

CHEMISTRY VCE UNITS 3&4 DIAGNOSTIC TOPIC TESTS 2008

TEST 2: SPECTROSCOPY AND CHROMATOGRAPHY

TOTAL 35 MARKS (45 MINUTES)

Student's Name: _____

Teacher's Name: _____

Directions to students

Write your name and your teacher's name in the spaces provided above.
Answer all questions in the spaces provided.

SECTION A: MULTIPLE-CHOICE QUESTIONS

Instructions for Section A

For each question in Section A, choose the response that is correct and circle your choice.

Choose the response that is **correct** or **best answers** the question.

A correct answer scores 1, an incorrect answer scores 0.

Marks will **not** be deducted for incorrect answers.

No marks will be given if more than one answer is completed for any question.

Question 1

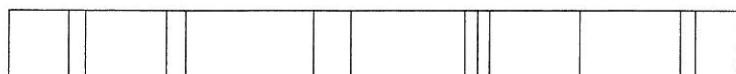
A sample of soil is removed from an industrial site to test for contamination by a highly toxic insecticide called dieldrin ($C_{12}H_8OCl_6$).

The most appropriate analytical technique to detect the presence of dieldrin in the soil is

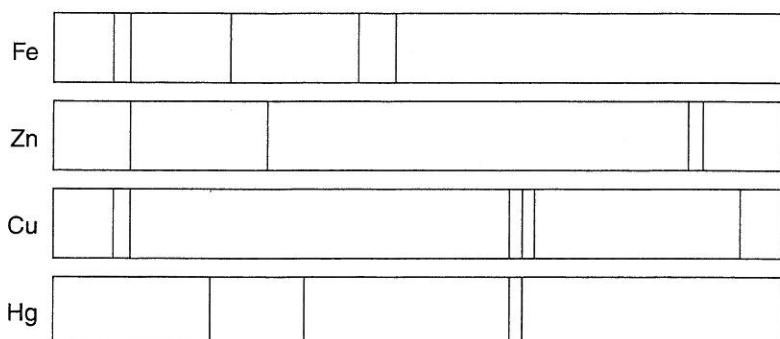
- A. atomic absorption spectroscopy.
- B. high performance liquid chromatography.
- C. UV-visible spectroscopy.
- D. paper chromatography.

Question 2

In June 2003 NASA sent two mobile rovers to Mars to explore the planet and test its soil and atmosphere. Four years later the spectrometers on board the rovers continue to relay valuable information back to Earth. Spectral analysis of a sample of Mars rock on the edge of an extinct volcanic crater generated the emission spectrum shown below.



The emission spectra of a number of elements are shown below.

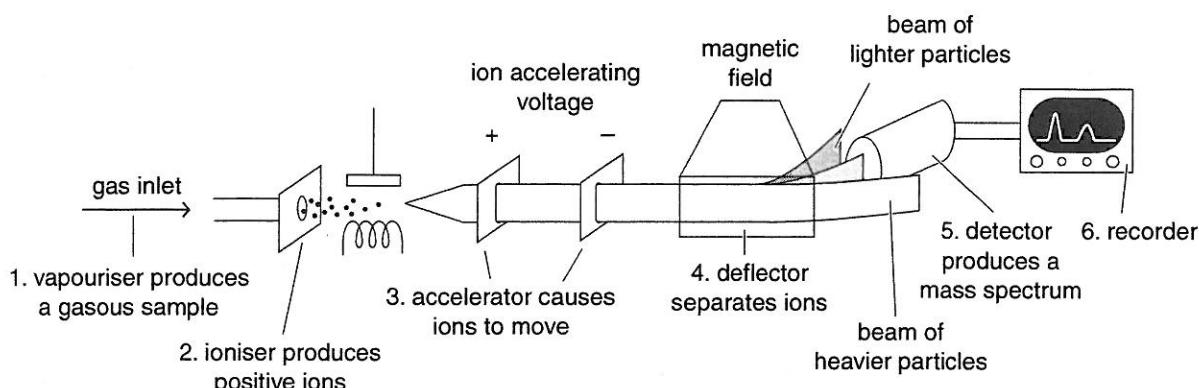


The elements present in the sample of rock from Mars include

- A. Fe and Cu.
- B. Fe and Hg.
- C. Zn and Cu.
- D. Zn and Hg.

