PEARSON EDEXCEL · INTERNATIONAL A-LEVEL · CHEMISTRY • EXERCISE SHEET

3.1.2 Organic unknowns and synthesis justification

Name: _____ Class: _____ Date: _____ **Total: 19 marks**

KEY WORDS drying agent • redox • deliquescent

Objective

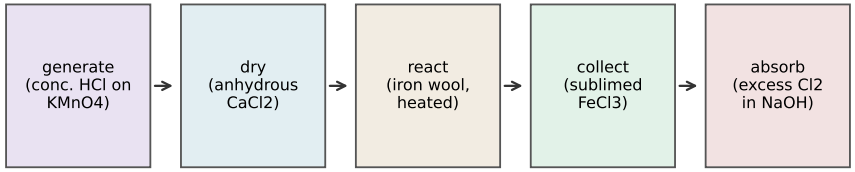
Identify organic unknowns from combined tests and spectra, and justify every stage of a gas synthesis: redox generation, drying, flushing air, absorbing exit gas, and the mass the product really weighs. Original practice for WCH13's organic-unknowns and synthesis demands (Summer 2025 Q1, Q4 pattern).

1 Key knowledge and worked examples

Two tests, one isomer set

Phosphorus(V) chloride on an alcohol (or carboxylic acid) releases misty fumes of **hydrogen chloride** – never "hydrochloric acid". Acidified potassium dichromate(VI) turns **orange to green** when primary or secondary alcohols are oxidised. With the molecular ion at m/z 60 (C_3H_8O), the strongest fragment separates the isomers: m/z 31 is CH_2OH^+ (primary – propan-1-ol); m/z 45 is CH_3CHOH^+ (secondary – propan-2-ol). Charges on fragments are required once; brackets optional.

The synthesis train, stage by stage



heat the iron only after the air is flushed out;

every junction dry; toxic exit gas absorbed, never released

- Generation: concentrated HCl on $KMnO_4$ is **redox** – chloride ions lose electrons ($2Cl^- \rightarrow Cl_2 + 2e^-$) while manganate(VII) is reduced.
- Drying: **anhydrous calcium chloride is a drying agent** (not "dehydrating agent"); ceramic wool stops it spreading so all gas passes through it.
- Timing: heat the iron only after ~half a minute, so the **air is flushed out** and iron meets dry chlorine, not oxygen.
- Exit: sodium hydroxide **absorbs the excess toxic chlorine**.
- Product: deliquescent iron(III) chloride is sealed quickly; any absorbed water makes the weighed mass *greater* than the calculated maximum.

2 Practice

2.1 Phosphorus(V) chloride is added to a liquid; misty fumes appear. Name the gas and the functional group it indicates. [2]

2.2 State the colour change when acidified dichromate(VI) oxidises propan-2-ol, and the functional group of the organic product. [2]

2.3 Give the formulae of the ions giving m/z 31 and m/z 45 in the mass spectra of the propanol isomers, and name each isomer from its strongest peak. [4]

2.4 In the $FeCl_3$ synthesis, state the purpose of the anhydrous calcium chloride and of the sodium hydroxide. [2]

3 Exam-style questions

3.1 Two isomeric liquids P and Q (C, H, O only, one functional group each, same group) both fume with PCl_5 and both turn acidified dichromate(VI) green on gentle heating. Their mass spectra both show M^+ at m/z 60; P's strongest peak is 31, Q's is 45. Deduce the structural formulae of P and Q, justifying from the fragments. [4]

3.2 Justify that the reaction between concentrated hydrochloric acid and potassium manganate(VII) is a redox reaction, including the ionic half-equation for chlorine formation. [2]

3.3 The iron wool is heated only after chlorine has been generated for about half a minute, and the product in the weighing bottle weighs more than the maximum calculated from the iron. Explain both observations. [3]

Solutions

Original-task marking: M1 method, A1 accuracy, B1 reasoning.

2.1 Hydrogen chloride gas (HCl); an –OH group – alcohol or carboxylic acid.

2.2 Orange to green; the product is a ketone (propanone) – secondary alcohol oxidation.

2.3 m/z 31: CH_2OH^+ (allow CH_3O^+) – propan-1-ol; m/z 45: CH_3CHOH^+ ($C_2H_5O^+$) – propan-2-ol.

2.4 Calcium chloride dries the chlorine gas (removes moisture); sodium hydroxide absorbs the unreacted excess chlorine.

3.1 Both are alcohols with $M_r = 60$, so C_3H_8O – the two propanol isomers. P's base peak at 31 is CH_2OH^+, the primary-alcohol fragment: P = $CH_3CH_2CH_2OH$. Q's base peak at 45 is CH_3CHOH^+, the secondary fragment: Q = $CH_3CHOHCH_3$.

3.2 Chloride ions lose electrons – oxidation number rises from -1 to 0 – while manganate(VII) ions gain electrons (Mn $+7 \rightarrow +2$); $2Cl^- \rightarrow Cl_2 + 2e^-$.

3.3 Waiting flushes the air (oxygen) out of the tube so the heated iron reacts with dry chlorine rather than air/oxygen. The product absorbs/reacts with water from the air to form hydrated iron(III) chloride, so the measured mass includes water.