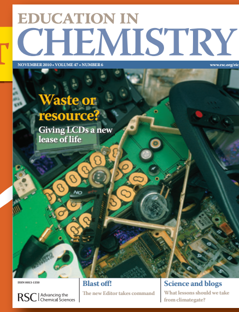
InfoChem
STUDENT SUPPLEMENT



ISSUE 125 NOVEMBER 2010

NANOPARTICLE PROTECTION

New inorganic nanoparticles that simultaneously restore and preserve ancient artworks have been developed by researchers in Italy. Many types of cultural heritage could be treated using this method, without causing further damage over time unlike some currently used restoration techniques and polymer coatings.


New method can restore and protect ancient art

THINKSTOCK

Preserving history

Preservation and restoration of artwork is important, as paintings such as frescos – Italian wall paintings applied straight onto plaster – give us important glimpses into history. A standard method used by conservators for protecting frescos is to apply an acrylic polymer coating, but such coatings can turn yellow, giving the surface a plastic appearance and damaging the artwork in the long term.

Piero Baglioni and colleagues at the University of Florence in Italy, have developed alkali metal hydroxide nanoparticles that can be applied to frescos and other pieces of art that not only provide a protective barrier against further damage, but can also help restore them to their former glory.

Baglioni explains that most wall paintings and monuments are made out of limestone – a sedimentary rock composed largely of calcium carbonate. When damaged by water, 'calcium carbonate is chemically converted into calcium sulfate and during this reaction you lose the painting,' Baglioni continues.

Baglioni's team has developed calcium hydroxide nanoparticles that react with carbon dioxide in the air to form calcium carbonate, replacing the calcium carbonate that has been lost due to water damage. This extra calcium carbonate can also help to reverse some of the damage caused by the calcium sulphate, something that none of the current coatings are able to do.

The nanoparticle coating that Baglioni's team has developed is very easy to use. The nanoparticles are first dispersed in propanol and then the propanol suspension is sprayed or brushed onto the surface of the artwork. In cases where the surface is very fragile, Japanese paper – a fine paper with pores – is laid on top of the painting to protect it from damage, allowing a thin coating to be applied through the paper onto the fragile image beneath.

Large potential

'We produced calcium, strontium, barium and magnesium hydroxide nanoparticles, and each of these are useful for different purposes. For example, you can use magnesium and calcium hydroxide for the conservation of paper, wood or cellulosic based materials,' Baglioni states. He believes the nanoparticle method can be used to protect most surfaces, apart from metal.

The spray can also be used in remote places where there is no electricity, and Baglioni has used his method in the jungle in Mexico. 'Hopefully, eventually all conservators will use this method as it is simpler and safer for the works of art and the conservator,' Baglioni concludes.

Mike Brown

IN THIS ISSUE

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CSI: CHEMICAL SCIEN

ISSUE 125 NOVEMBER 2010

This is the second in a short series of articles that explores the role of chemical scientists in forensic investigations.
In this issue: Poisoned or not? Napoleon's death

Napoleon Bonaparte suffered for years with a digestive condition that produced agonising pain leading up to his death in 1821. The cause of death was recorded as stomach cancer.

At the time Napoleon was being held by the English on Saint Helena. Foul play was suspected and arsenic named as the poison. Such poisoning was a distinct possibility as it would have produced symptoms identical with those of stomach cancer.

In those days there was no means of detecting arsenic in the body and many people are thought to have 'conveniently' died of food poisoning Fortunately, a sample of Napoleon's hair was retained and recently this was analysed and the presence of arsenic confirmed. How was this determined?

A common poison

Arsenic poisonings actually refer to highly toxic arsenic trioxide (As_2O_3) rather than the much less poisonous element itself. In years gone by, arsenic was commonly used use for fly-papers, pigments, cosmetics and even medicines. For example, in the eighteenth and nineteenth centuries Fowler's Solution – a tonic containing one per cent arsenic trioxide – was a favourite among men as it was thought to be an aphrodisiac. This household use resulted in many people dying due to accidental poisoning.

