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Pharmaceutical Inorganic and Analytical Chemistry

BP106T — B.Pharm Semester I

Rapid Revision Notes

One-night-pass companion: every topic, only the core

As per PCI B.Pharm (NEP 2020) syllabus

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Unit I — Pharmaceutical Analysis, Errors and Impurities

What pharmaceutical analysis is

- Pharmaceutical analysis answers two questions about a drug sample: what is in it (qualitative) and how much is there (quantitative) — identity, purity, strength.
- Every IP monograph's "Assay" section is built on these techniques.

Techniques of analysis

- Titrimetry (volumetric analysis) — measuring the volume of a standard solution needed to react completely with the sample. Fast, cheap, still the workhorse of IP assays.
- Gravimetry — converting the analyte into a pure, weighable precipitate. Slow but very accurate; used as a reference method.
- Instrumental methods — UV-Visible and IR spectroscopy, HPLC, gas chromatography, atomic absorption spectroscopy, and electroanalytical methods like pH-metry and potentiometry. You meet these properly in later semesters; here, just know what each one measures.

Methods of expressing strength of solutions

One-mark questions come straight from these definitions — learn every one.

Term	Definition
Molarity (M)	Moles of solute per litre of solution
Normality (N)	Gram-equivalents per litre; $N = M \times \text{n-factor (valency)}$
Molality (m)	Moles of solute per kg of solvent (temperature-independent)
% w/v, % v/v, % w/w	g per 100 mL; mL per 100 mL; g per 100 g
ppm	mg of solute per litre (very dilute solutions, e.g. impurities)
Ratio strength	1:1000 means 1 g in 1000 mL
Milliequivalents (mEq)	For electrolytes: $\text{mEq} = (\text{mg} \times \text{valency}) / \text{atomic weight}$

Primary and secondary standards

	Primary standard	Secondary standard
Definition	Weighed directly to prepare a standard solution	Strength found by standardisation against a primary standard
Properties	High purity, stable, non-hygroscopic, high equivalent weight	May be unstable, hygroscopic, or reactive
Examples	Anhydrous sodium carbonate, potassium hydrogen phthalate (KHP), oxalic acid, zinc oxide	NaOH, HCl, KMnO ₄ , sodium thiosulphate, AgNO ₃ , EDTA, perchloric acid

Remember: NaOH can never be a primary standard — it is hygroscopic and absorbs CO₂ from air, so a weighed mass is never pure NaOH.

Errors in analysis

- Sources: instrumental (uncalibrated burette, faulty balance), personal/operative (wrong endpoint judgement, parallax), method (incomplete reaction, co-precipitation). Spilling a sample is a mistake, not an "error" — it invalidates the analysis.
- Determinate (systematic) errors — reproducible, same direction every time; can be found and corrected. Constant and proportional subtypes.
- Indeterminate (random) errors — small, unpredictable fluctuations; reduced by replicates, never fully removed.
- Absolute error = measured value – true value. Relative error = (absolute error / true value) × 100.
- Minimising errors: calibrate instruments, run blank determinations, analyse replicates and take the mean, use control samples, weigh larger quantities to shrink relative error.

Accuracy, precision and significant figures

- Accuracy = closeness to the true value. Precision = reproducibility among repeats.
- Target analogy: a tight cluster off-centre is precise but not accurate; scattered shots around the bullseye average out to accurate but not precise. A good analysis needs both.

Remember: You can be precise without being accurate (reproducible wrong answers, e.g. an uncalibrated burette) — that is why calibration matters.

- Significant figures: report only the digits you can reasonably read. Zeros between non-zero digits are significant; trailing zeros after a decimal point are significant. In

multiplication/division the answer carries the fewest significant figures of the inputs; in addition/subtraction it follows decimal places.

Impurities in pharmaceuticals

- Definition: any unwanted foreign matter in a drug substance or formulation.
- Types: organic (starting materials, by-products, degradation products), inorganic (heavy metals like lead and arsenic, residual catalysts, reagents), residual solvents.
- Why regulators care: impurities can be toxic, reduce efficacy, or destabilise the product — so the IP prescribes a limit test for specific impurities in each monograph.
- Sources: raw materials → reagents and solvents → manufacturing process and equipment (metal leaching) → containers and closures (glass alkali leaching) → storage conditions (moisture, light, temperature) → decomposition of the drug itself.

Limit tests — learn as reagent → observation → standard

A limit test is a pass/fail comparison: the effect (opalescence, turbidity, colour) produced by the sample must be less than that from a standard solution, under identical conditions.

