

A Level Chemistry B (Salters)
H433/02 Scientific literacy in chemistry

Question Set 10

- 1 This question is based on the article **The Strange Story Of Napoleon's Wallpaper** which comes as an insert with this paper.
- (a) One reason arsenic is poisonous because it reacts with –SH groups in amino acids.
- Suggest how the removal of –SH groups might interfere with the way these amino acids form proteins. [1]
- (b) Arsenate(V) can replace phosphate(V) in nucleic acids.
- Draw the skeletal formula of a DNA nucleotide containing thymine and with As instead of P. [2]
- (c) Write an equation for the reaction of a solution of As^{3+} with hydrogen sulfide. Show state symbols. [2]
- (d) (i) A Marsh test is carried out for arsenic in a sample of As_2O_3 .
- Draw a labelled diagram of a suitable apparatus, showing the reactants and products. [3]
- (ii) Write equations for the formation and decomposition of arsine in the apparatus. [2]
- (e) (i) The structure of Scheele's green can be represented as $\text{Cu}^{2+}(\text{AsO}_2\text{OH})^{2-}$.
- Suggest a 'dot-and-cross' diagram for the anion in Scheele's green. [2]
- (ii) State which part of Scheele's green is responsible for the green colour. [1]
- (f) State and explain the C–As–C bond angle in trimethylarsine. [4]
- (g) Summarise the evidence that Napoleon was killed by his wallpaper. [3]

Total Marks for Question Set 10: 20

Resource Materials

Question Set No: 10

The Strange Story of Napoleon's Wallpaper

In 1815, after his defeat by the British at the battle of Waterloo, Napoleon Bonaparte was exiled to the remote island of St Helena. Just six miles by eight, St Helena is a tiny volcanic island south of the Equator, in the South Atlantic Ocean. The nearest land is Ascension Island, 700 miles to the north. Africa lies a thousand miles to the east, South America a thousand to the west.

During most of his exile, Napoleon lived in Longwood House with a small group of people – as well as servants, some of his generals had chosen to go into exile with him. He passed the time by dictating his memoirs, and by playing billiards, which he did rather badly.

Although Napoleon often dreamed of escape, he was never to leave the island, and he died there six years later in 1821.

The doctors who carried out the post-mortem on Napoleon were of the opinion that a perforated stomach ulcer which had turned cancerous was the main cause of his death. And there the matter might have rested, except that a number of his staff had kept locks of Napoleon's hair, which were subsequently passed down the generations, sometimes coming up at auction. Unbeknown to their owners, these treasured locks of hair contained something of a small historical time bomb.

One of those samples of Napoleon's hair, when analysed using modern scientific techniques in the 1960s, was found to contain significant quantities of arsenic. Suddenly the cause of Napoleon's death was being debated all over again. 'The Murder of Napoleon' was the title of one book that was published. But had the British really poisoned their most famous prisoner? Or were the French Bourbons so unwilling for Napoleon to return that they had him poisoned? Did one of his staff have a secret grudge?

Arsenic Poisoning

Since the Middle Ages, arsenic had been a popular way of poisoning people. Arsenic itself is a grey metal, which is not very poisonous. It generally occurs in nature as a mineral, arsenic sulphide (arsenikon is the latin word for yellow pigment), but another form is white arsenic, or arsenic oxide. This is extremely poisonous, although the symptoms of arsenic poisoning could be confused with those of many other illnesses, and it was also very difficult to detect arsenic after the death.

Arsenic poisoning happens because arsenic binds very strongly to sulfur groups. Many proteins contain one or more sulfur atoms, and enzymes (also proteins) are responsible for regulating the body's internal chemistry. An enzyme with an arsenic atom bound to the sulfur will not be able to function. Hair is interesting because the protein keratin contains sulfur atoms. If you ingest arsenic, then some of it will bind to the sulfur atoms in your hair, and a sample of hair will last a long time. Since hair is constantly growing, it can even show how the level of arsenic in someone's body can change over time.

Arsenic can also interfere with nucleic acids in the body by replacing phosphorus atoms.

However in 1832, 11 years after Napoleon's death, there was an interesting and significant development for the followers of arsenic poisoning. A certain John Bodle was brought to trial in the UK, accused of poisoning his grandfather. James Marsh was the chemist called by the prosecution.

He carried out the standard test of the time, which was to pass hydrogen sulfide gas (the one with the 'bad egg' smell) through the suspect solution. If arsenic was present, it would be shown by the appearance of a yellow precipitate of arsenic sulfide. Unfortunately, although James Marsh did find arsenic, the yellow precipitate doesn't keep very well, and by the time it was shown to the jury it had deteriorated. The jury were not convinced, and John Bodle was acquitted.