Today, the belief that Napoleon was poisoned

Exhiled and ill in St Helena

STEFANO BIANCHETTI/CORBIS

TISTS INVESTIGATE

Glory days

THINKSTOCK

persists. Arsenic's colourless and odourless properties made it a popular poison for sneaking into a victim's food or drink. With sufficient care in administering it, the poisoner could be reasonably confident that his crime would go undetected.

Arsenic in the body's chemistry

Arsenic forms strong bonds with amino acids that contain sulphur and so can become locked into proteins or interfere with the workings of enzymes. Where the toxic effect of arsenic is limited and the recipient continues to live, much of the arsenic will be excreted, although arsenic incorporated in the structure of hair and nail proteins will remain as a record until lost by normal growth or cutting.

Hair is especially stable and will remain chemically unchanged for centuries – even millennia in the right conditions. It is this permanence that is so beneficial for forensic analysis many years after the death – as in our Napoleon example. Hair grows at the rate of 10–15 mm per month. As the growth proceeds, the arsenic record formed can be quite precise in terms of when the person received a dose.

Detecting arsenic

Until the English chemist James Marsh demonstrated his test for arsenic, small amounts of arsenic could not be detected. Marsh's test played a key role in confirming the cause of death in an 1836 murder trial and represented a major step in the application of chemistry to crime investigation.

Today we have many techniques for arsenic analysis. Outstanding among them is Neutron Activation Analysis (NAA). Recently NAA was used at Harwell, Oxfordshire, to analyse samples of Napoleon's hair that had been preserved, samples taken just after his death and earlier samples from while he was still alive.

Conclusion

The truth of Napoleon's death may never be known. NAA showed that Napoleon was not just exposed to high levels of arsenic in the period leading up to his death, as might be expected by those proposing the arsenic poisoning theory. In fact samples from many years prior to his death contained alarmingly high concentrations of arsenic interspersed with low concentrations.

Was it that Napoleon had taken medication such as Fowler's Solution? Perhaps he was dosing himself with arsenic to build up a resistance to it to try and foil any attempt to poison him – long-term exposure to arsenic develops tolerance.

Focusing upon his living conditions on Saint Helena, we note that his room was decorated with wallpapers that had a pattern printed with a pigment known as Scheele's Green, a green insoluble compound copper arsenite ($CuHAsO_3$). While on dry wallpaper Scheele's

Napoleon's tomb

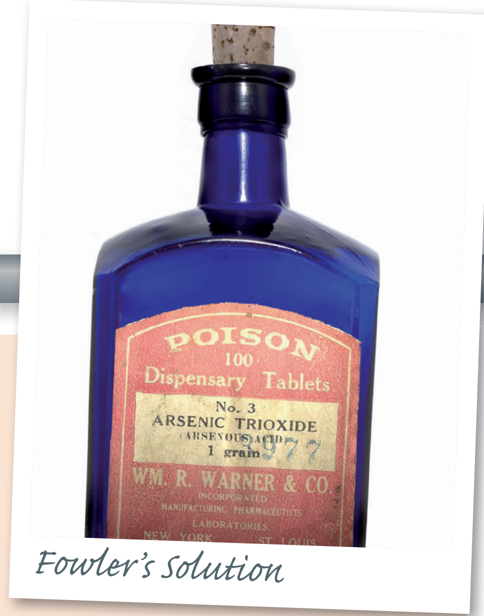
Green is not a problem. However, if the wallpaper becomes damp – and Saint Helena is a particularly damp place – the compound reacts and produces cacodyl (trimethyl arsenic, $As(CH_3)_3$) and a serious problem arises. For a start, cacodyl is volatile so it evaporates from the wallpaper and fills the room, and unlike the solid pigment copper arsenite cacodyl is much more toxic. Any occupant that spent any length of time in the affected room would inhale the cacodyl and absorb high doses of a treacherously poisonous compound.

It may well be that Napoleon did die of stomach cancer but suggestions of arsenic poisoning are plausible. However, if arsenic poisoning was the culprit it was highly likely to be unintentional and due to inhalation and absorption of cacodyl from the wallpaper. Of course, if Napoleon did die from stomach cancer the cancer could also have been caused by arsenic since arsenic and its compounds are carcinogenic.

