

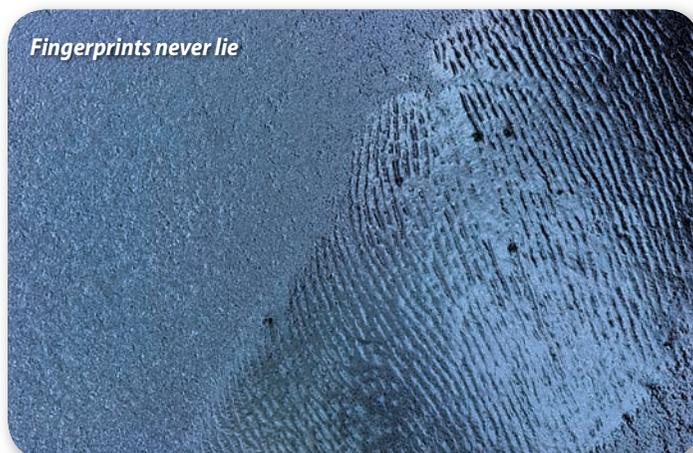
'INVISIBLE' CLUES

Fingerprints are unique. There is no surer way of establishing a person's identity at the scene of a crime than by their fingerprints. But often this crucial evidence is removed before the forensic team reach the scene and the criminal goes free. Now researchers in the department of chemistry at the University of Leicester, in collaboration with forensic scientists in the Northampton Police's scientific support unit, have come up with a method that will reveal fingerprints on metal objects, even when they have been wiped or washed away with soapy water.

How's it done?

According to Dr John Bond, reporting in the *American Journal of Forensic Science*, in May, the method works by exploiting the fact that the residue from a fingerprint corrodes metal surfaces, following precisely the ridge pattern of the prints as it does. The characteristics of the metal change, allowing forensics to enhance and reveal the print. In contrast, conventional fingerprinting methods rely on a physical or chemical interaction with the fingerprint residue, so once the residue has gone the technique would be of no use.

Bond explained to *InfoChem*, 'We take a metal that is thought to have a fingerprint on it – a gun



or bullet for example – and remove any residue. This ensures we are dealing with a corrosion reaction and not a reaction of the residue. We apply a potential across the metal of ca 2500V, at the same time dusting the metal with a conducting powder, *ie* very fine granular carbon. The powder preferentially adheres to the corroded parts of the metal, which we found to have a potential of about 10–12V less than other areas of the metal. In line with the laws of physics, the particles find the state of minimum energy.'

Fingerprint residues are typically made up from sweat from two different glands. Sweat from the eccrine glands, which exist in the pores on fingers, comprises 98 per cent water plus inorganic salts such as sodium and potassium chlorides. In contrast, sweat from

sebaceous glands, located in hair follicles, contains fats, oils and waxes. Bond suggests, based on what they know about corrosion science, that the Cl^- present in the residue from NaCl or KCl attacks the metal and causes it to dissolve. 'An aeration cell is formed', he says, 'with water and the ions acting as the electrolyte and the metal acting as both the anode and the cathode. Electron transfer through the metal results in dissolution of the metal in solution.'

Since the publication of Bond's article, two police forces have used the technique to help solve crimes. Meanwhile, a chemistry graduate is expected to take up a PhD studentship in the department of chemistry at the University of Leicester in the next academic year to unravel the fundamental chemistry and improve the technique.

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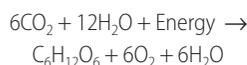
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ENERGY, NATURA

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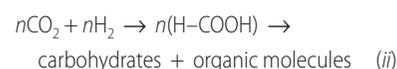
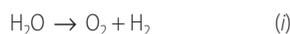
Natural photosynthesis produces billions of tonnes of energy in the form of sugar every year. In so doing carbon dioxide is removed from the atmosphere. Not surprisingly, scientists around the world are trying to emulate this process in the laboratory. But the promise of 'artificial photosynthesis' poses many challenges...