James Marsh was somewhat angry, especially when John Bodle later confessed that he had poisoned his grandfather after all. And so James Marsh set out to devise a better test. The result was the 'Marsh Test', which worked by adding zinc metal and sulfuric acid to the sample suspected of containing arsenic. If arsenic is present, the resulting chemical reaction converts the arsenic into arsine (each arsenic atom has three hydrogen atoms attached) which is a (very poisonous) gas. This gas is then passed along a heated glass tube, which causes the arsine gas to decompose, and the arsenic metal is deposited as a silvery-black film on the sides of the tube. The tube can then be sealed, and kept as evidence. Not only could minute amounts of arsenic be detected, but the test was very specific, since virtually no other element behaves in this way. With a chemical test this good, the age of the arsenic poisoners was drawing to a close! The only problem with the chemical test is that your arsenic containing sample is used up in the course of the test – in that sense it is a destructive test. And the Marsh Test is not sensitive enough to be able to detect arsenic in hair samples. In the 20th century, techniques such as X-ray fluorescence spectroscopy replaced the Marsh Test. These non-destructive tests are incredibly sensitive, and can detect really tiny quantities of elements. James Marsh would have been amazed!

Of course Napoleon had died some years before the Marsh Test was devised, and in any case no-one had suspected arsenic poisoning at the time.

The Wallpaper

The story of Napoleon's wallpaper really begins in 1980 when Dr David Jones, a chemist at the University of Newcastle, was making a radio programme that was broadcast on the BBC. 'I wonder if anyone listening', David Jones asked the radio audience, 'knows the colour of Napoleon's wallpaper on St Helena. Because if we knew, it might just help to clear up a scientific mystery'.

Why did David Jones want to know the colour of Napoleon's wallpaper? He wanted to know if it could have contained arsenic!

The subject of the radio programme had been vapour chemistry, and one of the stories that David Jones, himself a chemist, had told was the intriguing one of Gosio's Disease. During the 19th century there had been a number of cases of arsenic poisoning that had rather puzzled everyone. Some people just became sick, but others laid low with a lesser malady became sicker still, and died. Arsenic was found, using the Marsh Test, foul play was sometimes suspected, and relatives accused. But in many cases it just didn't seem possible that the person had been deliberately poisoned. Until in 1893 an Italian Biochemist called Gosio worked out what was happening.

Scheele's Green was a colouring pigment that had been used in fabrics and wallpapers from around 1770. It was named after the Swedish chemist Scheele who invented it. The pigment was easy to make, and was a bright green colour. But Scheele's Green was copper arsenite, CuAsHO_3 . And under certain circumstances it could be deadly. Gosio discovered that if wallpaper containing Scheele's Green became damp, and then became mouldy (this was in the days of animal glues) the mould could carry out a neat chemical trick to get rid of the copper arsenite. It converted it to a vapour form of arsenic. Normally a mixture of arsine, dimethyl and trimethyl arsine. This vapour was very poisonous indeed. Breathe in enough of the vapour, and you would go down with a nasty case of arsenic poisoning.

This was the reason for David Jones's question to the radio audience. David Jones knew of the arsenic found in Napoleon's hair. But if Napoleon's wallpaper had been green, it could possibly have contained arsenic, and this could have been the source of the arsenic in the hair sample. Napoleon might have been an early victim of Gosio's disease. It was rather a long shot, and David Jones didn't really expect anything to come of it.

But a few days after the broadcast David Jones received a letter from a woman called Shirley Bradley who lived in Norfolk, UK. The contents of her letter were to prove, according to David Jones, 'the greatest piece of scientific good fortune of my career'.

Shirley Bradley didn't have a theory or a story about the colour of Napoleon's wallpaper. She had an actual piece of the wallpaper itself. In fact, what Shirley Bradley had was a scrapbook, which had been handed down to her. The person who had owned the scrapbook had filled it with little poems and religious reflections. All the pages were dated. And one page was all about St Helena. The author of the scrapbook appeared to have visited St Helena in 1823. There was a leaf, taken from the tree that stood above Napoleon's grave. There were various observations about the island. And there, stuck to the page, was a small scrap of paper.

Next to the scrap of wallpaper, the old fashioned copper-plate handwriting reads: *'This small piece of paper was taken off the wall of the room in which the spirit of Napoleon returned to God who gave it'*.

The wallpaper showed a single star. The principal colours of this star were green and brown. It is possible that the brown had faded, and had originally been gold. Gold and green were the Imperial colours. The first question David Jones had was whether the wallpaper did actually contain arsenic. Shirley Bradley gave permission for the fragment of paper to be removed from the book, and subjected to the same non-destructive scientific tests that had originally found the arsenic in the hair sample. And yes, the green pigment did contain arsenic. David Jones remembers clearly standing in the lab with a colleague watching the arsenic peak appear on the print-out. As he says, 'It was a crazy, wonderful moment'.

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