Question 3

A simplified diagram of a mass spectrometer is shown below.



A quantity of methanol was passed through the device to generate a mass spectrum showing a number of peaks.

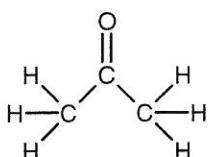
Of the particles listed below, the one that would be most strongly deflected by the applied magnetic field would be

- A. CH_4^+
- B. CH_2^{2+}
- C. CH_3^+
- D. CH_4^{2+}

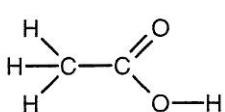
Question 4

Which one of the compounds listed below would have a major peak in its mass spectrum at a mass/charge ratio (m/e) of 31?

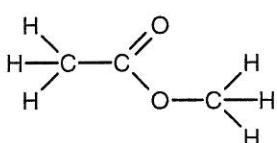
A.



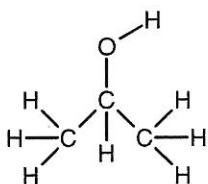
B.



C.

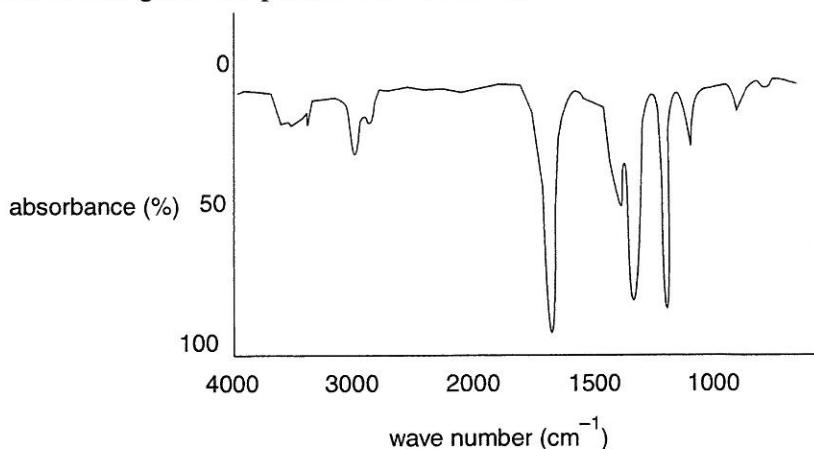


D.



Question 5

The infrared spectrum of an organic compound is shown below.



The compound could be

- A. propanol ($\text{CH}_3\text{CH}_2\text{OH}$).
- B. propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$).
- C. chloropropane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$).
- D. propanone ($\text{CH}_3\text{C=O}\cdot\text{CH}_3$)

Question 6

Which of the following processes is involved in analysis by ^1H NMR spectroscopy?

- A. the use of radio waves to align hydrogen nuclei with an applied magnetic field
- B. absorption of energy by molecules as they vibrate, rotate and stretch
- C. acceleration of electrons by a strong electric field
- D. the use of a monochromator to select the most strongly absorbed frequency

Question 7

A suitable material to be used as the stationary phase in a high performance liquid chromatograph is

- A. nitrogen gas.
- B. an inert, porous material coated with a high molecular mass liquid.
- C. a solid, polar material such as alumina with a high surface area.
- D. platinum metal in powder form.

