41st INTERNATIONAL

CHEMISTRY OLYMPIAD

2009

UK Round One

STUDENT QUESTION BOOKLET

* * * * *

- **The time allowed is 2 hours.**
- **Attempt all 6 questions.**
- **Write your answers in the special answer booklet.**
- **In your calculations, please write only the essential steps in the answer booklet.**
- **Always give the appropriate units and number of significant figures.**
- **You are provided with a copy of the Periodic Table.**
- **Do *NOT* write anything in the right hand margin of the answer booklet.**

Some of the questions will contain material you will not be familiar with. However, by logically applying the skills you have learnt as a chemist, you should be able to work through the problems. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may still find subsequent parts straightforward.

symbol
atomic number
mean atomic mass

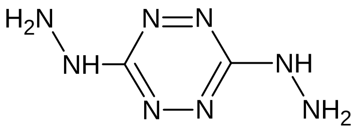
H 1 1.008																	**He** 2 4.003
Li 3 6.94	**Be** 4 9.01											**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
Na 11 22.99	**Mg** 12 24.31											**Al** 13 26.98	**Si** 14 28.09	**P** 15 30.97	**S** 16 32.06	**Cl** 17 35.45	**Ar** 18 39.95
K 19 39.102	**Ca** 20 40.08	**Sc** 21 44.96	**Ti** 22 47.90	**V** 23 50.94	**Cr** 24 52.00	**Mn** 25 54.94	**Fe** 26 55.85	**Co** 27 58.93	**Ni** 28 58.71	**Cu** 29 63.55	**Zn** 30 65.37	**Ga** 31 69.72	**Ge** 32 72.59	**As** 33 74.92	**Se** 34 78.96	**Br** 35 79.904	**Kr** 36 83.80
Rb 37 85.47	**Sr** 38 87.62	**Y** 39 88.91	**Zr** 40 91.22	**Nb** 41 92.91	**Mo** 42 95.94	**Tc** 43	**Ru** 44 101.07	**Rh** 45 102.91	**Pd** 46 106.4	**Ag** 47 107.87	**Cd** 48 112.40	**In** 49 114.82	**Sn** 50 118.69	**Sb** 51 121.75	**Te** 52 127.60	**I** 53 126.90	**Xe** 54 131.30
Cs 55 132.91	**Ba** 56 137.34	**La*** 57 138.91	**Hf** 72 178.49	**Ta** 73 180.95	**W** 74 183.85	**Re** 75 186.2	**Os** 76 190.2	**Ir** 77 192.2	**Pt** 78 195.09	**Au** 79 196.97	**Hg** 80 200.59	**Tl** 81 204.37	**Pb** 82 207.2	**Bi** 83 208.98	**Po** 84	**At** 85	**Rn** 86
Fr 87	**Ra** 88	**Ac**$^{+}$ 89															

***Lanthanides**	**Ce** 58 140.12	**Pr** 59 140.91	**Nd** 60 144.24	**Pm** 61	**Sm** 62 150.4	**Eu** 63 151.96	**Gd** 64 157.25	**Tb** 65 158.93	**Dy** 66 162.50	**Ho** 67 164.93	**Er** 68 167.26	**Tm** 69 168.93	**Yb** 70 173.04	**Lu** 71 174.97
$^{+}$**Actinides**	**Th** 90 232.01	**Pa** 91	**U** 92 238.03	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102	**Lr** 103

1. This question is about environmentally friendly fireworks

Recent research on fireworks has sought to reduce the quantity of heavy metal salts used for colouration, and perchlorate or chlorate(VII), an oxidiser that is also toxic. By employing a fuel that generates less smoke, less metal salt is required for the same visual effect.

Replacing the carbon and hydrogen in fuels by nitrogen can cut the smoke evolved, but many compounds containing mostly nitrogen are dangerously unstable. However, one compound finding favour as a fuel is *dihydrazinotetrazine* (shown below) which, despite its high nitrogen content, is remarkably stable.



dihydrazinotetrazine

(a) **i)** By considering the bonding in the ring suggest why this compound is so stable.

ii) It is possible to record nitrogen NMR spectra, due to the presence of the NMR-active ^{15}N isotope. Predict the number of signals you would expect to see in the ^{15}N NMR spectrum in dihydrazinotetrazine by working out how many different nitrogen environments are present in the molecule.