Impurity	Reagent	Observation
Chloride	Dilute nitric acid + silver nitrate	White opalescence of AgCl
Sulphate	Dilute hydrochloric acid + barium chloride	White turbidity of BaSO ₄
Iron	Citric acid + thioglycollic acid, made alkaline with ammonia	Purple colour of ferrous thioglycollate
Arsenic (Gutzeit test)	Zinc + HCl in a Gutzeit generator bottle → arsine gas stains mercuric chloride paper	Yellow-brown stain
Lead	Dithizone in chloroform at controlled pH	Violet-red lead dithizonate in the chloroform layer
Heavy metals	H ₂ S (or thioacetamide)	Brown-black precipitate of metallic sulphides

Mnemonic: match the metal to its reagent — AgNO₃ for Chloride, BaCl₂ for Sulphate. For iron, remember purple; for arsenic, the Gutzeit bottle makes gas (arsine).

- Why nitric acid in the chloride test? It keeps the medium acidic so silver carbonate or silver phosphate don't precipitate and confuse the result.
- Why citric acid in the iron test? It prevents iron from precipitating when ammonia is added.

- Gutzeit details examiners ask for: nascent hydrogen reduces arsenic to arsine (AsH_3); a lead acetate cotton plug traps H_2S that would give a false stain. Reaction: $\text{As}_2\text{O}_3 + 6\text{Zn} + 12\text{HCl} \rightarrow 2\text{AsH}_3 \uparrow + 6\text{ZnCl}_2 + 3\text{H}_2\text{O}$.

Remember: A limit test is semi-quantitative (is the impurity below the limit?) — an assay is quantitative (how much drug is present?). Limit tests control impurities; assays confirm strength.

Modified limit tests for chloride and sulphate

- The normal test fails when the substance itself interferes — e.g. a strongly coloured substance (like potassium permanganate) hides the opalescence, or the substance reacts with silver nitrate/barium chloride.
- The IP monograph then prescribes a modified procedure (decolourisation, filtration, or pH adjustment first). The exact pre-treatment differs per monograph — the exam point is why the modification is needed, not one fixed recipe.

Very short questions (2 marks)

- 1 Define molarity and normality, and give the relation between them.
- 2 Why cannot sodium hydroxide be used as a primary standard?
- 3 Name the gas evolved in the Gutzeit test and the colour of the stain it produces.
- 4 Why is dilute nitric acid added in the limit test for chloride?
- 5 Distinguish between accuracy and precision in one line each.

Short questions (5 marks)

- 1 Classify errors in analysis and describe the methods of minimizing errors.
- 2 Compare primary and secondary standards with two examples each.
- 3 Give the sources of impurities in pharmaceuticals and the regulatory importance of controlling them.

Long questions (10 marks)

- 1 Describe the principle and procedure of the limit tests for chloride, sulphate and iron, with the chemical reactions involved.
- 2 Explain the Gutzeit test for arsenic in detail — apparatus, reactions, and the role of lead acetate cotton.

How to approach these answers

- Very-short Q1: give both definitions plus the formula $N = M \times n\text{-factor}$; nothing more.
- Short Q1: open with the two error types, then list the five minimising methods as numbered points, close with one line on why blanks matter.

- Long Q1: structure — intro (principle of limit tests), main body under 3 subheads (one per test: reagent, observation, reaction), conclusion comparing with an assay.

Unit II — Acid-Base Chemistry, Buffers and Electrolytes

Acids and bases — the three definitions

Examiners ask these as a set; learn all three.

- Arrhenius: acid gives H^+ in water, base gives OH^- in water. Simple, but limited to aqueous solutions.
 - Bronsted-Lowry: acid is a proton donor, base is a proton acceptor. Gives conjugate acid-base pairs ($\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$).
 - Lewis: acid accepts an electron pair, base donates one. The broadest definition.
-

pH scale and its significance

- $\text{pH} = -\log_{10}[\text{H}^+]$. At 25 °C, 7 is neutral; below 7 acidic, above 7 alkaline. Each pH unit is a tenfold change in $[\text{H}^+]$.
 - Why pH matters in pharmacy: drug solubility, stability (many drugs hydrolyse at extreme pH), absorption (weak acids absorb better from the acidic stomach), and preservative efficacy all depend on pH.
-

Buffers

- Buffer: a solution that resists pH change when small amounts of acid or alkali are added.
- Acidic buffers: weak acid + its salt (acetic acid / sodium acetate). Basic buffers: weak base + its salt (ammonia / ammonium chloride). Pharmacy examples: citrate and phosphate buffers in injections and eye drops.
- Buffer equation (Henderson-Hasselbalch): $\text{pH} = \text{pK}_a + \log([\text{salt}] / [\text{acid}])$. For a basic buffer: $\text{pOH} = \text{pK}_b + \log([\text{salt}] / [\text{base}])$.
- Buffer capacity: moles of acid/base per litre needed to change pH by one unit. Maximum at $\text{pH} = \text{pK}_a$ (when $[\text{salt}] = [\text{acid}]$) and rises with total buffer concentration.