The above account usefully shows the application of modern analysis in the investigation of a situation that may turn out to be murder. However, what is also demonstrated here is that having a set of results does not lead us directly to a conclusion. As is often the case there may be many alternative explanations that fit the facts.

Tony Hargreaves

"Many alternative explanations fit the facts"



Fowler's Solution

Box 1. Analysis for arsenic. From laboratory wet method to nuclear reaction.

Marsh's test

Marsh's test is highly sensitive. In it, arsenic compounds react with nascent hydrogen formed by the reaction of zinc in acid. The arsenic and hydrogen form arsine (AsH_3) and this gas is passed through a small tube that is heated. Heating results in thermal decomposition of arsine to yield arsenic, which deposits as a stain inside the tube.

The size of the arsenic stain gives a semi-quantitative figure for the amount of arsenic when the procedure is run alongside standards with known amounts of arsenic.

This test is very specific for arsenic.

Neutron activation analysis (NAA)

This is one of the most sensitive methods available. NAA can determine the concentration of elements in large amounts of material. The method is non-destructive, so historical artifacts can be analysed without harming them.

When analysing a sample using NAA, neutrons bombard the sample and interact with stable isotopes of the target element, converting them to radioactive nucleii. A compound nucleus is formed which rapidly decays by a well studied decay path. The standard emissions that form this decay are particular for a specific element and can be detected. This means that the nuclei present can be identified.

However, although NAA is non-destructive, the technique leaves the sample radioactive for years afterwards, requiring special handling and storage.

magnificent molecules

Laura Howes, assistant editor, highlights one of her favourite molecules. In this issue: quinine

Quinine was the first successful anti-malarial, but it is now more familiar to us as the bitter taste in tonic water, but what is the story?

In Peru, the Quechua Indians would use the ground bark of the chinchona tree to treat shivering. In the 17^{th} century Agostino Salumbrino, an apothecary living in Lima, wondered if the bark could be used to treat the shivers and fevers of malaria sufferers. The bark worked, not just stopping the shivers, but the disease itself.

In 1820 quinine was isolated, so that people no longer had to drink powdered tree bark. Instead the quinine could be drunk directly. Quinine is very bitter and western explorers and colonists used to drink their quinine with gin as the sun went down and the mosquitoes came out. The refreshing drink of gin and tonic water became a popular drink in its own right, and although better anti-malarials are now used when travelling, tonic water it still flavoured with the bitter flavour of quinine.

Purely medicinal

THINKSTOCK

Fluorescence

The popular drink of gin and tonic also led to the first observation of fluorescence – the phenomenon of a substance emitting light of a different wavelength to that that hit it. In 1845 Sir John Frederick William Herschel reported that under certain conditions his tonic water gave a 'beautiful celestial blue colour'. You can see this colour yourself by looking at the surface of a glass of tonic water at an angle that is approximately at 90 degrees to the sunlight shining on the liquid and the effect is even more dramatic under UV light, for example at a disco.

While Hershel found fluorescence interesting, his main interest was astronomy. In fact, for around 100 years the science of fluorescence was perhaps more of a curiosity. In World War II the allies were interested in monitoring anti-malarials, including quinine , and this lead to the first practical spectrofluorometer to measure fluorescence spectra. Fluorescence is now widely used in analytical chemistry, forensics and medicine as well as other applications.

Jonathan Hare asks...

NATIONAL TREASURE: *can lemon juice and hot breath reveal invisible ink?*

In *National Treasure*[1] Benjamin Gates (Nicholas Cage) is the latest in a long line of treasure hunters in his family. They have all been searching for a 'mountain of treasure' apparently hidden 100s of years ago by the founding fathers of the USA. Early on in the film Ben's troubles really start when he learns that the key information he seeks is written in invisible ink on the back of what is arguably the USA's most important historical document – the Declaration of Independence!