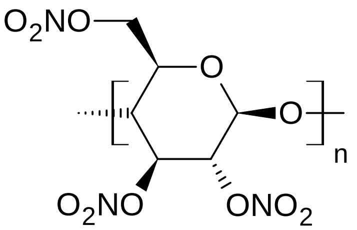
iii) When dihydrazinotetrazine is burnt in excess oxygen the products are nitrogen gas and two other substances. Write a balanced equation for this combustion in excess oxygen.

Octanitrocubane is another potential fuel. Its structure has a cage of carbon atoms at the corners of a cube with each carbon atom bonded to a nitro group ($–NO_2$). Due to bond strain, the molecule is difficult to make and less stable than dihydrazinotetrazine.

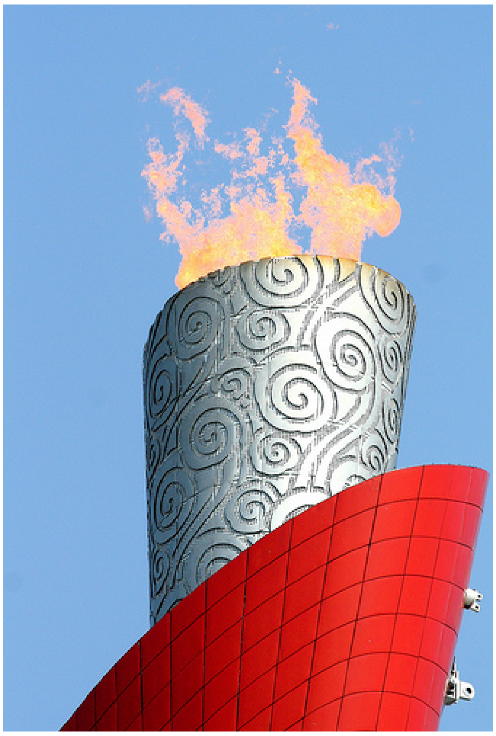
(b) **i)** How many degrees smaller is the C–C–C bond angle in octanitrocubane compared with that in a straight-chained alkane?

ii) Give a balanced chemical equation to show that no additional oxygen – and therefore no (toxic) oxidiser – is required when octanitrocubane is used as a fuel.

(c) Another nitrogenated fuel is the polymer nitrocellulose whose repeat unit is shown below. Give the empirical formula of nitrocellulose, and hence write an equation for the combustion of this formula unit in excess oxygen.



2. This question is about the unnecessary production of carbon dioxide



Outdoor flames, such as patio heaters and the Olympic flame, contribute to global warming. This is not only due to the heat released, but also due to the carbon dioxide produced from the combustion of hydrocarbons.

Most patio heaters are powered by small cylinders of propane gas. A typical patio heater designed to produce 15 kW of energy runs from a cylinder containing 13 kg of propane. A 'completely full' cylinder at a pressure of 140 psi (9.52 atmospheres) is in fact only filled to about 87% capacity with liquid propane, the remaining volume being taken up by propane vapour. The standard enthalpy change of combustion of propane is –2220 kJ mol^{-1}.

Assume 1 mole of a gas occupies 24 dm^3 under the conditions of this question.

(a) **i)** Calculate the number of moles of propane contained in a cylinder.

ii) Calculate the mass of carbon dioxide produced when all of the propane in a cylinder is burnt completely.

iii) Calculate the total amount of heat energy released by combustion of all the propane in a cylinder.

iv) Calculate the rate at which propane must leave the cylinder (in $cm^3\ s^{-1}$) to produce 15 kW (ie 15 kJ s^{-1}).

v) Estimate the equilibrium pressure when the cylinder is only 'half full'.

Because pure propane gas is odourless, small amounts of another compound are usually added so that gas leaks can be detected. An example of such an odorant is ethyl mercaptan (ethanethiol, C_2H_5SH); this is chosen since the human nose can detect its presence at levels of only about 0.02 ppb (parts per billion).

