JEE MAIN · PAPER 1 · CHEMISTRY

13 Purification & Characterisation of Organic Compounds

Formula & concept sheet

How an organic compound is purified (sublimation, crystallisation, distillation in its three forms, extraction, chromatography) and how it is identified and its formula found: Lassaigne's test for N, S, halogens and P, and the quantitative methods of Liebig, Dumas, Kjeldahl and Carius with the percentage formulas. Each idea is explained first, then the formulas and the worked numericals.

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READ ALONGSIDE NCERT XI · Organic Chemistry: Some Basic Principles and Techniques

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

Practise this chapter with real past-paper questions on Prep Vault. Written for revision, not as a first read.

CHAPTER 13

Purification & Characterisation of Organic Compounds

NCERT XI · Organic Chemistry: Some Basic Principles and Techniques

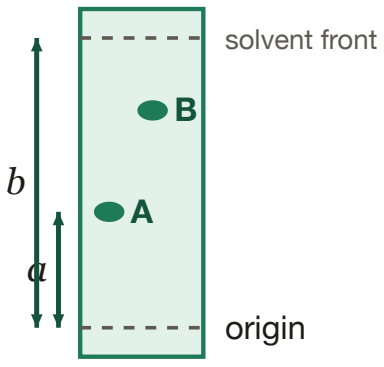
Covers: sublimation, crystallisation, distillation (simple, fractional, reduced pressure, steam), differential extraction, chromatography (column, TLC, paper) · detection of C, H, N, S, halogens, P (Lassaigne's test) · estimation of C, H (Liebig), N (Dumas, Kjeldahl), halogens, S, P (Carius), O by difference · empirical and molecular formula.

1 Methods of purification

A compound is judged pure by a **sharp melting point** (solid), a sharp **boiling point** (liquid) or a **single spot** on a TLC plate. The method is chosen from the property that differs between the compound and its impurities: volatility, solubility, adsorption.

TECHNIQUES: PRINCIPLE AND EXAMPLES

TECHNIQUE	PRINCIPLE AND WHEN IT IS USED	EXAMPLE
sublimation	a solid passes to vapour without melting; separates a sublimable solid from a non-sublimable one	camphor, naphthalene, anthracene, benzoic acid
crystallisation	different solubility at high and low temperature; charcoal removes coloured impurities; fractional crystallisation separates two compounds of different solubility	sugar, impure solids
simple distillation	volatile liquid from a non-volatile impurity, or liquids whose boiling points differ by a lot	chloroform (334 K) and aniline (457 K)
fractional distillation	liquids with close boiling points: a fractionating column gives many vaporisation-condensation steps	acetone (329 K) and methanol (338 K); crude oil fractions
distillation under reduced pressure	a liquid that decomposes at or below its normal boiling point; lower pressure lowers the boiling point	glycerol from spent lye (soap industry)
steam distillation	a steam-volatile, **water-immiscible** liquid (or solid); boils below 373 K because $p_{org} + p_{\mathrm{H_2O}} = P_{atm}$	aniline, essential oils, turpentine; o-nitrophenol from p-nitrophenol
differential extraction	different solubility in two immiscible solvents (water and ether); repeated extraction is more efficient	organic compound from an aqueous solution with ether
chromatography	different adsorption on a stationary phase (column, TLC: silica, alumina) or partition (paper)	mixtures of dyes, amino acids, purity checks



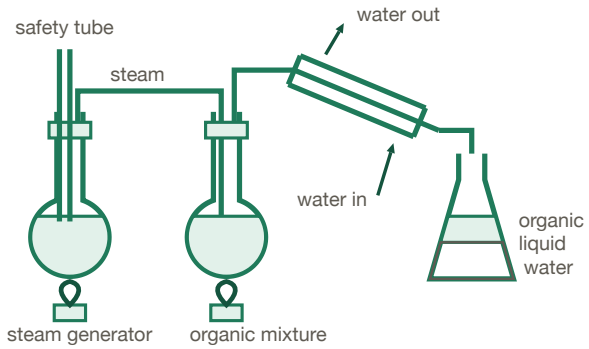
Rf = a / b, $0 < Rf < 1$

Rf is the ratio of the distances moved by the substance and by the solvent front; the less polar compound runs further on silica