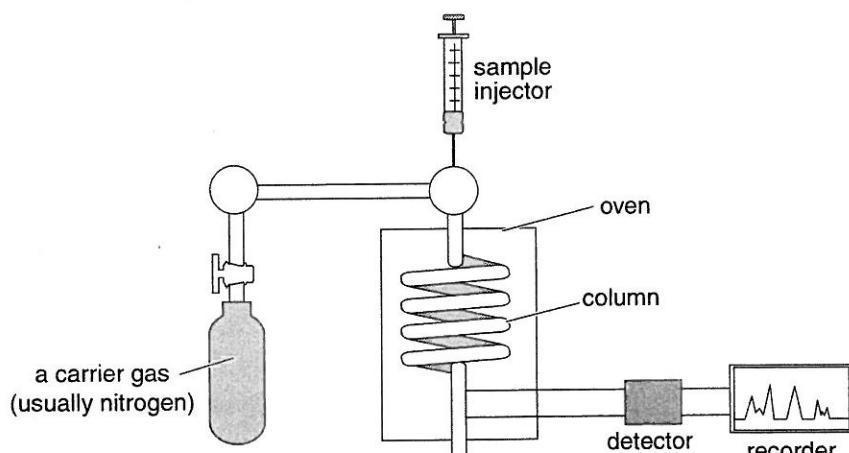
Question 8

Gas–liquid chromatography is best suited to determining the presence of

- A. the cause of a foul odour in the effluent from a factory outlet.
- B. particular proteins in cancerous body tissue.
- C. coloured dyes in a marker pen.
- D. mercury in a sample of contaminated fish.

Question 9

A mixture of the alcohols ethanol, propanol and butanol is made up in the proportions 30%, 50% and 20% by mass respectively. A small quantity of this mixture is then injected into the column of a gas–liquid chromatograph and is allowed to pass through the device.



The smallest peak and longest retention time respectively are recorded for

- A. ethanol and propanol.
- B. butanol and propanol.
- C. ethanol and butanol.
- D. butanol in both cases.

Question 10

The key factors which influence the length of time that a compound requires to move through the column of a high performance liquid chromatograph are

- A. the length of the column and the amount of chemical injected.
- B. the temperature of the column and the polarity of the liquid mobile phase.
- C. the polarity of the solid stationary phase and the amount of chemical injected.
- D. the sensitivity of the detector and the temperature of the column.

SECTION B: SHORT-ANSWER QUESTIONS

Instructions for Section B

Answer **all** questions in the spaces provided.

To obtain full marks you should

- give simplified answers with an appropriate number of significant figures to all numerical questions; unsimplified answers will not be given full marks.
- show all working in your answers to numerical questions. No credit will be given for an incorrect answer unless it is accompanied by details of the working.
- make sure chemical equations are balanced and that the formulas for individual substances include an indication of state; for example $\text{H}_2(\text{g})$; $\text{NaCl}(\text{s})$.

Question 1

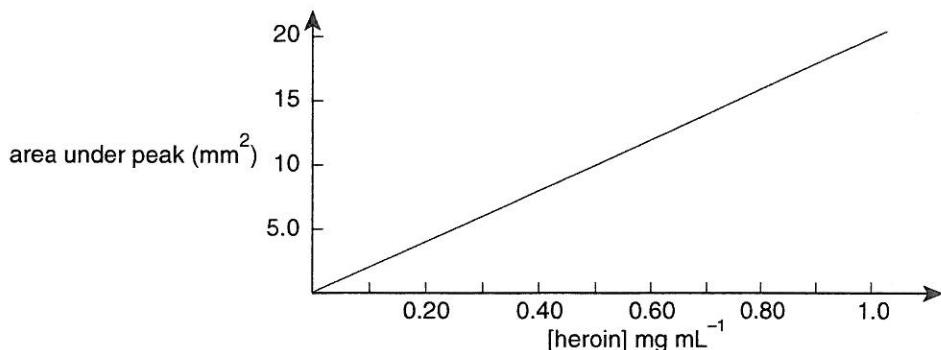
An unconscious person is brought into a hospital emergency department having suffered from a suspected heroin overdose. Doctors take a blood sample from the patient and run it through a HPLC. The chromatogram generated contains over one hundred peaks.

- a. i. Why are there so many peaks present in the chromatogram generated?

- ii. How can the doctors determine whether or not the person has heroin in their bloodstream?

1 + 2 = 3 marks

- b. A series of pure heroin samples of different concentrations are passed through the same HPLC as that used to test the patient's blood. The results obtained are shown in the graph below.