(b) **i)** Draw a diagram to show how the atoms are bonded together in ethyl mercaptan and predict the bond angle around the sulphur atom.

ii) Calculate the mass of ethyl mercaptan which must be added to 13 kg of propane to produce 0.02 molecules of it per billion (10^9) molecules of propane.

The Olympic flame on top of the Bird's Nest Stadium which burned throughout the Beijing Olympics consumed 6000 m^3 of methane per hour and was kept alight for 16 days.

(c) Calculate the total mass of carbon dioxide produced from the flame during the Olympics, assuming complete combustion.

3. This question is about the chemistry of matches

The heads of strike-anywhere matches contain a mixture of phosphorus sesquisulfide P_4S_3 and potassium chlorate(V) $KClO_3$. When the match is struck across a rough surface the heat of friction is sufficient to ignite the phosphorus sesquisulfide; the potassium chlorate(V) decomposes to provide the oxygen needed for combustion.

(a) **i)** Write an equation to show the combustion of phosphorus sesquisulfide into phosphorus(V) oxide and sulfur dioxide.

ii) Write an equation to show the decomposition of potassium chlorate(V) into potassium chloride and oxygen.

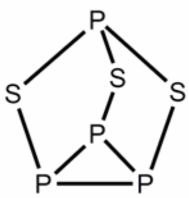
iii) Hence or otherwise write a single equation to show the reaction that takes place between these two substances when a match-head ignites.

iv) Calculate the mass ratio in which phosphorus sesquisulfide and potassium chlorate(V) should be combined on the match-head.

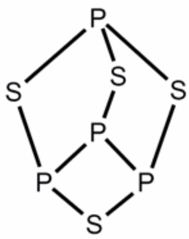
v) Given the following standard molar enthalpy changes of formation, calculate the standard enthalpy change for the reaction in part **(iii)**.

	KCl (s)	$KClO_3$ (s)	SO_2 (g)	P_4S_3 (s)	P_4O_{10} (s)
$\Delta_f H^\ominus$ kJ mol^{-1}	–436.7	–397.7	–296.8	–154.0	–2948

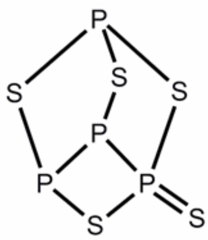
Phosphorus sulfides can be made by heating white phosphorus with sulfur. When this reaction is carried out at low temperature a range of products from P_4S_3 to P_4S_{10} are produced. ^{31}P NMR spectroscopy has been used to determine the structures of many of the phosphorus sulfides:



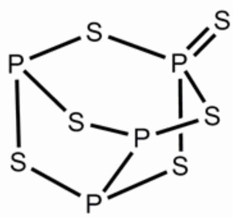
P_4S_3



P_4S_4



P_4S_5



P_4S_6

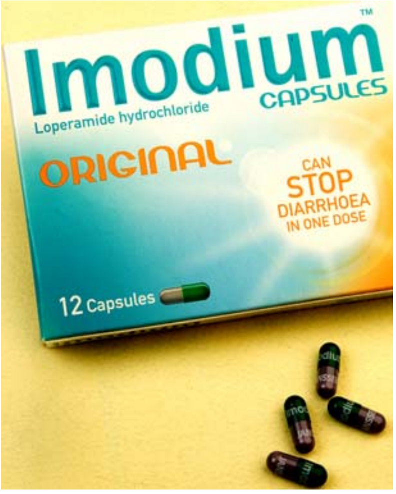
In ^{31}P NMR spectroscopy the number of peaks seen corresponds to the number of different P environments, for example P_4S_3 has two different P environments so shows two peaks in the ^{31}P NMR spectrum.

(b) Using the structures above, predict how many peaks would be seen in the ^{31}P NMR spectrum of: **i)** P_4S_4 **ii)** P_4S_5 **iii)** P_4S_6.