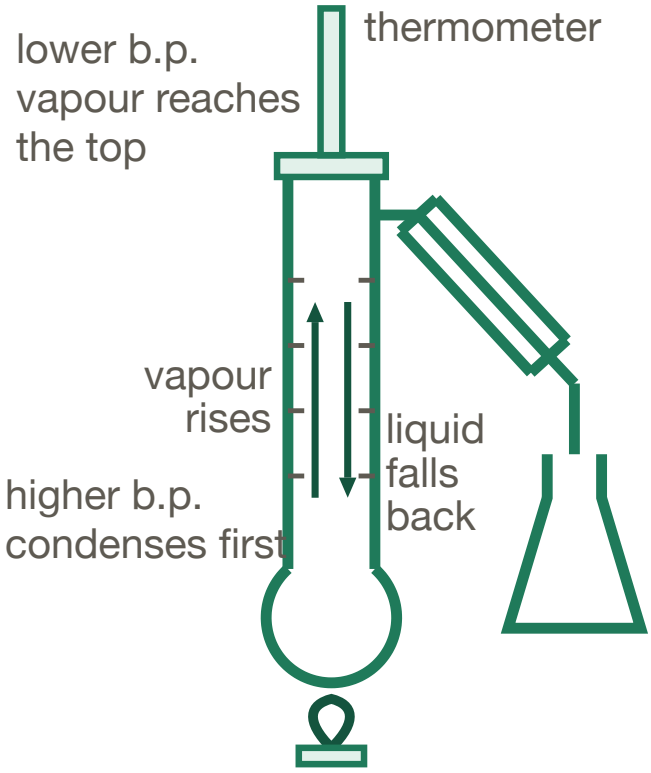
RETARDATION FACTOR $R_f = \dfrac{\text{distance moved by the substance from the base line}}{\text{distance moved by the solvent front}}$, always $0 < R_f < 1$, with no unit; it is constant for a given compound, solvent and adsorbent. On silica (a polar stationary phase) the **less polar** compound moves further (higher R_f): alkenes $>$ alcohols. Colourless spots are seen under UV (fluorescent plate), with iodine vapour (brown) or a reagent (ninhydrin for amino acids).

KEY IDEA

Steam distillation works when the liquid is immiscible with water and steam-volatile: the total vapour pressure is the sum of the two, so the mixture boils below 373 K without decomposition. In fractional distillation the vapour that reaches the top of the column is richer in the lower-boiling liquid.



the mixture boils below 373 K because p(organic) + p(water) = atmospheric pressure



repeated vaporisation-condensation steps enrich the top in the lower-boiling liquid

STEAM DISTILLATION RATIO

$$\frac{m_{org}}{m_{\mathrm{H_2O}}} = \frac{p_{org}\,M_{org}}{p_{\mathrm{H_2O}}\,M_{\mathrm{H_2O}}}$$

from Dalton's law: the moles in the distillate are proportional to the vapour pressures

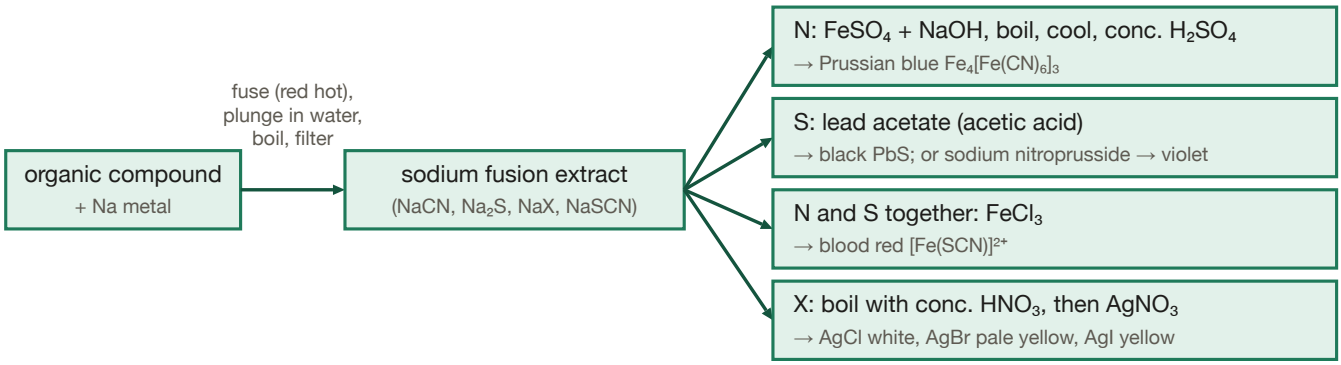
QUICK CHECK

Which method for: glycerol, aniline from water, a mixture of acetone (329 K) and methanol (338 K), o- and p-nitrophenol?