Remember: The worked pattern examiners repeat — for 0.1 M acetic acid + 0.1 M sodium acetate (pK_a 4.76), $\text{pH} = 4.76 + \log(1) = 4.76$. Change the ratio and the log term shifts the pH. Practise two or three such sums before the exam.

Isotonicity

- Isotonic = same osmotic pressure as body fluids — equivalent to 0.9% w/v NaCl, freezing point $-0.52\text{ }^{\circ}\text{C}$. Hypertonic = more concentrated; hypotonic = less.
- IV fluids: a hypotonic injection makes water rush into red cells → haemolysis; a hypertonic one draws water out → crenation (shrinking). Large-volume parenterals must be isotonic.
- Ophthalmic solutions: a non-isotonic eye drop stings and irritates, causing tearing that washes the drug out. Isotonicity adjustment keeps the drop comfortable.
- Methods of adjusting isotonicity: freezing-point depression method, sodium chloride equivalent method, White-Vincent method, Sprowls method. The freezing-point method is asked most: calculate the freezing-point lowering of the drug solution, then add enough NaCl to bring the total depression to $0.52\text{ }^{\circ}\text{C}$.

Major extra- and intracellular electrolytes

- Extracellular: Na^+ , Cl^- , HCO_3^- . Intracellular: K^+ , Mg^{2+} , phosphate, protein.
- Functions of major physiological ions: maintaining fluid balance and osmotic pressure, acid-base balance, nerve impulse transmission, and muscle contraction (Ca^{2+} in excitation-contraction coupling; Na^+/K^+ in the membrane potential).

Electrolytes used in replacement therapy

- Sodium chloride* — 0.9% w/v "normal saline" for fluid and electrolyte replacement; also the reference for isotonicity and a primary standard in argentometric titrations.
- Potassium chloride — treats hypokalaemia (e.g. after diuretic therapy or vomiting). Given diluted, never as a rapid IV bolus — concentrated KCl can cause cardiac arrest.
- Calcium chloride — hypocalcaemia, and in cardiac resuscitation; supplies Ca^{2+} rapidly.
- Oral Rehydration Salt (ORS) — for dehydration in diarrhoea. WHO reduced-osmolarity formula per litre of water: sodium chloride 2.6 g, potassium chloride 1.5 g, anhydrous glucose 13.5 g, trisodium citrate dihydrate 2.9 g (245 mOsm/L). Glucose is essential — sodium is absorbed with glucose by sodium-glucose co-transport in the gut, which is why sugar + salt works better than salt alone.

Physiological acid-base balance

- Blood pH is held at 7.35–7.45 by the bicarbonate buffer system ($\text{H}_2\text{CO}_3/\text{HCO}_3^-$), plus phosphate and protein buffers. Lungs (CO_2 removal) and kidneys (H^+ excretion, HCO_3^- reabsorption) are the long-term regulators.
- Acidosis = pH below 7.35; alkalosis = above 7.45.

Mnemonic: for ORS, remember 2.6 – 1.5 – 13.5 – 2.9 (salt, KCl, glucose, citrate) — and always write the glucose co-transport point; that is the mark-fetching line.

Very short questions (2 marks)

- 1 State the Henderson-Hasselbalch equation.
- 2 What is buffer capacity, and when is it maximum?
- 3 Why must large-volume IV fluids be isotonic? Name the two cell injuries involved.
- 4 List the major extracellular and intracellular ions.
- 5 Give the composition of WHO reduced-osmolality ORS per litre of water.

Short questions (5 marks)

- 1 Define acids and bases according to Arrhenius, Bronsted-Lowry and Lewis.
- 2 Explain isotonicity and its application in IV fluids and ophthalmic solutions.
- 3 Write a note on the physiological acid-base balance of blood.