Plants and trees do it. Algae do it. Even primitive bacteria do it. They capture energy from the Sun and use it to convert water and carbon dioxide into oxygen and carbohydrates, such as glucose.



This is photosynthesis, and began on Earth over two billion years ago, changing our

atmosphere from an oxygen-poor to an oxygen-rich one. In a two-stage process, water is first split into hydrogen and oxygen (reaction (i), sometimes referred to as the 'light' reaction because light is needed) and the hydrogen then reduces carbon dioxide to carbohydrates and other organic molecules (reaction (ii), the 'dark' reaction because no light is needed).



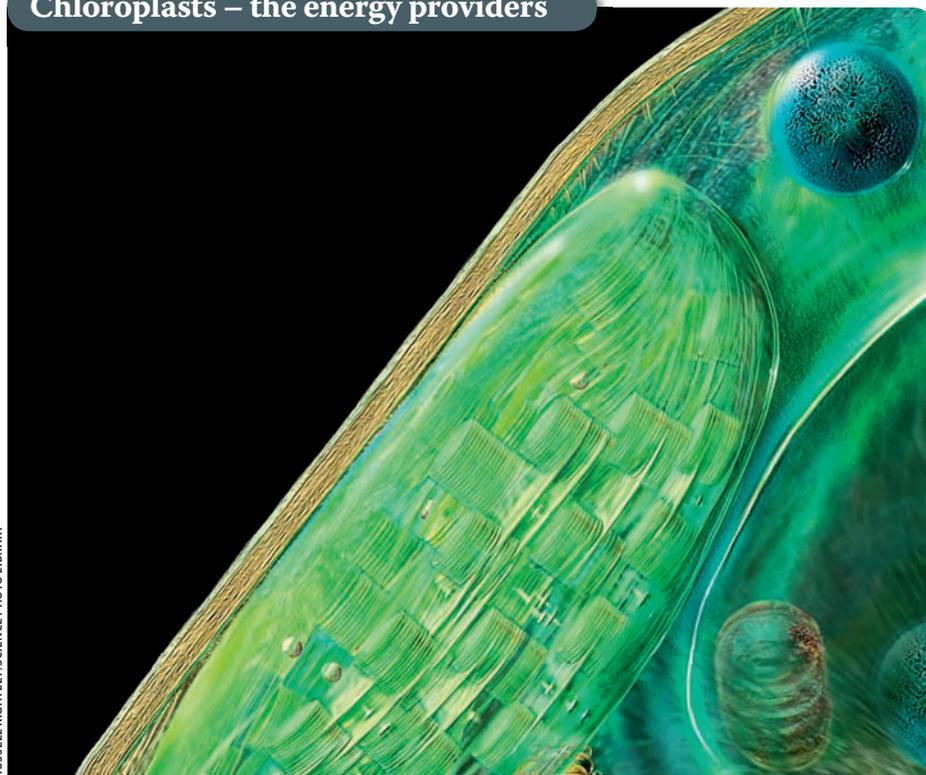
Today many scientists around the world believe that if this process could be reproduced in the laboratory and developed on an industrial scale, we would have the perfect solution to our energy problem. By 2050 scientists estimate that there will be an energy shortfall of 14TW (1TW = 10^{12} W). With over 100 000TW falling on the Earth as sunlight, the potential of 'artificial photosynthesis' is huge. Not only does it offer a route to sustainable hydrogen production and other useful fuels such as methane and ethanol, but it also removes CO_2 from the atmosphere, a key process with the potential to build other useful chemicals.

A CHALLENGING PROBLEM

By the 1970s, interest in artificial photosynthesis began in earnest. Scientists knew from earlier work on 'photogalvanic cells' (basically a dye in water plus a couple of electrodes) that they could generate electricity via charge separation and electron transfer reactions, but they had severe limitations. The amount of electricity produced was very small and the cells had to be extremely thin otherwise the ions would react in solution. So sustaining the output from such cells was difficult and scientists looked towards Nature for a better solution.