Answer: Reduced-pressure distillation; steam distillation; fractional distillation; steam distillation (only the ortho isomer, with the intramolecular H bond, is volatile).

2 Qualitative analysis: detecting the elements

- **Carbon and hydrogen**: heat the compound with dry CuO; carbon is oxidised to $\mathrm{CO_2}$ ($\mathrm{C + 2\,CuO \longrightarrow 2\,Cu + CO_2}$, turning lime water milky: $\mathrm{Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O}$) and hydrogen to water ($\mathrm{2\,H + CuO \longrightarrow Cu + H_2O}$, turning anhydrous $\mathrm{CuSO_4}$ blue: $\mathrm{CuSO_4 + 5\,H_2O \longrightarrow CuSO_4 \cdot 5\,H_2O}$).
- **Lassaigne's test** (sodium fusion extract, SFE): fusing with sodium converts the covalent elements into ionic sodium salts, $\mathrm{Na + C + N \longrightarrow NaCN}$, $\mathrm{2\,Na + S \longrightarrow Na_2S}$, $\mathrm{Na + X \longrightarrow NaX}$ (with N and S together $\mathrm{Na + C + N + S \longrightarrow NaSCN}$); the fused mass is boiled with water and filtered.



fusion with sodium turns covalent N, S, X into ionic NaCN, Na_2S, NaX

LASSAIGNE TESTS IN DETAIL

ELEMENT	TEST ON THE SFE	OBSERVATION AND CHEMISTRY
nitrogen	boil with $FeSO_4$ + NaOH, then acidify with conc. H_2SO_4	Prussian blue: $6\,CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$; $3\,[Fe(CN)_6]^{4-} + 4\,Fe^{3+} \longrightarrow Fe_4[Fe(CN)_6]_3$ (some Fe^{2+} is oxidised by air)
sulphur	acetic acid + lead acetate	black PbS: $S^{2-} + Pb^{2+} \longrightarrow PbS$
sulphur	sodium nitroprusside	violet: $S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$
nitrogen and sulphur together	$FeCl_3$	blood red $[Fe(SCN)]^{2+}$ (from NaSCN; no Prussian blue; excess sodium decomposes NaSCN to NaCN and Na_2S)
halogens	boil with conc. HNO_3 (destroys CN^- and S^{2-}, which would also precipitate with Ag^+), then $AgNO_3$	AgCl white (soluble in NH_3 solution); AgBr pale yellow (sparingly soluble); AgI yellow (insoluble)
phosphorus	oxidise to phosphate by fusion with Na_2O_2, boil with conc. HNO_3 + ammonium molybdate	yellow precipitate of ammonium phosphomolybdate $(NH_4)_3PO_4 \cdot 12MoO_3$

TRAP

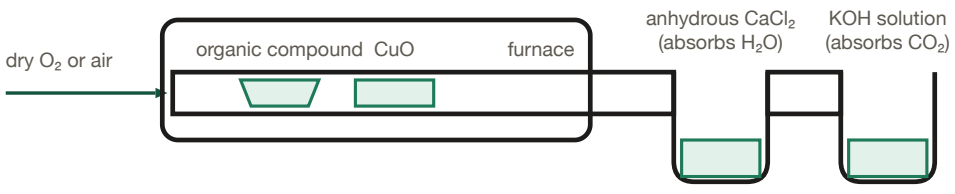
Compounds that lose their nitrogen as N_2 on fusion (hydrazine, some diazonium salts) or have no carbon (NH_2NH_2) do not give the N test. Heating the SFE with HNO_3 before $AgNO_3$ removes CN^-/S^{2-}, it does not oxidise halides. The Beilstein green-flame test for halogens also gives false positives (urea, thiourea). With too little sodium and both N and S present you get blood red, not Prussian blue.

