network & Trevor Farren**

Second Result of the New Scientist Article

Continuous Reactions in $scCO_2$

Vending Machine Chemistry

"The chemist will simply press a button and the machine will add the appropriate reagents to the supercritical CO_2 and pump the mixture into the reactor."

Thomas Swan OBE

Thomas Swan & Co. Ltd.

Consett, County Durham, UK

Why collaborate on SCFs ?

- Mid 1990s fear of ban on all chlorinated solvents
- " Vending machine chemistry"
  "dial a molecule"

A New Approach to Hydrogenation of Organic Compounds

- Wide range of compounds
- High selectivity
- Heterogeneous Catalyst
- High throughput: tons per year
- **Environmentally “Clean”**


DELOXAN®
Degussa

Timescale

New Scientist article	Aug 1994
First Discussions	**Nov 1994**
First Reaction	**Nov 1995**
Start Building Plant	**Feb 2001**
Commissioning	Feb 2002
Official Opening	**July 2002**

TOP 20 INNOVATORS

3M	Inhale
Albemarle	Kao
Avecia	Lubrizol
Baxenden	MediChem
Cambrex	PCAS
Degussa	Rohm and Haas
Dow CMS	Rhodia ChiRex
Ecolab	Sensient Technologies
Engelhard	Sigma-Aldrich
IFF	Thomas Swan