But it's not that simple. Natural photosynthesis is incredibly complex. The energy of sunlight is transferred in the form of electrons and positive charges throughout a pathway of

Chloroplasts – the energy providers



RUSSELL KIGHTLEY/SCIENCE PHOTO LIBRARY

myriad steps before the final products – carbohydrates – are formed. Crucially, these steps often require up to four electrons. This presents an enormous challenge to chemists because they need to be able to store electrons and use them at just the right time. All chemical reactions done in the laboratory involve transferring just one electron at any one time. To stand any chance of replicating and exploiting photosynthesis, scientists need to know exactly what is going on in the natural systems.

By this time they knew that natural photosynthesis occurs in specific membranes – chloroplasts – in plant cells. These high surface area membranes contain proteins and light-absorbing pigments such as chlorophyll and carotenoids. Chlorophyll captures the light and transfers it to the reaction centre, *ie* the catalytic site where the water-splitting reaction takes place. Chlorophyll is regenerated frequently during this process. This, Tony Harriman, professor of physical chemistry at the University of Newcastle, explains to *InfoChem*, raises another big challenge for an artificial system based on organic molecules. 'Organic molecules, such as dyes, when exposed to sunlight for an extended period will degrade. How such molecules can be renewed or repaired in an artificial system presents a huge challenge for chemists', he says.

UNDERSTANDING NATURE'S MASTERPIECE

Originally chemists thought that photosynthesis was occurring through a random distribution of chlorophyll in the chloroplasts, which they reasoned should be possible to replicate in the lab. However, over the past 30 years scientists have uncovered a different picture. They now know that Nature has learnt to position chlorophyll molecules in precise positions in the chloroplasts – at exactly the

same angle and same orientation in every chloroplast. This was confirmed by Professor Richard Cogdell and his team at the University of Glasgow in the 1990s by using X-ray diffraction studies.

Harriman explains, 'Within the chloroplast, there are a series of precisely placed chlorophyll molecules in a protein matrix which is *ca* 60 Å (1 Å = 10⁻¹⁰m) thick. It is a masterpiece of engineering. Shine light on one side and an electron will move in a series of jumps until it reaches the other side of the membrane. The result is a battery with a positive charge on the top of the membrane and a negative charge on the bottom. The catalyst is able to store these until it gets either four electrons or four positive charges, and then it will make oxygen on one side and reduce carbon dioxide on the other side. The way the chlorophyll species are arranged ensures that the positive and negative charges never come together otherwise they would annihilate each other and there would be no potential to do work. When you try to design this system in the laboratory it is impossible to arrange the chlorophyll species in precisely the correct positions so that these electron transfer reactions take place to split water'.



Chlorophyll in position

Another breakthrough in our understanding of natural photosynthesis was the elucidation of the structure of the catalytic reaction centres in chlorophyll in 2004 by Professor Jim Barber and his team at Imperial College, London. There are two very complex enzyme systems which carry out the light reaction – called photosystem 1 (PSI) and photosystem 2 (PSII). Barber identified the precise location and geometry of a few critical ions – manganese, oxygen and calcium – within the core of PSII, and this has led to research teams around the world looking for more robust catalysts that will do the same job outside of the natural environment. The problem with the natural systems, explains Harriman, is that they are very elaborate and totally unstable once they are removed from their protein environment.

Most of the current research in this area is focusing on ruthenium and iridium oxides as potential catalysts for an artificial system

Powered by fossil fuels, courtesy of photosynthesis



“...THE PERFECT SOLUTION TO OUR ENERGY PROBLEM.”

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based on dye molecules. So far, however, scientists have only been able to achieve efficiencies of *ca* 0.3 per cent with such laboratory-based systems.