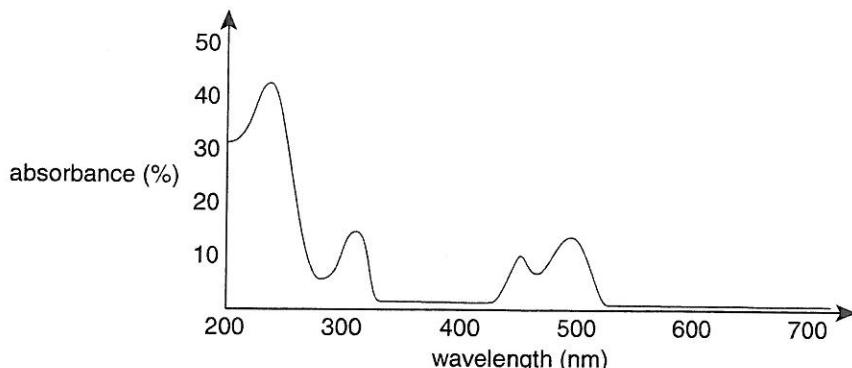
The patient's blood sample generated a heroin peak with an area of 13 mm^2 .

Calculate the concentration of heroin in the patient's blood sample in mg mL^{-1} .

1 mark
Total 4 marks

Question 2

The compound fluorescein ($C_{20}H_{12}O$) is used as a synthetic colouring agent in cosmetics. In alkaline solutions, fluorescein glows with an intense green colour that is visible to very low concentrations. The UV-visible spectrum of fluorescein is shown below.

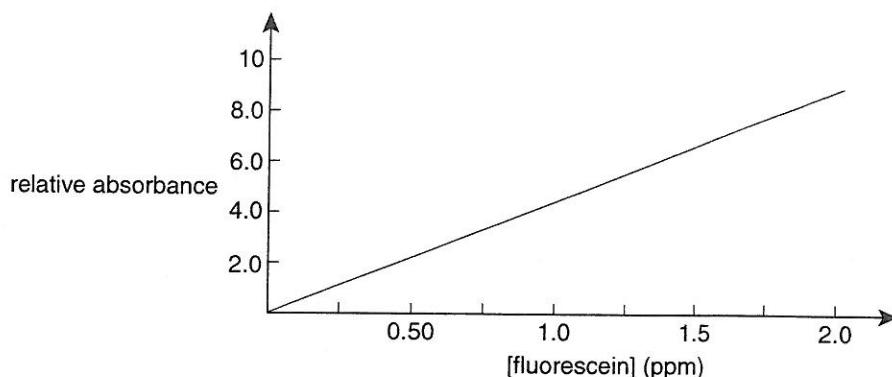


- a. i. Given that red light has a wavelength of around 700 nm and blue/violet light wavelengths are in the range of 400–490 nm, explain why fluorescein appears as a green colour in solution.

- ii. What frequency should be selected to generate a calibration curve of the relative absorbances of a set of standard solutions of known fluorescein concentrations using UV-visible spectroscopy? Explain your answer.

1 + 2 = 3 marks

- b. By using a suitable wavelength the absorbance of a set of fluorescein solutions was measured using a UV-visible spectrometer. The results are shown below.



A 0.520 g sample of ‘Skin-Glo’ anti-ageing cream was dissolved in 100.0 mL of distilled water and a small quantity of this solution was passed through the UV-visible spectrometer. An absorbance reading of 3.5 units was recorded.

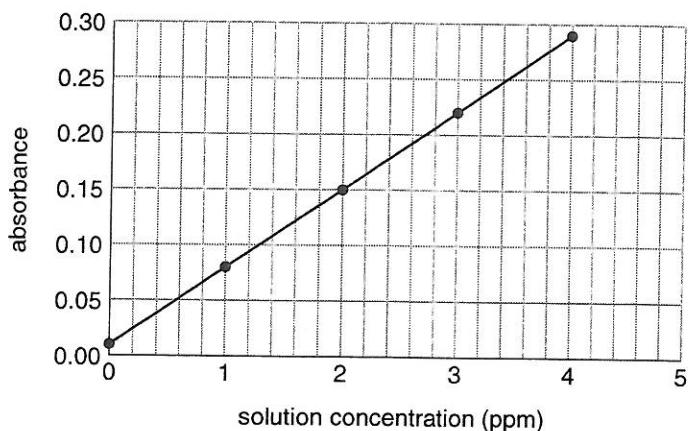
- i. Determine the concentration of fluorescein in the solution in parts per million.

- ii. Calculate the percentage mass of fluorescein in the 0.520 g sample of ‘Skin-Glo’ anti-ageing cream.