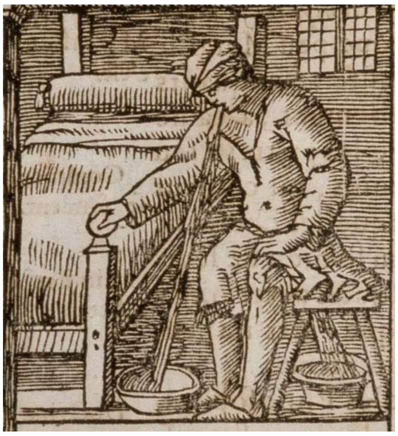
P_4S_4 has, in fact, been shown to exist in two different isomeric forms. You are given the structure of one isomer above. The second isomer shows only one peak in the ^{31}P NMR spectrum.

(c) Suggest a structure for the second isomer of P_4S_4.

4. This question is about stopping diarrhoea

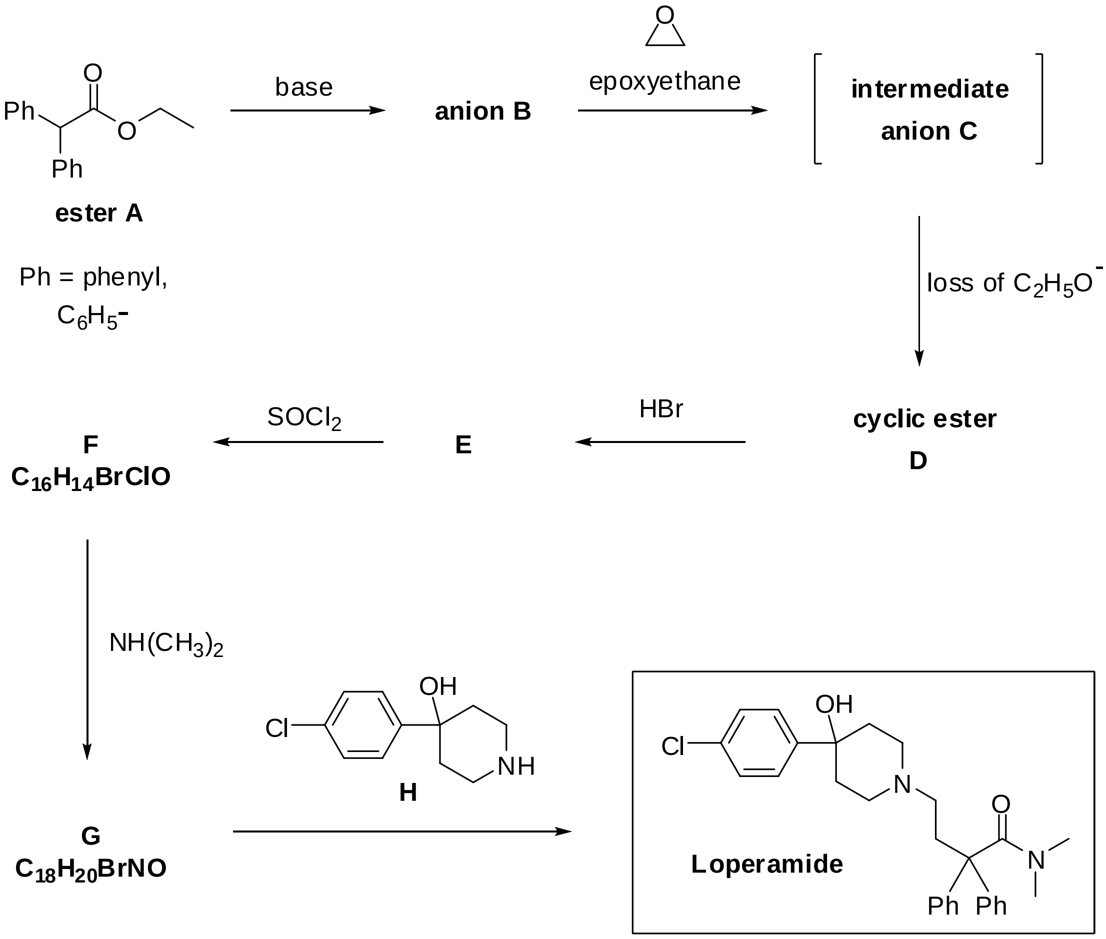


The active ingredient in anti-diarrhoea medicines such as imodium, is *loperamide*, whose structure is given below. As with many drugs, loperamide is often sold as the hydrochloride salt since this is more soluble in water.