In a daring and exciting mission Gates and his collaborators steal the priceless manuscript but with the police hot on their trail they only have a short time to reveal and decode any hidden message. Using lemon juice they tentatively start testing the manuscript but are crestfallen when nothing immediately appears. Then one of the team suggests that heat might be required and so, using their hot breath they breathe on the lemon-soaked paper and the invisible messages start to appear!

What is eventually revealed is a list of numbers in sets of three (*e.g.* 11-22-33) known as Ottendorf ciphers.[2] Each set of three will lead them, one letter at a time, to spell out the secret code or message. In this example the three numbers could correspond to the first letter of the 33rd word in the 22nd paragraph of an 11th manuscript.

Ideally, invisible inks need to dry transparent, leave no tide mark or stain and also not wrinkle the paper.[3] An old parchment is probably better at covering up these tale-tale signs than a modern flat piece of bright white paper, so it's not improbable that an invisible message may have gone unnoticed. Many 'invisible' inks can be made from simple or common

They found the document, but how did they read it?

chemicals and in emergencies even bodily fluids such as saliva can be used.[3] Dried writing from bodily fluids can be made visible again under a UV light but of course these were not available way back in the 1800's.

Perhaps the simplest 'invisible ink' is lemon juice or vinegar. To reveal the writing all you need to do is carefully heat the manuscript. Heat oxidises the organic acid making it brown and therefore visible. In the film they initially breathed onto it but this would not be enough heat; later they used a hair dryer which would be better. Another option is to use a dilute solution of Cobalt chloride which is slightly red and if written on slightly pink paper is quite invisible. When the paper is warmed it shows up as a brilliant blue colour. However if it was breathed on the moisture would make it disappear again.

In the film they brush lemon juice all over the manuscript using it as they would a 'developer' rather than an ink. Some invisible inks made from indicators can be made visible using acids or bases. Phenolphthalein 'ink' for example, goes bright pink when exposed to ammonia (alkali) fumes. However if they are using the lemon juice as an acid developer with an indicator ink why then do they also need to heat it up, which would have oxidised the lemon juice covering up all the writing. They seem to mix-up different methods and would probably just have ruined the unique historical treasure!

REFERENCES

1. *National Treasure, Walt Disney Pictures, 2004*
2. *http://en.wikipedia.org/wiki/ottendorf_cipher*
3. *http://en.wikipedia.org/wiki/invisible_ink*

Dr Jonathan Hare, The CSC Centre, chemistry department, University of Sussex, Brighton BN1 9ET (www.creative-science.org.uk/TV.html).

Did you know?

As well as the Nobel Prizes, there are also Ig Nobel Prizes. The Ig Nobel Prizes are awarded to scientific research that 'first makes people laugh, and then makes them think'. This year's Ig Nobel Prize for Chemistry was awarded to American scientists Eric Adams, Scott Socolofsky and Stephen Masutani who showed that oil and water do mix. The scientists were investigating how oil spills at sea disperse as part of **Project DeepSpill.**

BACKYARD CHEMISTRY

DR HAL SOSABOWSKI PRESENTS EXPERIMENTS YOU CAN DO ON YOUR OWN

IN THIS ISSUE: how to freeze soda instantly

We have previously examined the effect of dissolved carbon dioxide on fizzy drinks. You may have seen the cola–Mentos experiment whereby addition of Mentos to cola causes the dissolved carbon dioxide to fall out of solution causing a huge pressure rise in the bottle which results in a spectacular cola shower (see *Infochem*, 2008, **112**(5), 6). In this article we will examine the effect of carbon dioxide as an impurity on the freezing point of cola.

The melting point/freezing point of a liquid is affected by its purity. Impurities will lower freezing points, because atoms/ions/molecules of impurity can get in the way of the formation of the crystal lattice of the solid. This is why we add salt to ice on our paths. Antifreeze (a mixture of ethylene glycol (ethan-1,2-diol) and corrosion inhibitors) is also added to the coolant in the engine of cars. The reason for this that a volume of ice occupies more space than the equivalent liquid water and since the coolant system of an engine is sealed the expansion of ice in the system can crack an engine block.

Materials

You will need:

- thermometer;
- salt;
- ice cubes;
- pudding basin;
- 500 ml bottles of cola or lemonade.