1 + 2 = 3 marks
Total 6 marks

Question 4

Brazil nuts are an important source of the metal selenium, which is essential in trace quantities in virtually all animals. A 3.50 g sample of brazil nuts was finely chopped and dissolved in 20.0 mL of acid. The mixture was filtered and diluted to 100.0 mL with distilled water. A small quantity of this solution was then passed through an atomic absorption spectrometer along with a number of solutions of known selenium concentration. The calibration curve generated by this experiment is shown below.



The absorbance of the diluted nut solution was recorded as 0.19.

- a. Why was it necessary to generate a calibration curve for various selenium concentrations in this experiment?

1 mark

- b. The calibration curve shows that a small absorbance reading was made for the solution of zero selenium metal concentration.

State a possible reason for this observation.

1 mark

- c. Determine the concentration of selenium in the **undiluted** acid solution in parts per million.

2 marks

- d. Calculate the mass of selenium (in mg) present in the sample of brazil nuts.

2 marks

- e. Name another analytical technique that might be used to determine the presence of selenium in the brazil nuts.

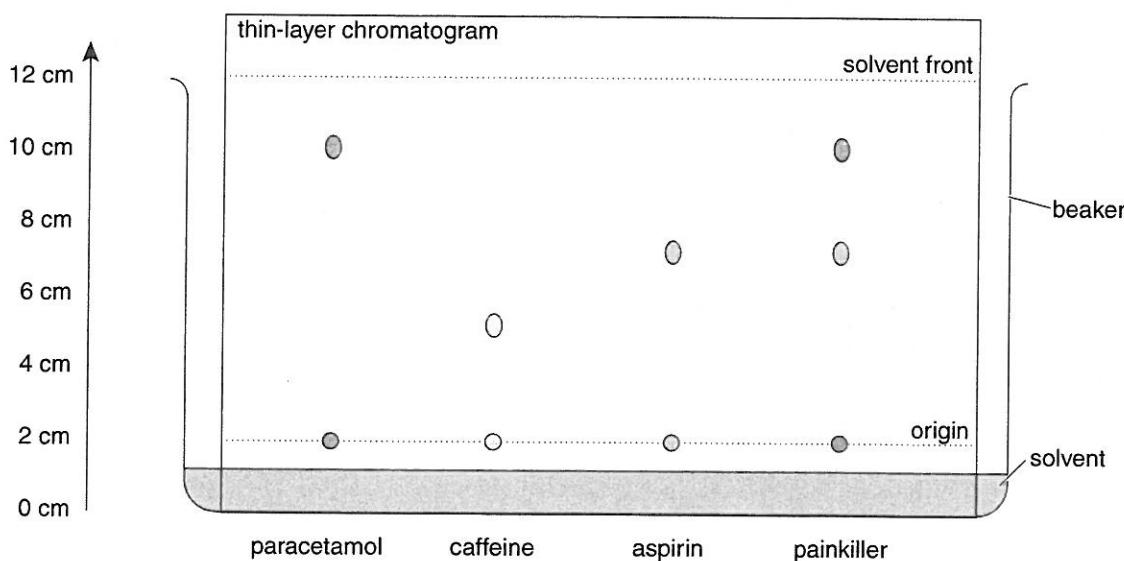
1 mark

Total 7 marks

Question 3

Thin-layer chromatography is a similar technique to paper chromatography for separating chemicals according to the extent to which they adsorb onto a stationary phase. In the case of TLC, a slurry of calcium sulfate and silica gel is applied to a glass plate and is allowed to dry. An origin line is drawn in pencil 2.0 cm from the base of the glass plate and drops of the chemicals to be tested are placed at equal intervals along the origin. The plate is then lowered into a vessel containing sufficient solvent to cover the base of the plate without immersing the origin.

A student wished to determine the principal active ingredients in a painkilling tablet. He was aware that the manufacturers of painkillers in the United States replace codeine with caffeine and wished to determine whether or not the tablet contained caffeine. He set up a thin-layer chromatogram by spotting the origin with pure samples of paracetamol, aspirin and caffeine along with the unknown painkiller. The solvent used as the mobile phase is a mixture of butyl ethanoate ($\text{CH}_3\text{COO}(\text{CH}_2)_3\text{CH}_3$) and trichloroethane (CHCl_3) and the final results are observed under UV light. The results obtained are shown below.