(a) On the structure in your answer booklet, circle the atom in loperamide which will be protonated in the salt.

A synthesis of loperamide is shown below.



(b) **(i)** Ester **A** may be made by treating a mixture of an alcohol and a carboxylic acid with a catalytic quantity of concentrated sulfuric acid. Give the structures of the alcohol and carboxylic acid.

(ii) Ester **A** is deprotonated by a base to give the anion **B**. Draw the structure of **A** and indicate clearly which proton is removed by the base to form anion **B**.

Anion **B** then opens up the three-membered ring of epoxyethane to form an intermediate, anion **C**. This intermediate then cyclizes and eliminates ethoxide, $C_2H_5O^-$, to form ester **D**.

(c) Draw the structures of anion **C** and cyclic ester **D**.

Ester **D** reacts with bromide which opens the ring to give carboxylic acid **E**. **E** then reacts with $SOCl_2$ to give **F**.

(d) Draw the structures of compounds **E** and **F**.

F reacts with dimethylamine to form **G**. Two isomeric structures may be drawn for **G**; either an open-chain amide, or a cyclic bromide salt. There are *ten* signals in the ^{13}C NMR spectrum of the cyclic bromide salt.

(e) Suggest structures for **G** in (i) the amide form and (ii) the bromide salt form.

5. This is a question about arsenic.

Arsenic, As, atomic number 33, is an element infamous for its toxic compounds. The presence of naturally occurring arsenic compounds in groundwater currently affects millions of people throughout the world.
A number of different techniques for removing arsenic compounds from water have been developed, but research to improve these methods is ongoing.

Marsh gas test

In 1836 British chemist James Marsh developed the first reliable test for the detection of arsenic(III) oxide. In the Marsh test arsenic(III) oxide is first converted to arsine gas (AsH_3) which is then ignited leaving a silvery-black deposit of arsenic.

a) **i)** Draw the structure of arsine indicating the geometry.

ii) Write a balanced equation for the combustion of arsine as used in this test.

Arsine is formed when arsenic(III) oxide is reacted with zinc and sulfuric acid.

b) **i)** Give the formula for arsenic(III) oxide.

ii) Write a balanced equation for the reaction of arsenic(III) oxide with zinc and sulfuric acid.

The Marsh test is no longer used to detect arsenic; today spectroscopic methods allow the concentration of arsenic in a sample to be determined rapidly and with great sensitivity.

In groundwater the most prevalent arsenic species at high pH is $HAsO_4^{2-}$.

c) **i)** What is the oxidation number of arsenic in $HAsO_4^{2-}$?

ii) Draw a diagram to show the three-dimensional structure of $HAsO_4^{2-}$.

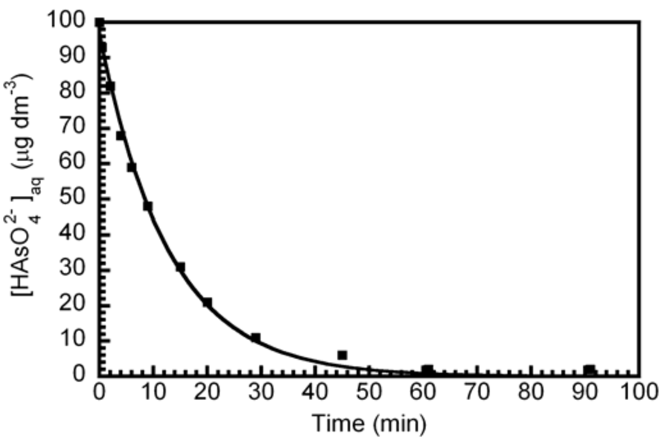
$HAsO_4^{2-}$ can be removed from water by adsorption on to particles of iron(III) hydroxide. The variation in the concentration of aqueous $HAsO_4^{2-}$ with adsorption time can be described by the equation:

$$[HAsO_4^{2-}{}_{(aq)}]_t = [HAsO_4^{2-}{}_{(aq)}]_0\, e^{-(kt)}$$

where $[HAsO_4^{2-}{}_{(aq)}]_t$ is the concentration of aqueous $HAsO_4^{2-}$ at time t, $[HAsO_4^{2-}{}_{(aq)}]_0$ is the initial concentration of aqueous $HAsO_4^{2-}$ and k is the rate constant for the adsorption reaction. The rate constant is related to the half-life of the reaction ($t_{1/2}$) by the equation:

$$t_{1/2} = \frac{\ln 2}{k}$$

The graph to the right shows how the concentration of aqueous $HAsO_4^{2-}$ varies with adsorption time at 40 °C. According to the World Health Organization the safe level for dissolved arsenic species in water is < 10μg dm^{-3}.