Method

Using the ice cubes and pudding basin make a slush by crushing the ice cubes, adding salt then adding some water. The ice and water were in equilibriam, but the addition of the salt causes the freezing point of ice to lower. The ice to melts, but for that it needs energy (the latent heat of fusion) which it takes out from the surrounding water, reducing the temperature to a potential -18 ºC. Allow the temperature of the ice slush to reach about -3 to -5 ºC and place the bottles of soda into the bath. The drinks should be allowed to cool to the point just before ice begins to form inside.

When the bottles are at the correct temperature take one out and unscrew the tap. There should be a hiss of escaping gas and then, if the conditions are correct, ice will begin to form spontaneously until the whole mass of soft drink turns to solid.

The science

The carbon dioxide inside the soda is effectively an impurity; therefore the freezing point of the liquid is depressed. When the pressure inside the bottle is lowered by the cap being unscrewed, some of the carbon dioxide escapes and so there is effectively less impurity in the soda. The freezing point of the drink therefore rises and the soda freezes spontaneously. The process is also helped along by the same process which causes the cola–Mentos fountain, that of nucleation. The bubbles of carbon dioxide 'seed' the formation of ice crystals, and as soon as ice crystals form, they cause the formation of others, causing a wave of freezing throughout the body of the liquid.

Did you know

Before the advent of freezers, ice cream was made by mixing ingredients in an ice/salt bath in the same way.

Health & Safety

There are no particular health & safety issues with this experiment.

With acknowledgement and thanks to www.thenakedscientists.com

MATTHEW J INGRAM

INK DEVELOPMENT MANAGER

Josie Harries

Josie Harries has been working for Domino Printing Sciences for five years and has been an ink development manager there for the last year. She talks to Laura Howes about her typical day.

Josie Harries

Domino Printing Services is a global company that provides the inks and printers for 'coding' onto packaging and products. The coding might be the best before dates on your crisps or a 2D barcode on your shampoo that allows the manufacturer to track that individual bottle. Domino's products have to print variable data quickly and legibly on a huge variety of surfaces – the technology that prints the lion on your egg won't be right for printing on a shiny metal surface for example – and as more and different products are created, Domino have to come up with new ways to print onto them. Ink Development Manager Josie's job is to manage a team of chemists and develop new inks for people to use.

Market forces

Josie explains that inks may need to be developed for many reasons but often it's market led – a company will come to Domino with a problem and Josie's team have to create a new dye based on their brief. Other reasons for ink development include new legislation that means that existing dye formulations can't be used anymore, or because a company want a new colour. Josie describes formulating new colour inks as quite easy but fun because most of the inks she works with are black. The black inks are also why Josie wears a dramatic black lab coat, rather than the white ones you might be more used to.

Josie currently manages a team of four chemists, who will be working on several projects at the same time. When Josie first gets in, after a coffee, she will sit down and look at the plans of the team and how their projects are progressing. Josie tries to have a weekly one-to-one meeting with each of her staff so that they can talk through their results and make sure everything's OK.

The team also have planning meetings where they talk about problems they are aware of and how to solve them, for example reducing the environmental impact of current ink formulations. After talking about new materials they've heard of, or new samples from a supplier, the team might play around in the lab to experiment with their idea.

PATHWAY TO SUCCESS:

- 2009-present, ink development manager, Domino Printing Sciences, Cambridge
- 2007-2009, Senior Chemist, Domino Printing Sciences, Cambridge
- 2005-2007, Chemist, Domino Printing Sciences, Cambridge
- 2005, PhD in Chemistry from The University of Manchester
- 2002, Chemist, Avencia, Manchester
- 2001, BSc in Chemistry from The University of Manchester
- 1998, Chemistry, Biology and Physics A-levels, Simon Langton Girls School, Canterbury.

Jet set printing

Domino is a global company and the inks that Josie designs in Cambridge might also get sold in China. Because of this, Josie sometime goes out to Domino's other offices around the world to meet the sales teams in those countries. It's important that Josie can make personal contacts and learn about problems that people face in other countries. For example, if the sales team are having trouble selling a product, Josie can find out why that is and then go back to her team in Cambridge to work on that problem.