Long questions (10 marks)

- 1 Define a buffer. Derive the Henderson-Hasselbalch equation and explain buffer capacity with the significance of $\text{pH} = \text{pK}_a$.
- 2 Describe the electrolytes used in replacement therapy — sodium chloride*, potassium chloride, calcium chloride and ORS — with their functions and the role of glucose in ORS.

How to approach these answers

- Very-short Q1: just the equation with each term defined; no derivation.
- Short Q2: open with the definition of isotonic (0.9% NaCl), then 4–5 points on IV fluids and eye drops, close with one line on adjustment methods.
- Long Q2: structure — intro (why electrolytes are replaced), main body under 3 subheads (the three salts + ORS with composition table), conclusion tying to fluid therapy.

Unit III — Titrimetric Analysis

This is the largest unit (14 hours) and the most scoring one — almost every technique here doubles as a BP111P practical. Learn each titration as: principle → titrant → indicator → endpoint → example assay.

FIVE TITRATION FAMILIES AT A GLANCE (BP106T Unit III-IV)

ACID-BASE	Titrant: standard HCl / NaOH Indicator: methyl orange, phenolphthalein <i>Endpoint: colour change at equivalence pH</i>
NON-AQUEOUS	Titrant: perchloric acid (acidimetry) / sodium methoxide (alkalimetry) Indicator: crystal violet / thymol blue <i>Endpoint: violet to green (acidimetry)</i>
PRECIPITATION	Titrant: standard AgNO ₃ Indicator: K ₂ CrO ₄ (Mohr) / ferric alum (Volhard) / fluorescein (Fajans) <i>Endpoint: red Ag₂CrO₄ / red Fe-SCN complex / adsorbed colour</i>
COMPLEXOMETRIC	Titrant: disodium EDTA (1:1 metal complexes) Indicator: Eriochrome Black T (pH 10) <i>Endpoint: wine red to blue</i>
REDOX	Titrant: KMnO ₄ / Ce(IV) / I ₂ / Na ₂ S ₂ O ₃ / KIO ₃ Indicator: self (KMnO ₄) / starch (iodine) / ferroin <i>Endpoint: colour appears / disappears</i>

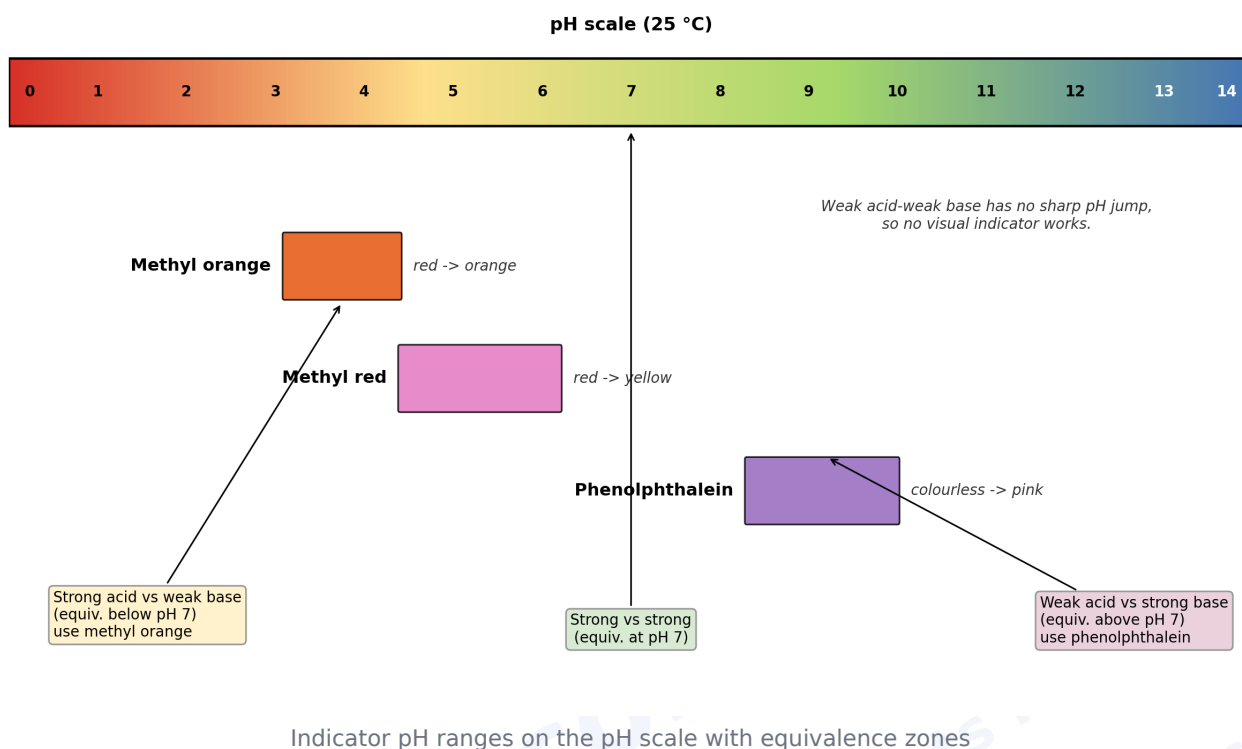
Five titration families compared: titrant, indicator and endpoint