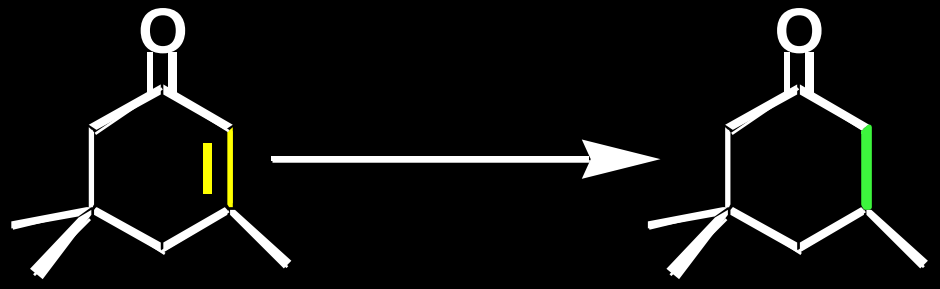
Thomas Swan

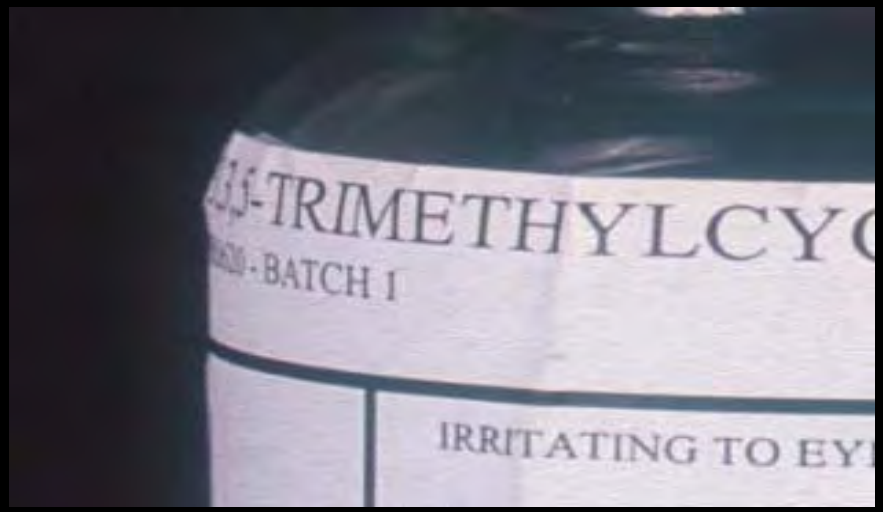
Chemical Specialties
Sept/Oct 2001

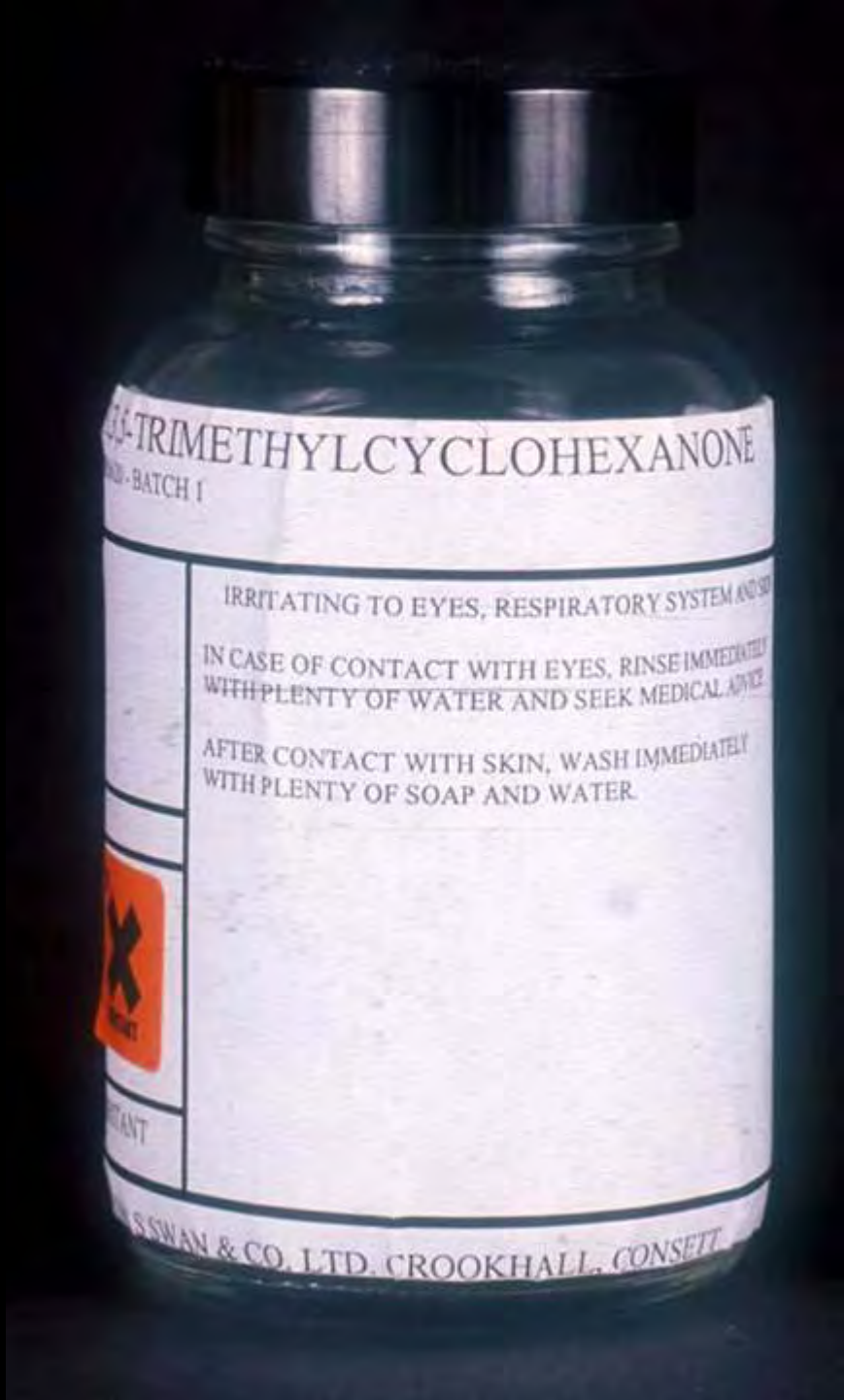
$scCO_2$ Chemical Plant

- continuous
- multipurpose
- 1000 ton p.a.

The First Product!







Thomas Swan Outcomes

- 4 co-workers got jobs with Swans
- High quality publications
- Several patents
- Additional funding EPSRC and EU
- New collaborations: AstraZeneca, Uniqema/Croda, SI Group, etc
- Research continuing
- **Phase behaviour capability**