QUICK CHECK

A compound gives a blood-red colour with $FeCl_3$ in Lassaigne's test. Which elements are present?

Answer: Both N and S (as NaSCN in the extract); also carbon.

3 Quantitative analysis and the formula



%H = 2/18 × (mass of H_2O) / (mass of compound) × 100
%C = 12/44 × (mass of CO_2) / (mass of compound) × 100

the increase in mass of each absorber gives the mass of water and carbon dioxide

% CARBON (LIEBIG)

$$\%\mathrm{C} = \frac{12}{44} \times \frac{m_{\mathrm{CO_2}}}{m} \times 100$$

$\mathrm{CO_2}$ absorbed in KOH; compound burnt in $\mathrm{O_2}$ over CuO

% HYDROGEN (LIEBIG)

$$\%\mathrm{H} = \frac{2}{18} \times \frac{m_{\mathrm{H_2O}}}{m} \times 100$$

water absorbed in anhydrous $\mathrm{CaCl_2}$

% OXYGEN

$$\%\mathrm{O} = 100 - \sum(\text{other }\%)$$

oxygen is found by difference (or by a direct method)

% NITROGEN, DUMAS

$$\%\mathrm{N} = \frac{28}{22400} \times \frac{V_0}{m} \times 100$$

V_0 mL of $\mathrm{N_2}$ at STP; over aqueous KOH: $V_0 = \dfrac{(P - p_{aq})VT_0}{P_0T}$ (subtract the aqueous tension); m in g

% NITROGEN, KJELDAHL

$$\%\mathrm{N} = \frac{1.4 \times N_{acid} \times V_{acid}}{m}$$

V in mL of acid neutralised by $\mathrm{NH_3}$ (acid taken minus the back-titrated excess); $N = 2M$ for $\mathrm{H_2SO_4}$

digest: compound + conc. $\mathrm{H_2SO_4}$ (+ $\mathrm{K_2SO_4}$, $\mathrm{CuSO_4}$) → $(\mathrm{NH_4})_2\mathrm{SO_4}$

add excess NaOH, heat: $\mathrm{NH_3}$ released

$\mathrm{NH_3}$ distilled into known excess of standard $\mathrm{H_2SO_4}$; back-titrate unused acid with NaOH



%N = 1.4 × N × V / m (V in mL of acid used)

not for nitro, azo and ring-nitrogen compounds

KJELDAHL IN THREE STEPS

- **Digestion**: heat with conc. $\mathrm{H_2SO_4}$ (+$\mathrm{K_2SO_4}$, $\mathrm{CuSO_4}$): nitrogen becomes $(\mathrm{NH_4})_2\mathrm{SO_4}$.
- **Release**: boil with excess NaOH: $(\mathrm{NH_4})_2\mathrm{SO_4} + 2\,\mathrm{NaOH} \longrightarrow \mathrm{Na_2SO_4} + 2\,\mathrm{NH_3} + 2\,\mathrm{H_2O}$.
- **Absorb and titrate**: $\mathrm{NH_3}$ into a known excess of standard acid; titrate the unused acid with NaOH; milli-equivalents of acid used = milli-equivalents of $\mathrm{NH_3}$.

OTHER PERCENTAGE FORMULAS

ELEMENT	FORMULA	PRECIPITATE (MOLAR MASS)
halogen (Carius)	$\%\mathrm{X} = \frac{A_X}{M_{AgX}} \times \frac{m_{AgX}}{m} \times 100$	AgCl 143.5, AgBr 188, AgI 235
sulphur (Carius)	$\%\mathrm{S} = \frac{32}{233} \times \frac{m_{BaSO_4}}{m} \times 100$	$\mathrm{BaSO_4}$ 233 (S oxidised to $\mathrm{H_2SO_4}$ by fuming $\mathrm{HNO_3}$, then $\mathrm{BaCl_2}$)
phosphorus	$\%\mathrm{P} = \frac{62}{222} \times \frac{m_{Mg_2P_2O_7}}{m} \times 100$ or $\frac{31}{1877} \times \frac{m_{(NH_4)_3PO_4.12MoO_3}}{m} \times 100$	$\mathrm{Mg_2P_2O_7}$ 222; ammonium phosphomolybdate 1877
empirical formula	mole ratio $= \frac{\%}{A}$, divide by the smallest, multiply to clear fractions	molecular formula $= n\times$ empirical, $n = \frac{M}{M_{EF}}$, $M = 2\times$ vapour density