MOVING TO THE DARK SIDE

Mimicking the dark reaction is also highly desirable. Again, in natural systems this involves a very elaborate mechanism – the Calvin cycle, named after Melvin Calvin one of the chemists at the University of California, Berkeley who discovered it. In this process a co-enzyme system, NADP⁺/NADPH, moves

back and forth, picking up a proton and two electrons and depositing them for use in the production of carbohydrates.

Chemists, notably in the US and Germany, are looking for a catalyst that will mimic the natural co-enzyme in the lab. Etsuko Fujita and her team at the Brookhaven National Laboratory in New York, recently reported a new catalyst for CO₂ reduction based on ruthenium, which holds much promise for fuel production.

At the present time, despite having taken huge steps in our understanding of the

Engineering plant...

natural process, artificial photosynthesis is still considered as ‘blue-sky’ research. Its further development and exploitation lie in the hands of policy makers and funding agencies, and a supply of high quality chemists and engineers in the future to deliver the breakthroughs.

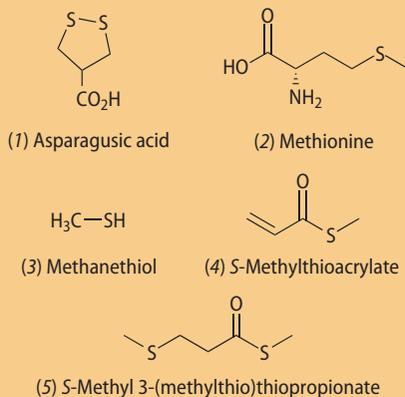
Kathryn Roberts

that's chemistry!

Simon Cotton, chemistry teacher at Uppingham School, looks at the molecules in our lives. In this issue: **asparagus and its after effects**

I like asparagus, but why does it makes my urine smell funny?

You are not alone. Some 43 per cent of people find that after eating asparagus (*Asparagus officinalis*) their urine smells of rotten vegetables. Asparagus contains sulfur compounds such as asparagusic acid (1) and sulfur-containing amino acids such as methionine (2). These chemicals are broken down in the body into small, smelly, sulfur-containing molecules such as methanethiol, CH₃SH (3). This smelly compound is mixed into our domestic



Asparagus tip – sulfur compounds smell

gas supply so that gas leaks can be detected by methanethiol's familiar bad odour.

Are other compounds involved?

In 1975 scientists analysed ‘asparagus-tainted’ urine samples, using gas chromatography coupled with mass spectroscopy, and identified two larger molecules, S-methyl thioacrylate (4) and S-methyl-3-(methylthio)thiopropionate (5), but not methanethiol.

However, further research in 1987 showed that methanethiol was present in similar urine samples along with other different sulfur-containing compounds, including dimethyl sulfide and dimethyl disulfide. So it's possible that different people produce different ‘blends’.

Can we detect these blends?

Some researchers say that the ability to produce smelly urine is an autosomal (sex-independent) inherited trait. Other scientists have reported that anyone who can smell this bad odour in their urine can smell it in the urine of anyone else who has eaten asparagus, with *ca* 10 per cent able to detect the smell at very low concentrations. This suggests a genetically-determined hypersensitivity to these smelly sulfur compounds. ■

If you want to test your chemical knowledge with an ‘asparagus pee’-related problem, ask your teacher for your institution's copy of the Royal Society of Chemistry book *Kitchen chemistry* and turn to page 109.

ON-SCREEN CHEMISTRY

Jonathan Hare asks...

AVOIDING DETECTION: *can you fool an infrared security camera?*

In *The Thomas Crown affair*, Pierce Brosnan is Thomas Crown, a rich playboy who spends his time stealing priceless pieces of art. In one scene Crown steals a precious painting from an art gallery. The painting is in a room with thermal imaging (infrared) security cameras. These cameras image heat rather than light so they work well during the day or at night. Before Crown steals the painting he leaves a suitcase in the room containing a heater, switched on. He does this to raise the temperature of the room and swamp the

sensitivity of the camera – producing a ‘white-out’ on the screens – which allows him to go about his business unseen. So can you fool a state-of-the-art thermal camera by using this trick?