Grand Opening 12th July 2002
Lord Sainsbury Minister of Science

Carbon Capture and Storage

phase behaviour of CO_2 is crucial

Projects: Mike George & Trevor Drage

Supercritical Water

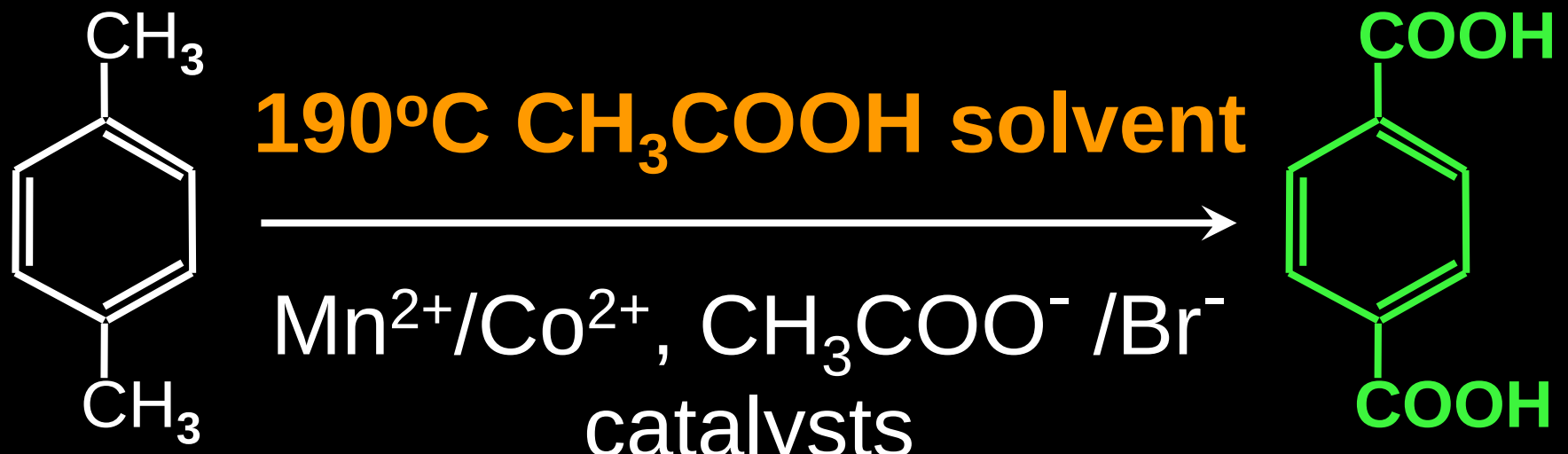
T_c 374 ^oC, p_c 221 bar

At high T, H_2O has solvent power similar to acetone

COST Action D6 Meeting