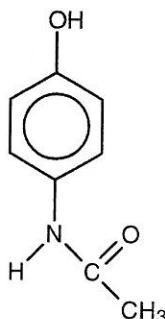


- a. Explain why the paracetamol, aspirin and caffeine travel different distances in the chromatogram.

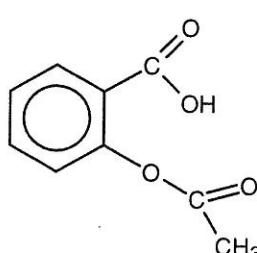
1 mark

- b. i. Calculate the R_f values of paracetamol, caffeine and aspirin.

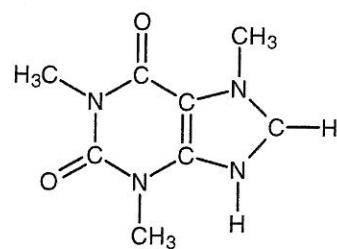
The structural formulas of paracetamol, aspirin and caffeine are provided below.



paracetamol



aspirin



caffeine

- ii. In terms of structure, explain why caffeine has the smallest R_f value of these three compounds.

- iii. Why is water not suitable as a solvent/mobile phase for this experiment?

2 + 2 + 1 = 5 marks

- c. Has the student proved that the unknown painkiller contains codeine and not caffeine? Explain your answer.

2 marks

Total 8 marks

CHEMISTRY VCE UNITS 3&4 DIAGNOSTIC TOPIC TESTS 2008

TEST 2: SPECTROSCOPY AND CHROMATOGRAPHY

SUGGESTED SOLUTIONS AND MARKING SCHEME

SECTION A: MULTIPLE-CHOICE QUESTIONS

Question 1 B

Atomic absorption spectroscopy is best suited to determining the presence of trace quantities of metals (so **A** is incorrect). UV-visible spectroscopy is generally used to test for the presence of coloured organic molecules or those that absorb in the UV region of the electromagnetic spectrum. It is generally not used for large, complex molecules such as dieldrin (so **C** is incorrect). Paper chromatography is a relatively simple technique that separates (often) coloured compounds such as dyes (so **D** is incorrect). High performance liquid chromatography (HPLC) is a highly sensitive technique particularly well suited to determining the presence of small quantities of large, complex molecules, even in the presence of structurally similar molecules.

Question 2 A

Emission spectra are highly characteristic of the elements present in a sample. If a particular metal is present in the Mars rock being tested, then all of the spectral lines for that metal must be present in the emission spectrum of the rock. This is the case only for iron and copper, so **A** is the correct response.

Question 3 B

The magnetic field deflects particles according to their mass and charge. The lesser the mass and the greater the charge on the particle, the more strongly it will be deflected by the applied magnetic field. Mathematically, the amount of deflection is directly proportional to the charge and inversely proportional to the mass. CH_2^{2+} carries a +2 charge and is lighter than the CH_4^{2+} fragment and so will be deflected to the largest extent.

Question 4 C

A major peak in the mass spectrum will occur for a fragment of a molecule that is likely to be created when the molecule is subjected to the strong electric field within the spectrometer. Methyl ethanoate (option **C**) would be expected to produce fragments such as CH_3^+ ($m/e = 15$), CH_3CO^+ ($m/e = 43$) and CH_3O^+ ($m/e = 31$) and so this is the correct response. Propanone (option **A**) would produce fragments including CH_3^+ ($m/e = 15$), CH_3CO^+ ($m/e = 43$) and CO^+ ($m/e = 28$). Ethanoic acid (option **B**) would produce fragments including CH_3^+ ($m/e = 15$), COOH^+ ($m/e = 45$) and OH^+ ($m/e = 17$). Propan-2-ol (option **D**) would produce fragments including CH_3^+ ($m/e = 15$), CH_3CHOH^+ ($m/e = 45$) and CHOH^+ ($m/e = 30$).