Thermal cameras

Modern thermal cameras are sensitive to a wide range of infrared energy produced by the temperature of the objects around them. They give a false colour image on a TV screen that depicts the variations in heat energy coming from the objects in view. However, if you heat up everything to exactly the same temperature it won't necessarily make everything look the same on the screen. This is because different objects emit and absorb infrared radiation at different rates even if they are at the same temperature – it's called their emissivity. So the thermal camera records the heat they emit rather than their temperature.

If you take a tray of different objects, put them in an oven for enough time for them all to reach the same temperature and look at them with a thermal camera they will appear distinct because they all have different emissivities. So heating everything up to the same temperature won't fool the cameras.

Modern thermal cameras are very sensitive and will operate over a very wide range of intensities. So would it be possible to raise the temperature of the room by enough so that the thermal energy would be too great for the range of the camera and thus produce a white-out on the screen as seen in the film?

It is possible to produce an effect like this by carefully adjusting the setting of the

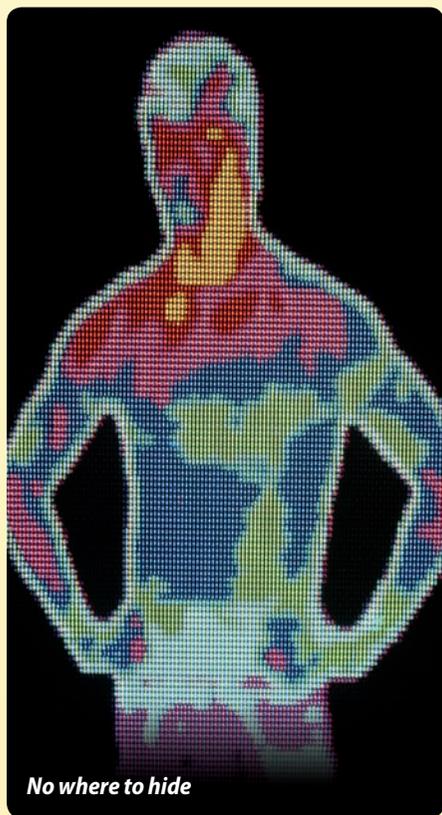
thermal camera. I tried observing a person through the camera in a small room as the heater was turned up to maximum and I was able to create just such a ‘white out’ on the screen. But this was a deliberate attempt to try to produce this effect. In normal use the thermal cameras have such a wide response that this would never happen. Certainly not over the sort of temperature rise you would expect with a small briefcase heater in the centre of a large room.

Thermal cameras are usually set-up with what's called ‘automatic gain control’ (AGC) which automatically adjusts the camera sensitivity (gain) for any changes in the overall background. The AGC extends the useful range of the camera which will stop ‘white-out’ occurring.

Caught (infra)red handed

So with a correctly set-up camera it would be extremely unlikely that such a simple stunt could work. Since the security team had several of these cameras around the room I think they would have been able to see exactly what the thief was doing and so catch him before he left the building. ■

Dr Jonathan Hare, The Creative Science Centre, Chemistry Department, University of Sussex, Brighton BN1 9ET (www.creative-science.org.uk/TV.html).



No where to hide

Q&A

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Looking for answers to chemically related issues? Why not put them to InfoChem's professional chemists ...

Q: How accurately can we measure Avogadro's constant? (From Jason Hui of Bristol Grammar School.)

Dr Michael Laing, University of KwaZulu-Natal says:

In 1986, the International Union Of Pure and Applied Physics published the value: $6.022\ 136\ 7\ (36) \times 10^{23}$ as being the best value. This number was determined by accurate measurement of the diffraction of monochromatic x-rays from a pure, single crystal of silicon. The accuracy of the technique rests on the accuracy of the x-ray wavelength, the density of the crystal, and the molar mass of silicon. These values were known to seven significant figures. The earliest measurements of Avogadro's constant were by French physicist Jean Perrin in 1909, who used the Brownian motion of small particles in suspension. He found values between 6.5 and 7.2×10^{23} .