d) **i)** Using the graph, determine the rate constant for the adsorption of $HAsO_4^{2-}$ on to iron(III) hydroxide particles stating the units.

ii) In a different water sample it took 55 minutes for the concentration of aqueous arsenic to reach the safe level. What was the initial concentration of aqueous $HAsO_4^{2-}$?

Under certain conditions the equilibrium constant, K, for the adsorption of $HAsO_4^{2-}$ can be defined as:

$$K = \frac{[HAsO^{2-}_{4\,(adsorbed)}]}{[HAsO^{2-}_{4\,(aq)}]}$$

At 20 °C the value of K is 186.

e) If the initial concentration of aqueous $HAsO_4^{2-}$ was 30 μg dm^{-3}, what is the concentration of aqueous $HAsO_4^{2-}$ at equilibrium at 20 °C?

6. This question is about revealing a hidden van Gogh painting

In 2008, a team of Dutch analytical chemists used a technique called *Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping* to discover a hidden van Gogh painting. The original painting of a woman's head had been lost when van Gogh painted his '*Patch of Grass*' over the top.
The technique works by firing monochromatic, high-energy X-rays at the target. This causes core electrons, such as those in the 1s shell, to be knocked out. Electrons from other shells drop down to replace the lost electron, and energy is given out in the form of a lower-energy X-ray. Measuring the exact frequency of the emitted X-ray can tell us which element is present.

The painting of a woman's head hidden under the *Patch of Grass*.

The energy, E_n, of an electron in a hydrogen atom, or a one-electron ion, is given by the equation:

$$E_n = -R_H \frac{Z^2}{n^2}$$

where R_H is a constant known as the Rydberg constant, Z is the nuclear charge (Z = 1 for hydrogen) and n is the principal quantum number of the shell the electron is in. If the electron is in the **1**s shell, n = **1**; if in the **2**s or **2**p, n = **2**; if in the **3**s, **3**p, or **3**d, n = **3** etc.

When dealing with the energies of electrons in atoms, a convenient unit is the electron volt, eV, where 1eV ≡ 1.6022 ×10^{-19} J. Expressed in these units, R_H = 13.6 eV. The Avogadro constant = 6.022×10^{23} mol^{-1}.

(a) **i)** What is the energy, in eV, of the electron in a hydrogen atom when in the 1s orbital?

ii) What happens to the energy of the electron as it is moved into higher shells, further from the nucleus, so that the atom <u>just</u> becomes ionized? Tick the correct box in the answer booklet.

The energy of the electron tends to:

– infinity –13.6 eV –1 eV zero +1 eV + 13.6 eV + infinity

iii) Calculate the ionization energy of a hydrogen atom in kJ mol^{-1}.

For atoms or ions with more than one electron, the charge an electron experiences is less than the full nuclear charge Z since the electrons shield one another.

The equation may be modified to become:

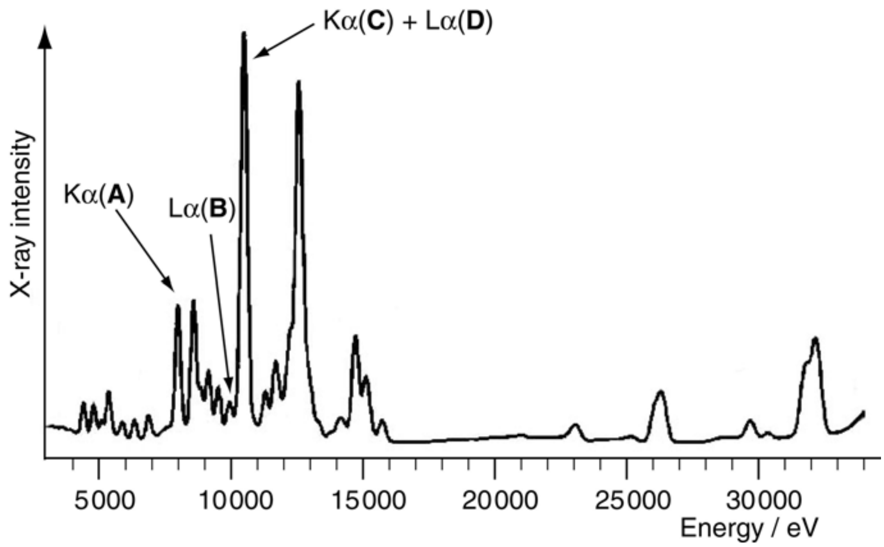
$$E_n = -R_H \frac{(Z-S)^2}{n^2}$$

where S is a shielding constant.

The quantity ($Z - S$) is sometimes known as the *effective* nuclear charge, Z_{eff} , that an electron experiences.

(b) Given the first ionization energy of sodium is 495.8 kJ mol^{-1}, calculate Z_{eff} for an electron in the valence shell of a sodium atom.

An X-ray fluorescence spectrum recorded from the van Gogh painting is shown below.



The peaks marked Kα are due to transitions from the 2p shell to the 1s shell. For such transitions, S is taken to be 1.

(c) Calculate the atomic number, and hence element symbol **A**, which gives rise to the line marked Kα(**A**) in the spectrum.

The lines marked Lα are due to transitions from the 3d shell to the 2p shell. For such transitions, S may be taken to be 7.4.

(d) **i)** Calculate the atomic number and hence element **B**, which gives rise to the peak marked Lα(**B**) in the spectrum.

ii) This peak is especially strong in the region around the lips of the face in the portrait since a red pigment (the sulfide) is used in that area. Suggest the formula of the pigment.

(e) **i)** The peak at 10500 eV is due to the Kα transition for element **C** and the Lα transition for element **D**. Calculate the atomic numbers and hence give the symbols of these elements.

ii) Element **C** is present in a green pigment called known as Scheele's green. It has the formula (**A** **C** H O_x). Given that element **C** is the +3 oxidation state, suggest a formula for Scheele's green.

(f) Calculate the energy for the Kα transition of antimony, Sb.

In actual fact, the peak in the spectrum due to the Kα transition is slightly different from the calculated value. Comparison with known compounds tells us that this is because the compound contains Sb in its highest oxidation state.

(g) One possible pigment is Naples yellow which has the formula (**D**$_2$Sb$_2$O$_7$). What is the oxidation state of element **D** in this compound?

Acknowledgements & References

References for questions

Q1 Pyrotechnics For The Planet *Chemical & Engineering News,* 2008, Vol 86, p 14-18.

Q4 Synthetic antidiarrheal agents. 2,2-Diphenyl-4-(4'-aryl-4'-hydroxypiperidino)butyramides R. A. Stokbroekx et al. Journal of Medicinal Chemistry 1973, Vol 16, p 782-786.

Q5 Kinetic and thermodynamic aspects of adsorption of arsenic onto granual ferric hydroxide. K. Banerjee *et al.* *Water Research*, 2008 Vol 42, p 3371-3378.

Q6 Visualization of a Lost Painting by Vincent van Gogh Using Synchrotron Radiation Based X-ray Fluorescence Elemental Mapping. J. Dik *et al.* *Analytical Chemistry*, 2008, Vol 80, p 6436-6442.

The Chemistry Olympiad Committee would like to thank the following people / organisations for their help and advice in the preparation of this paper.

Joris Dik of Delft University of Technology for helpful advice and for the permission to use the image of the van Gogh painting.

The photography department of the University of Cambridge, Department of Chemistry for the photographs used in question 4.

The UK Chemistry Olympiad is supported by INEOS

INEOS is a leading global manufacturer of petrochemicals, specialty chemicals and oil products. It comprises 19 businesses each with a major chemical company heritage. The production network spans 73 manufacturing facilities in 19 countries throughout the world. The chemicals INEOS produce enhance almost every aspect of modern life.