Question 5 D

To answer this question you will need to refer to the data sheets which provide the infrared absorption data. The spectrum provided shows strong absorbance at a wave number of 1720 cm^{-1} . This significant peak is strongly indicative of the presence of the carbonyl ($\text{C}=\text{O}$) functional group. Propanone (option D) is the only molecule which has this functional group present. A is incorrect as there must be a strong and broad peak present for the alcohol functional group at $3200\text{--}3500\text{ cm}^{-1}$. While there is some absorbance at these frequencies, it is insufficient to indicate the presence of the $-\text{OH}$ group. Similarly, B and D are incorrect as the spectrum does not exhibit absorbances at $2500\text{--}3300\text{ cm}^{-1}$ and $700\text{--}800\text{ cm}^{-1}$ respectively.

Question 6 A

^1H nuclear magnetic resonance (NMR) spectroscopy uses radio waves to align hydrogen nuclei with an applied magnetic field (so A is correct). Infrared spectroscopy measures the absorption of energy by molecules as they vibrate, rotate and stretch (so B is incorrect). One of the key stages in mass spectrometry is the acceleration of electrons by a strong electric field to ionise and fragment molecular species (so C is incorrect). Atomic absorption spectroscopy uses a monochromator to select the most strongly absorbed (characteristic) frequency as light passes through the vapourised sample (so D is incorrect).

Question 7 C

In high performance liquid chromatography (HPLC), the stationary phase is a solid consisting of small, tightly packed particles packed into a column (so C is correct). An inert gas such as nitrogen or argon is used as the mobile phase in gas chromatographic techniques (GSC and GLC) (so A is incorrect). B refers to the stationary phase in gas–liquid chromatography and so is incorrect. Platinum metal is an outstanding catalyst, but is not used in chromatography (so D is incorrect).

Question 8 A

Gas–liquid chromatography is widely used to separate and identify volatile (low molecular mass) organic compounds from complex mixtures of similar substances. The substance is producing an unpleasant odour, so it must be gaseous and must have a relatively low molecular mass, making A the best answer. Proteins in cancerous tissue are large molecules with high molecular weights. These molecules would be destroyed if they were to be vapourised in a GLC and so are best separated and identified using HPLC (so B is incorrect). Coloured dyes from marker pens can be separated using either paper chromatography or perhaps UV–visible spectroscopy (so C is incorrect). To determine the presence of mercury in a sample of fish the most appropriate technique is atomic absorption spectroscopy (AAS) (so D is incorrect).

Question 9 D

The area under the peak of a chromatogram is proportional to the amount of substance present, so in this case the propanol (50% of the mixture) will have the largest peak, followed by ethanol (30%) and butanol (20%). The longer the retention time the more strongly the molecule has interacted with the stationary and mobile phases. All three of these alcohols have the same hydroxyl ($-\text{OH}$) functional group, and so the strength of interaction will depend on the magnitude of the dispersion forces, which in turn depends on molecular mass. Ethanol will have the shortest retention time as it is the smallest organic molecule present, followed by propanol and then butanol. Thus, the smallest peak and longest retention time are both recorded for butanol, so D is correct.

Question 10 B

There are a number of factors that affect the time required for compounds to pass through, or elute from, a HPLC column. The length of the column and the material with which it has been packed are both significant factors. The column is maintained at a constant temperature, as the temperature affects the viscosity and rate of movement of the compounds along the column material. The amount of material injected into the column should have no significant influence on the retention time (so A and C are incorrect). The sensitivity of the detector will only impact on the accuracy of the results (so D is incorrect).

SECTION B: SHORT-ANSWER QUESTIONS

Question 1

- a. i. Blood is a complex mixture of many different compounds, including numerous proteins, enzymes, lipids, hormones and other molecules required for life. If drugs have been recently ingested both these and their metabolic by-products will be found in the bloodstream. 1 mark
- ii. To ascertain whether the patient's blood contains heroin, it would be necessary to know the precise HPLC retention time for heroin (or its by-products) using the same temperature, column length, packing material, eluent etc. as was used when the patient's blood was tested. All of these factors affect the rate at which the chemical components of blood dissolved in the mobile phase will elute from the column, and will consequently affect the retention time. 1 mark
The chromatogram of the blood sample would then need to be analysed to determine whether there is a peak with the same retention time as heroin. 1 mark
- b. Reading from the graph, a peak area of 13 mm^2 corresponds to a heroin concentration of approximately 0.65 mg mL^{-1} . 1 mark