Getting a good, accurate and dependable number is not easy. Chemistry books of 1950 quote many different values: 6.0220 , 6.0225 , 6.020 , 6.025×10^{23} .

You can rely on this new value to be accurate to about one part in 600 000. How does this compare in simple terms? This is equivalent to 1 cm in 6 km. Can you detect this with the naked eye? Or with any simple instrument? For practical purposes the value 6.022×10^{23} is a good number for use in normal calculations. (For fun you might like to look up 'Determination of Avogadro's constant' on Google.)

SEND YOUR QUESTIONS TO:

The Editor, *Education in Chemistry*, the Royal Society of Chemistry, Burlington House, Piccadilly, London W1J 0BA or e-mail: eic@rsc.org.

All questions published will receive a £10 HMV token.

Organic Prize Quiz winner

The winner of the Organic Prize Quiz published in May's issue of InfoChem was Charlotte Lynch of Birkenhead, Merseyside. Answers to quiz, along with a downloadable pdf version of InfoChem, can be found at <http://www.rsc.org/Education/EiC/issues/2008July/Infochem.asp>

GO FOR GOLD!

Test yourself with questions from the International Chemistry Olympiad

This question is adapted from Q3 of the 2005 UK Round 1 Chemistry Olympiad paper.

The 'simplest' carboxylic acid is called methanoic acid and has formula HCOOH. It occurs naturally in ants and used to be prepared by distilling them! When an ant bites, it injects a solution containing 50 per cent by volume of methanoic acid. A typical ant may inject around $6.0 \times 10^{-3} \text{ cm}^3$ of this solution.

- Given that the density of methanoic acid is 1.2 g cm^{-3} , how many moles of methanoic acid does the 'typical ant' inject?
- As soon as the methanoic acid is injected it dissolves in water in the body to produce a solution of methanoic acid. Assuming that it dissolves immediately in 1.0 cm^3 of water in the body calculate the concentration of the methanoic acid solution that is formed. (You may ignore the volume of the methanoic acid itself in this calculation.)

The pH of a solution is related to the concentration of hydrogen ions as: $\text{pH} = -\log[\text{H}^+]$, where $[\text{H}^+]$ stands for the concentration of hydrogen ions in mol dm^{-3} .

- The pH of the methanoic acid solution produced above was 2.43. What is the concentration of hydrogen ions in this solution?

Methanoic acid is a weak acid and so is only partly ionised in solution:



- Calculate the percentage of methanoic acid molecules which are ionised in this solution.

The acid dissociation constant, K_a , is a measure of how ionised a weak acid is. For methanoic acid it is defined by the following expression where again square brackets written round a formula mean the concentration of that substance in mol dm^{-3} : $K_a = \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]}$

- Calculate the acid dissociation constant for methanoic acid.

WEB RESOURCES

To see the 2005 Olympiad paper (and answers!) go to: www.chemsoc.org/olympiad

To find out more about how to take part in the RSC Olympiad competitions for UK sixthform students go to:

www.rsc.org/olympiad

A DAY IN THE LIFE OF...

REGULATORY AFFAIRS CONSULTANT: Adesola Obunge

Adesola has spent the past three years working for Parexel Consulting as a regulatory affairs consultant. She talks to James Berressem about her typical day.

Parexel Consulting is a life sciences consultancy firm that provides scientific, regulatory and business advice to help healthcare companies bring their products (drugs or medical devices) to market quickly. Clients include several pharmaceutical and biotechnology companies in the UK and worldwide. Based in offices in Uxbridge, Adesola is one of *ca* 70 staff in the regulatory affairs department.