WHY IT WORKS

Kjeldahl digestion (conc. $\mathrm{H_2SO_4}$ with $\mathrm{K_2SO_4}$ to raise the boiling point and $\mathrm{CuSO_4}$ catalyst) turns N into $(\mathrm{NH_4})_2\mathrm{SO_4}$; NaOH liberates $\mathrm{NH_3}$, which is absorbed in a known excess of acid. It fails for **nitro, azo** and ring-nitrogen compounds (pyridine), whose N does not become $(\mathrm{NH_4})_2\mathrm{SO_4}$; Dumas works for all nitrogen compounds.

QUICK CHECK

In Kjeldahl's method 0.5 g of compound liberates $\mathrm{NH_3}$ neutralising 30 mL of 0.1 M $\mathrm{H_2SO_4}$. %N?

Answer: $N = 0.2$ N: $\dfrac{1.4 \times 0.2 \times 30}{0.5} = 16.8\%$.

4 Worked examples

LIEBIG TO FORMULA

0.3 g of an organic compound gives 0.44 g CO_2 and 0.18 g H_2O. Empirical formula?

$\%C = \frac{12}{44} \times \frac{0.44}{0.3} \times 100 = 40$; $\%H = \frac{2}{18} \times \frac{0.18}{0.3} \times 100 = 6.67$; $\%O = 53.3$; ratio $3.33 : 6.67 : 3.33 = 1 : 2 : 1$: CH_2O

DUMAS

0.30 g gives 50 mL of N_2 at 300 K and 715 mm Hg (aqueous tension 15 mm). %N?

$V_0 = \frac{(715 - 15) \times 50 \times 273}{760 \times 300} = 41.9$ mL; $\%N = \frac{28 \times 41.9}{22400 \times 0.30} \times 100 = 17.5$

CARIUS SULPHUR

160 mg of a compound gives 466 mg $BaSO_4$. %S?

$\frac{32}{233} \times \frac{466}{160} \times 100 = 40\%$ (2 mmol S)

CARIUS BROMINE

0.15 g of a bromo compound gives 0.20 g AgBr. %Br?

$\frac{80}{188} \times \frac{0.20}{0.15} \times 100 = 56.7\%$

RF VALUE

A spot moves 3.2 cm while the solvent front moves 8.0 cm. R_f?

$\frac{3.2}{8.0} = 0.40$ (no unit)

CHOOSE THE METHOD

Separate: sugar and common salt (crude); a mixture of chloroform and aniline; camphor from sand; acetone and methanol.

crystallisation from a solvent; simple distillation (large b.p. gap); sublimation; fractional distillation

5 Last-minute checklist

BEFORE YOU ANSWER

Which property differs: volatility (distillation), solubility (crystallisation, extraction), adsorption (chromatography), ability to sublime? In a percentage problem: which precipitate, which molar mass?

- Sublimation (camphor, naphthalene), crystallisation, simple, fractional, reduced-pressure (glycerol) and steam distillation (aniline, *o*-nitrophenol); chromatography: adsorption (column, TLC) or partition (paper); $R_f = a/b < 1$.
- Lassaigne: Prussian blue (N), black PbS or violet nitroprusside (S), blood red (N + S), AgCl white, AgBr pale yellow, AgI yellow (halogens, after HNO_3), yellow phosphomolybdate (P).
- $\%C = \frac{12}{44}\frac{m_{CO_2}}{m}100$; $\%H = \frac{2}{18}\frac{m_{H_2O}}{m}100$; Dumas $\%N = \frac{28V_0}{22400m}100$; Kjeldahl $\%N = \frac{1.4NV}{m}$ (not for nitro, azo, ring N); Carius: AgX (143.5, 188, 235), $BaSO_4$ (233), $Mg_2P_2O_7$ (222).
- Empirical formula from % by moles; $M = 2\times$ vapour density; oxygen by difference.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**