Total 4 marks

Question 2

- a. i. Fluorescein absorbs light with wavelengths 420–520 nm quite strongly. This corresponds to the blue and violet end of the spectrum. As these colours are absorbed, light from the other end of the spectrum (reds and yellows) will be transmitted. The combination of these transmitted frequencies of light is the green colour observed. The very strong absorbance in the UV range is not visible to the human eye and so has no bearing on the colour perceived. 1 mark
- ii. 240 nm 1 mark
This is the most strongly absorbed wavelength of light, and so will be the most sensitive indicator of the presence of fluorescein in any solution. 1 mark
- b. i. From the graph, the concentration of fluorescein in the solution is 0.75 ppm. 1 mark
- ii. $c(\text{fluorescein}) = 0.75 \text{ ppm} = 0.75 \text{ g of fluorescein per } 10^6 \text{ g of solution}$
 $= x \text{ g of fluorescein per } 100 \text{ g of solution}$
 $x = \frac{0.75 \times 100}{10^6} = 7.5 \times 10^{-5} \text{ g}$ 1 mark

Given that $7.5 \times 10^{-5} \text{ g}$ of fluorescein are present in 0.520 g of cream, the

$$\text{percentage mass} = \frac{7.5 \times 10^{-5}}{0.520} \times \frac{100}{1} = 0.014\% \text{ m/m}$$
 1 mark

Total 6 marks

Question 3

- a. Paracetamol, aspirin and caffeine travel different distances in the chromatogram as they adsorb onto the stationary phase (the calcium sulfate attached to the glass plate) at varying rates. As the molecules have different structures and polarities, they will interact with the stationary and mobile phases to differing extents. 1 mark
- b. i. paracetamol: $\frac{8}{10} = 0.8$; caffeine: $\frac{3}{10} = 0.3$; aspirin: $\frac{5}{10} = 0.5$ 2 marks
- 2 marks for all three correct values
1 mark for two correct values*
- 1 mark if the student ignores that the origin is at '2 cm', but otherwise correctly calculates all three values*
- ii. Caffeine has the smallest R_f value of these three molecules as it has travelled the shortest distance. This means that it is the molecule adsorbed most strongly onto the stationary phase. 1 mark
Caffeine has the largest molecular mass of the three analgesic molecules shown and also has a number of polar nitrogen and oxygen atoms bonded into its structure. This explains why it bonds more strongly to the polar stationary phase. 1 mark
- iii. Water is not suitable as a solvent/mobile phase for this experiment as all three molecules to be analysed are relatively large, non-polar, organic molecules and so will not be very soluble in the polar solvent water. 1 mark
- c. The student has not proven that the unknown painkiller contains codeine and not caffeine. The chromatogram for the unknown painkiller has shown that it does (most likely) contain paracetamol and aspirin as the R_f values of the spots on the painkiller chromatogram match the R_f values for these two compounds. Caffeine is not present. To prove the existence of codeine in the painkiller, it would be necessary to repeat the experiment with a sample of the painkiller alongside a small quantity of pure codeine. 1 mark
- Total 8 marks

Question 4

- a. A calibration curve is required so that the absorbance reading of the unknown solution can be converted into a concentration measurement reading. 1 mark
- b. There may have been a small amount of contamination in the 'zero concentration' test solution. Alternatively, there may have been a small amount of light scattering by the cell holding the sample. 1 mark
- c. From the graph, [Se] in the diluted solution = 2.6 ppm. 1 mark
[Se] in the undiluted solution = $\frac{100}{20.0} \times 2.6 = 13$ ppm 1 mark
- d. The concentration of selenium in the nuts is 13 ppm, so there is 13 g of selenium per 10^6 g of brazil nuts. 1 mark
 x g of selenium per 3.50 g of brazil nuts
 $x = \frac{3.50 \times 13}{10^6} = 4.6 \times 10^{-5}$ g = 0.046 mg 1 mark
- e. atomic absorption spectroscopy (AAS) 1 mark
- Total 7 marks