REGULATING HEALTHCARE PRODUCTS

The healthcare industries are regulated by international government agencies, *eg* the European Medicines Agency (EMA), and the Food and Drugs Administration (FDA) in the US, which ensure that medicines and medical devices work and are safe. These agencies set out laws relating to the testing, manufacture and marketing of new drugs and medical devices. Adesola works with healthcare companies to ensure that their processes and procedures meet the regulators' requirements.

Her day-to-day work is varied and depends on the clients' needs. She always has several projects on the go at once and these can

range from writing applications to start clinical trials, through preparing product licence applications to manufacture and sell a new drug, to auditing manufacturers' processes and procedures to check that they adhere to current regulations.

Much of her day is spent at her desk reviewing product data and proposals provided by clients, writing technical reports for clients, and contacting and meeting with clients and the agencies. Although based in the UK, Adesola's projects tend to be international because clients usually want to test, manufacture and sell their products globally. So she contacts clients and the regulators by phone or e-mail and holds frequent telephone conferences, which can mean early and late starts to her day because of international time differences.

For each project, *eg* seeking authorisation to manufacture a new drug, Adesola first checks what the regulations are and compares these with the client's proposals, checking that supporting data submitted by the client is accurate and complete. Adesola's chemistry training helps her to understand the data provided by clients, which include information on the drug's mode of action and how it is manufactured. And if a topic is unfamiliar, she consults colleagues with specialist knowledge, *eg* in pharmacology. She collates these data in the application, presenting in a logical manner complex information in straightforward language. Having submitted an application, Adesola awaits the verdict and feedback from the regulators, who may want the client to supply additional data prior to approval. Most of her time is spent negotiating with the client and regulators on changes to the application, sourcing additional data, and then re-writing the application until it receives approval.

CHALLENGE AND DIVERSITY

The diversity of the job attracted Adesola to a role in regulatory affairs and she enjoys the challenge of working on new projects with different people. She is pleased to be in a career that requires her to use the chemical knowledge she developed at university. ■



Adesola Obunge

PATHWAY TO SUCCESS

- 2008–present, regulatory affairs consultant, Parexel Consulting, Uxbridge
- 2005–08, regulatory affairs associate consultant, Parexel Consulting, Uxbridge
- 2004–05, regulatory affairs officer, Waymade Healthcare, Basildon
- 2001–04, quality control scientist, GlaxoSmithKline, Ware
- 1996–2001, BSc (Hons) Chemistry with year in industry (2.ii), University of St Andrews
- 1995–1996, chemistry, physics, biology A-levels, Oxbridge College, Nigeria

£50 OF HMV TOKENS TO BE WON!

Benchtalk

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PRIZE WORDSEARCH No. 40

Students are invited to find the 29 words/expressions associated with synthetic diamonds hidden in this grid. Words read in any direction, but are always in a straight line. Some letters may be used more than once. When all the words are found, the unused letters, read in order, will spell a further 10-letter word. Please send your answers to the Editor at the usual address to arrive no later than Monday 4 August. First correct answer out of the editor's hat will receive a £20 HMV token.

D	S	R	D	C	L	E	P	O	R	T	O	L	L	A	A	Y
N	R	E	E	R	S	T	R	U	C	T	U	R	E	C	R	H
O	O	Y	P	Y	S	E	N	O	T	S	M	E	G	T	E	O
M	S	A	O	S	U	B	S	T	R	A	T	E	S	I	A	T
A	N	L	S	T	S	U	R	F	A	C	E	I	G	V	C	B
I	E	N	I	A	N	O	B	R	A	C	M	B	A	A	T	A
D	S	O	T	L	F	I	L	A	M	E	N	T	S	T	I	L
C	D	I	I	L	M	O	T	A	H	A	R	D	E	I	O	L
I	N	S	O	I	R	E	A	C	T	A	N	T	S	O	N	S
T	O	U	N	S	O	H	E	A	T	S	I	N	K	N	C	O
E	M	F	S	E	N	S	O	R	T	R	E	N	I	B	H	F
H	A	F	D	I	A	M	O	N	D	F	I	L	M	A	A	P
T	I	I	R	H	A	R	E	S	E	A	R	C	H	R	M	L
N	D	D	P	T	T	S	Y	L	A	T	A	C	O	R	B	A
Y	R	S	L	O	O	T	G	N	I	T	T	U	C	I	E	S
S	A	S	T	N	A	L	P	M	I	A	N	I	T	E	R	M
G	C	R	Y	S	T	A	L	G	R	O	W	T	H	R	Y	A