Lahnstein, March 1995

Derek Graham,
ICI Strategic Technology Group

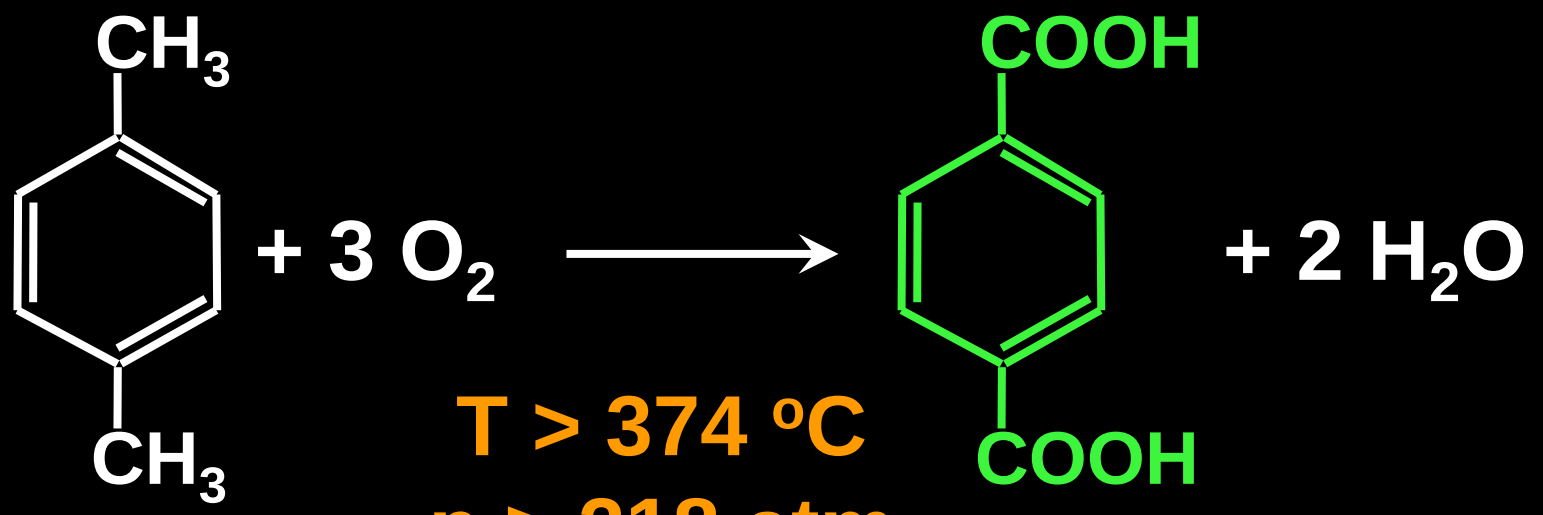
Oxidation of *p*-Xylene



0.5 Mton p.a. per plant

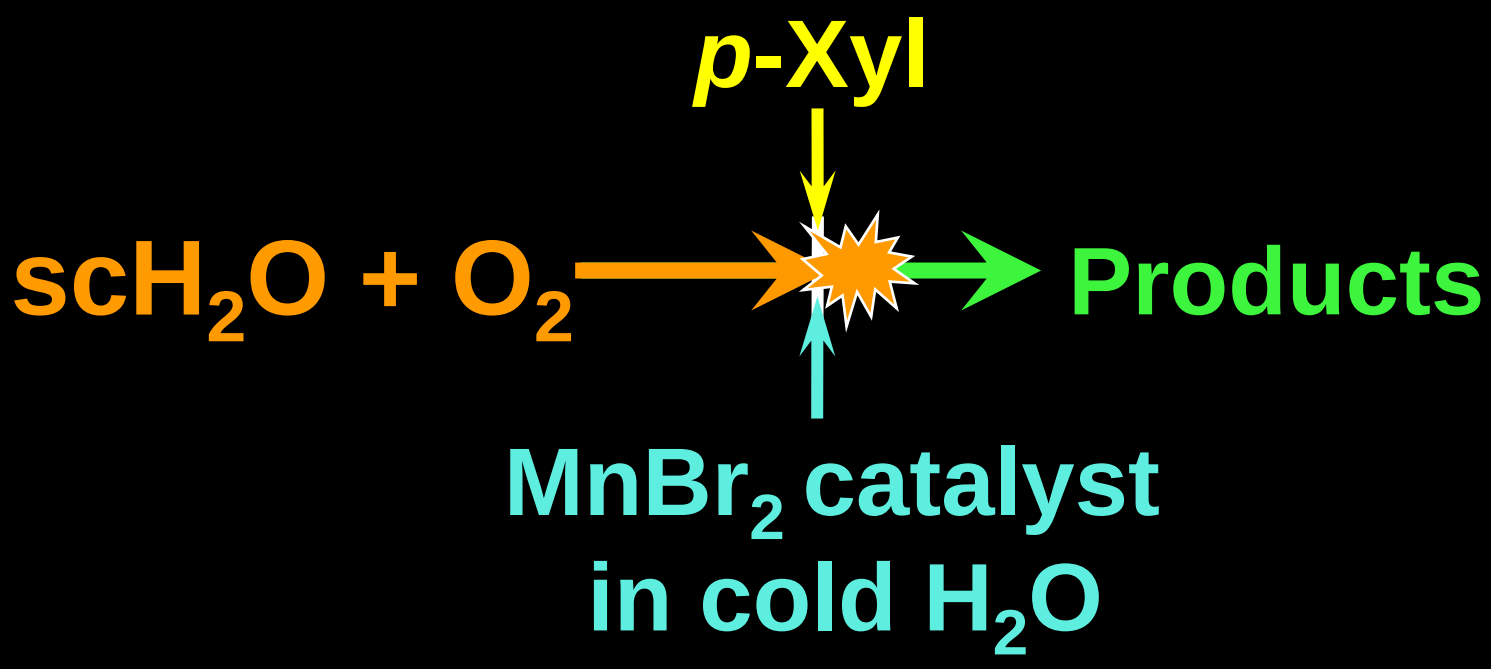
- TA insoluble in CH_3COOH
- **18% of world production of CH_3COOH lost in the process**

Continuous Oxidation of *p*-Xylene in scH_2O?