The best bits

Like other people at Domino, Josie attends scientific conferences that are not necessarily in the precise area that she works in. This allows her to find out about different areas of science and technology that she can apply back in the lab, introducing novel things into her products and bringing innovation into the company.

However, Josie also admits that one of the best bits of her job is being able to make a mess in the lab.

£50 OF TOKENS TO BE WON!

Benchtalk

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PRIZE WORDSEARCH No. 53

Students are invited to find the 28 words/expressions associated with batteries 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 8-letter word. Please send your answers to the Editor at the usual address to arrive no later than Thursday 2 December. First correct answer out of the editor's hat will receive a £20 HMV token.

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

ALKANES
BIODIESEL
BIOMASS
CARBON DIOXIDE
CARBOXYLIC ACID
CHEMICALS
CHILLER
CORNSTARCH
CRITICAL POINT
CROP
DENSITY
EXTRACT
FEEDSTOCK
GLYCEROL
HEAT EXCHANGERS
LONG CHAIN ALCOHOLS
NON POLAR SOLVENT
ORGANIC CHEMICALS
PHARMACOLOGICALLY
PHASE DIAGRAM
POLAR SOLVENT
POLYMER
RESOURCES
SOLVENT FREE
STEROLS
TERPENE
WHEAT STRAW WAXES
WAX ESTERS

July PRIZE WORDSEARCH No. 52 winner

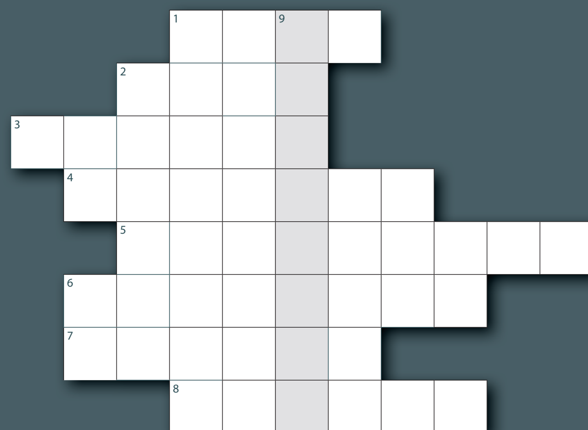
The winner was Janna Aziz Ria, Sir John Cass Sixth Form College, London. The ten-letter word was COLOURLESS.

FIND THE ELEMENT No. 16

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

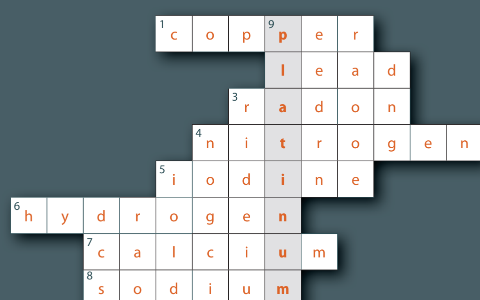
ACROSS

1. Metal used to make the plates in traditional car batteries.
2. Main metal used to make magnets.
3. This metal formes a blue chloride with formula MCl_2, which turns pink when water is added. It is therefore used in testing for water.
4. This metal is essential in bone function.
5. The main ore of this metal is bauxite.
6. The nucleus of this element is called a proton.
7. When added to this element, starch gives an intensive blue-black colour.
8. Element present in alcohols but not in hydrocarbons.



If you have completed this correctly, in 9 down you will have generated the name of an element with the unusual property of expanding when it freezes. It is therefore able to make sharp castings and traditionally was used in the alloy to make type metal for printers.

Please send you answers to: the Editor, *Education in Chemistry* the Royal Society of Chemistry, Thomas Graham House, Cambridge CB4 0WF, to arrive no later than Thursday 2 December. First out of the editor's hat to have correctly completed the grid will receive a £30 HMV token.



Find the element no. 15 solutions and winner

The winner was Chloe Hosker, Colmers School, Rednal, Birmingham.