ACTIVATION	DEPOSITION	GEMSTONES	RESEARCH
BARRIER	DIAMOND FILM	HARD	RETINA IMPLANTS
ALLOTROPE	DIAMOND	HEAT SINK	SENSOR
ATOM	SENSORS	HOT BALLS OF	STRUCTURE
CARBON	DIFFUSION LAYER	PLASMA	SUBSTRATE
CATALYST	FILAMENT	INERT	SURFACE
CRYSTAL GROWTH	GASES	REACTION	SYNTHETIC
CRYSTALLISE	GAS PHASE	CHAMBER	DIAMOND
CUTTING TOOL	CHEMISTRY	REACTANTS	

May PRIZE WORDSEARCH No. 39 winner

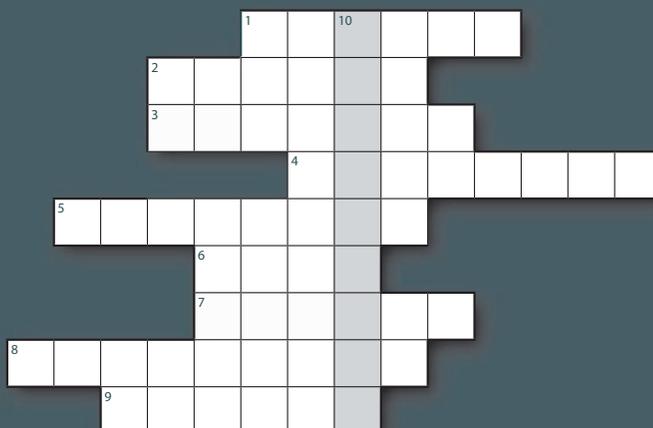
The winner was ChemNet member Robert Alford from St Nicholas Catholic High School, Hartford, Cheshire. The five-letter word was CURRY.

FIND THE ELEMENT No. 3

Students are invited to solve Benchtalk's *Find the element* puzzle, contributed by Dr Simon Cotton of Uppingham School. Your task is to complete the grid by identifying the 10 elements using the clues below.

ACROSS

- _____ fibres are used as a strengthening material; found in charcoal and all organic compounds.
- Metals found in all salts that give a yellow flame test.
- Inert gas that reminds you of Superman.
- Poisonous green-yellow gas used as a disinfectant.
- Used to make ammonia by the Haber process; found in air.
- Second most common metal in the Earth; corrodes in moist air.
- Used in antiseptic solutions; black solid that forms purple vapour when heated.
- Silvery metal that reacts with steam but only slowly with cold water.
- Least dense inert gas (whose name means 'sun' in Greek).



If you have found the correct nine elements, in 10 down you will have generated the name of an uncommon member of the platinum metal family. Its name begins with a girl's name.

Please send your answers to: the Editor, *Education in Chemistry*, the Royal Society of Chemistry, Burlington House, Piccadilly, London W1J 0BA, to arrive no later than Monday 4 August. First out of the editor's hat to have correctly completed the grid will receive a £30 HMV token.

Ne	<	Ar	He	Xe	Kr		
^					v		
Kr	Xe	Ne	He	<	Ar		
Xe	>	Kr	>	Ar	Ne	>	He
Ar	He	Xe	>	Kr	Ne		
He	Ne	Kr	Ar	Xe			

Futoshiki chemical elements no. 1 winner

The winner was Chloë Guppy from Broadlands School, Keynsham, Bristol.