Potential major improvement over existing process

Oxidation of *p*-Xylene / scH_2O



PA Hamley, et al. *Green Chem.* (2002) ***4***, 235; (2005) ***7***, *294;* (2007) ***9***,*1238*

Oxidation of *p*-Xylene in scH_2O

- > 80% yield of TA
- > 90% selectivity for TA

Selective Oxidation in scH_2O

If our results are scalable,

- **total elimination of CH_3COOH**
- **increased energy recovery compared to existing process**
- **significant reduction in cost of manufacturing TA**

P-Xylene Outcomes

- On-going project (after 13 years)
- Papers, patents, funding
- 2 co-workers now with INVISTA
- New collaborations: GSK, Lucite
- **Behaviour of metal catalysts in scH_2O**

Formation of Oxides in scH_2O

$$ML_x + x\ H_2O \longrightarrow M(O)_{x/2} + x/2\ H_2O$$

where L = NO_3^-; M = Ce, Cr, Pr, Fe, *etc.*

K. Arai, T. Adschiri et al. in *High Pressure Chemical Engineering*; Elsevier:, 1996; p 315.

$$(1\text{-}x)[NH_4]_2\,Ce(NO_3)_6 + xZr(Ac)_4 \xrightarrow{H_2O} Ce_{1-x}Zr_xO_2\ ?$$

Continuous Reactions in ncH_2O

Solid solutions: Ce:Zr, Pr:Ce, Pr:Ce:Zr

~10 g / hour

A. Cabañas, J. A. Darr, E. Lester, M. Poliakoff, Chem. Commun. 2000, 901

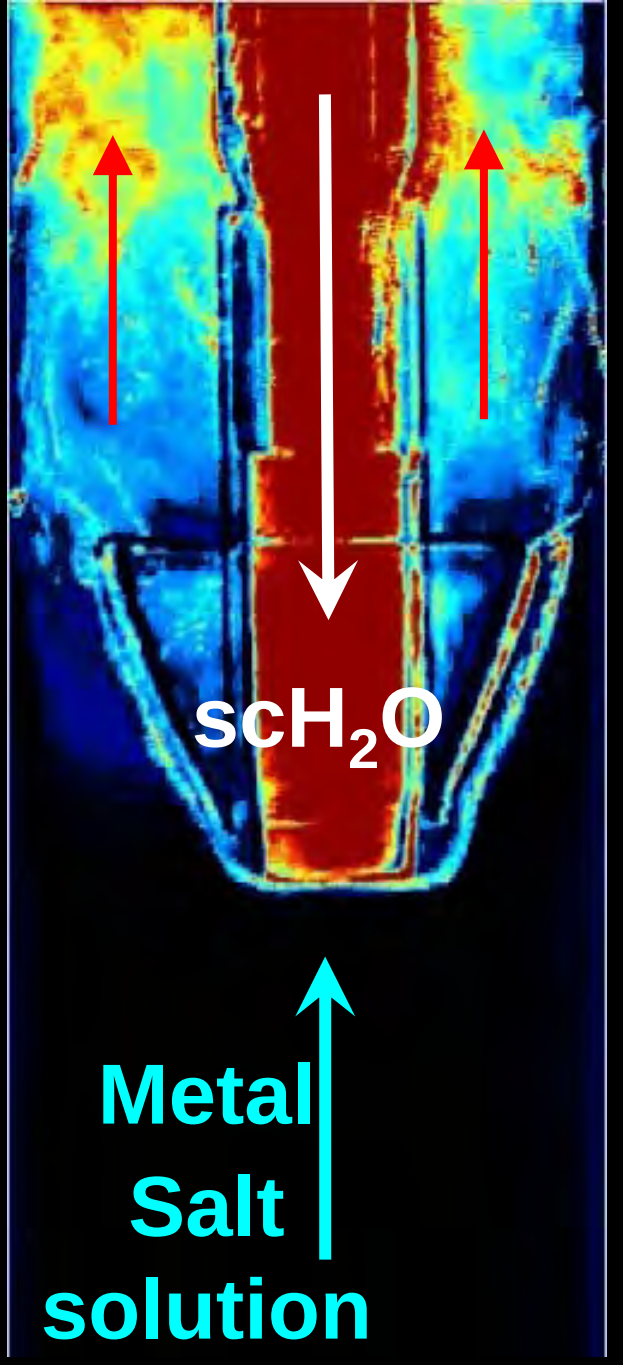
The Nozzle Reactor: Ed Lester

Exploit the density differential between scH_2O and the metal salt solution

Now being developed in spin-out company

PrometheanParticles

Formulating solutions with nanomaterials

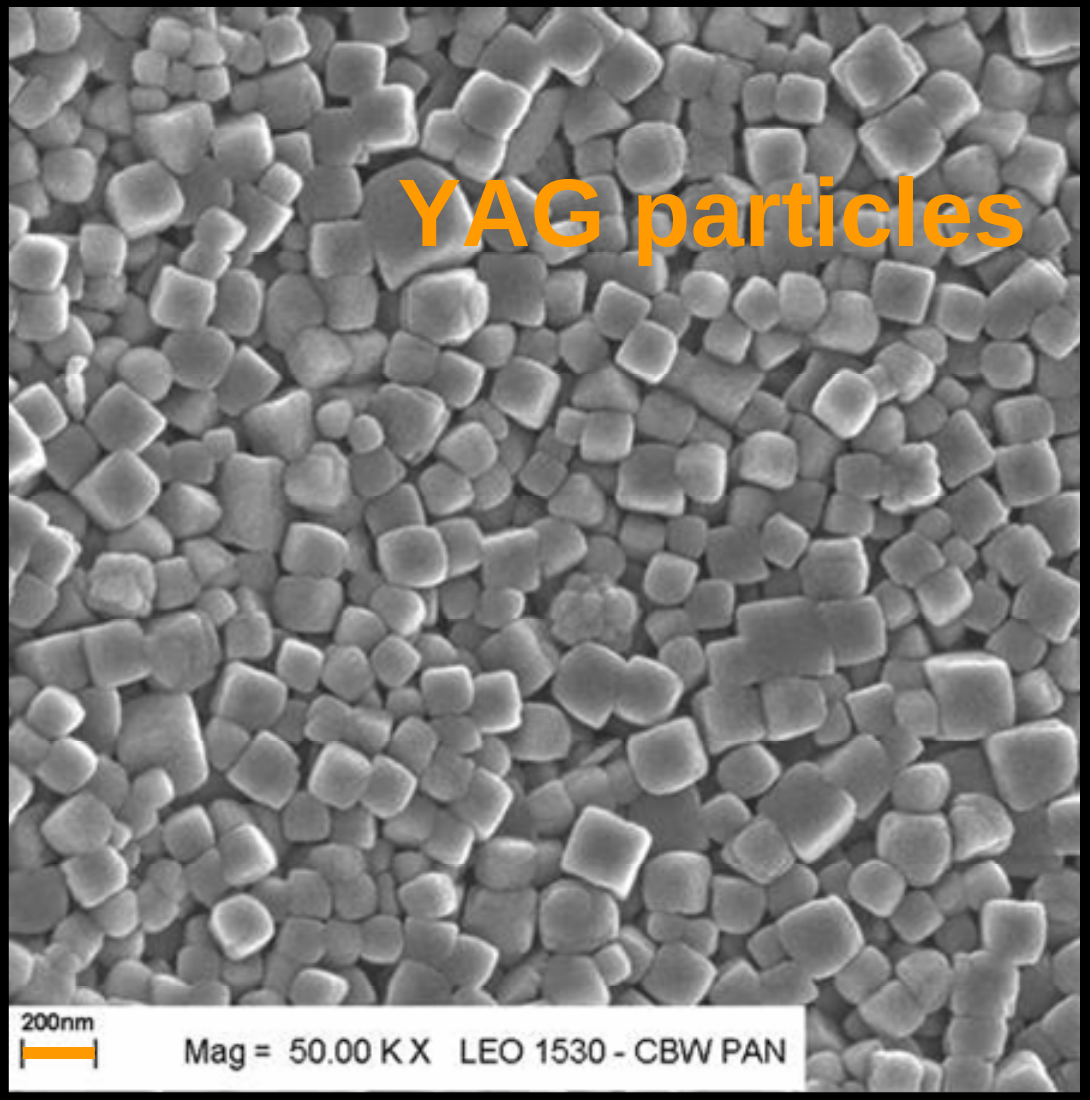


Synthesis of YAG in H_2O/EtOH

$Y(ac)_3$
$Al(acac)_3$

H_2O/EtOH 40/60
350 ºC, 240 bar

A Cabañas
E Lester, et al
J. Supercrit. Fluid
40 (2007) 284



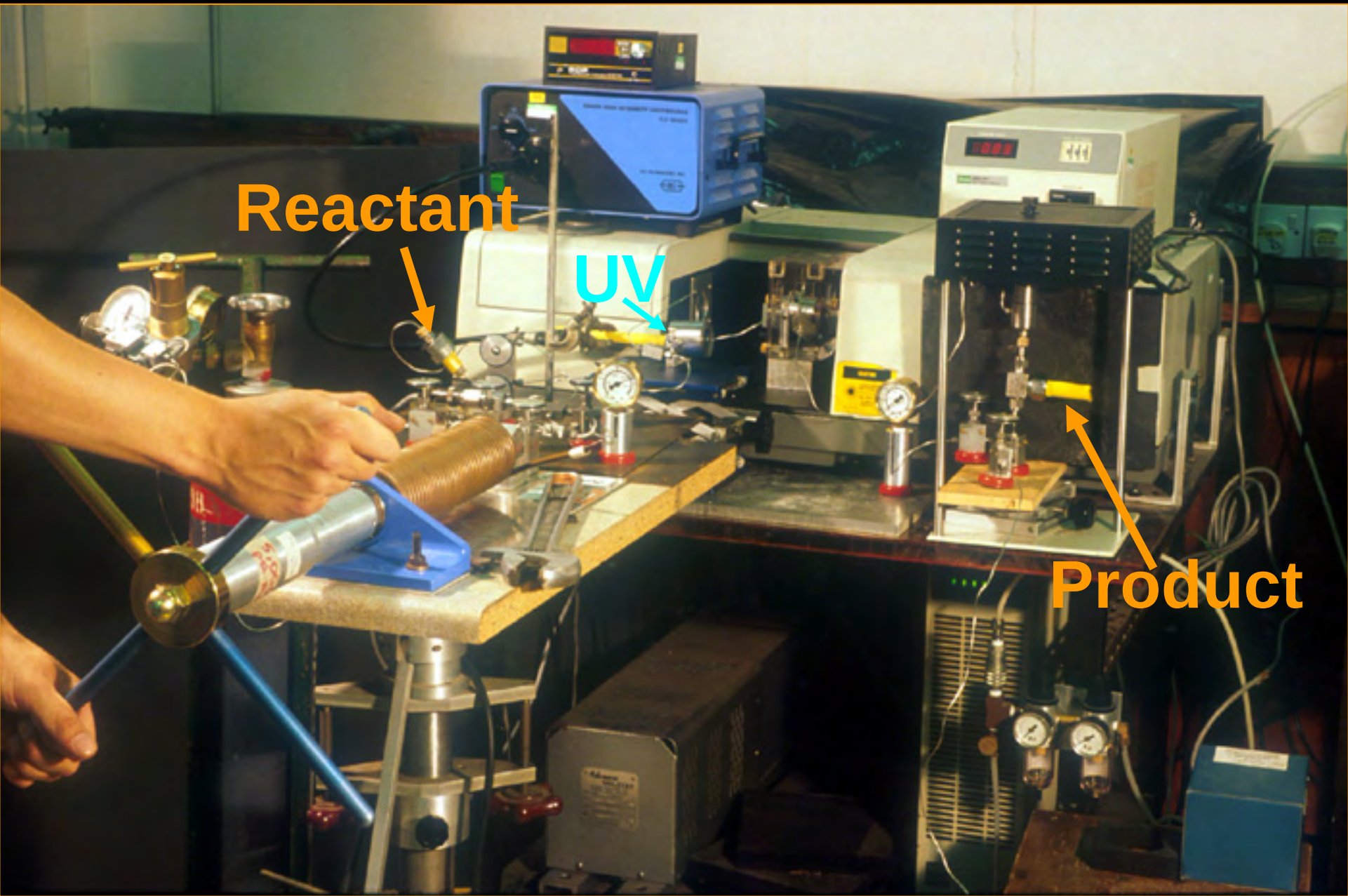
Scale-up

Nanoparticles in scH_2O

- Only requires simple salts
- Scalable
- Particles delivered in water – no dry handling

www.prometheanparticles.co.uk

Where has this led??



Overall Outcomes for me

- Taken me into new areas of science
- > 100 publications
- > 20 patent filings
- Involvement in CIKTN
- Council member of IChemE
- **Lots of fun!**

Outcomes for Nottingham

- New industrial collaborations
- Many supercritical patents
- **2 spin-out companies**
- £4.5M EPSRC DICE project
- **Strong collaboration between Chemistry & Engineering**

www.periodicvideos.com

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The University of Nottingham

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Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr


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"a brilliant idea" Guardian Media, Sept 8th
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Is commercialisation is an activity for a gentleman?

Definitely Yes!!!