Acid-base titrations: indicator theories

- Ostwald's (ionisation) theory: the indicator is a weak acid or base whose ionised and unionised forms have different colours; colour change follows the shift in ionisation with pH.
- Quinonoid theory: the indicator exists in two tautomeric forms — benzenoid and quinonoid — with different colours; pH shifts the equilibrium between them. Phenolphthalein (colourless benzenoid in acid, pink quinonoid in alkali) is the classic example.

Classification of acid-base titrations

- 1 Strong acid vs strong base (HCl vs NaOH) — sharp pH jump; methyl orange or phenolphthalein both work.
- 2 Strong acid vs weak base (HCl vs NH₄OH) — equivalence below pH 7; methyl orange or methyl red.
- 3 Weak acid vs strong base (CH₃COOH vs NaOH) — equivalence above pH 7; phenolphthalein.
- 4 Weak acid vs weak base — no sharp pH jump at equivalence, so no direct visual titration is possible.



Preparation and standardisation of titrants

- Hydrochloric acid: standardised against weighed anhydrous sodium carbonate (primary standard) with methyl orange. $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$.
- Sodium hydroxide: standardised against potassium hydrogen phthalate (KHP) with phenolphthalein. Prepare with carbon-dioxide-free water and protect from air — NaOH absorbs CO_2 to form carbonate, which causes titration errors.

Neutralisation (titration) curves

- Plot pH against volume of titrant; the steep vertical portion marks the equivalence point.
- An indicator is suitable only if its colour-change range falls on that steep part — which is exactly why indicator choice depends on the titration type above.

Assay of ammonium hydroxide

- Ammonia solution is assayed by titration with standard acid using methyl red indicator.
- Because ammonia is volatile, the assay is done quickly in a cooled, stoppered flask — a detail examiners like.

Non-aqueous titrations

- Why non-aqueous? Water has a levelling effect — it is too good a proton donor/acceptor, so very weak acids and bases (many drugs) give no sharp endpoint in water. A non-aqueous solvent sharpens the endpoint.
- Types of solvents: aprotic — inert, neither donate nor accept protons (benzene, chloroform, toluene); protophilic — basic, accept protons; enhance acidity of dissolved acids (dimethylformamide, pyridine, liquid ammonia); protogenic — acidic, donate protons; enhance basicity of dissolved bases (glacial acetic acid — the most used solvent); amphiprotic — can both donate and accept (glacial acetic acid, alcohols).
- Acidimetry (titration of bases): titrant is perchloric acid in glacial acetic acid, standardised against KHP; indicator crystal violet (violet → green endpoint). Used for weakly basic drugs.
- Alkalimetry (titration of acids): titrant is sodium or lithium methoxide in methanol-benzene, standardised against benzoic acid; indicator thymol blue. Used for weakly acidic drugs.
- Estimation of sodium benzoate — the classic example: dissolve in glacial acetic acid, titrate with perchloric acid (crystal violet). Sodium benzoate is too weak a base to titrate in water, which is precisely why the non-aqueous route is needed.

◆ **Mnemonic: solvent types — "A Proti Prefers Amphi"**

Aprotic, Protophilic, Protonic, Amphiprotic.

Precipitation titrations and gravimetry

- Gravimetric analysis — principle: the analyte is converted into a pure compound of known composition, precipitated, filtered, washed, dried/ignited and weighed.
- Steps: precipitation (with digestion to grow filterable crystals) → filtration → washing → drying or ignition to constant weight → weighing and calculation via the gravimetric factor.
- A good gravimetric precipitate must be highly insoluble, pure, easily filterable, and of definite composition after ignition.
- Estimation of barium sulphate by gravimetry: Ba^{2+} precipitated with dilute sulphuric acid as BaSO_4 , digested, filtered through ashless paper, ignited and weighed as BaSO_4 . Digestion grows larger crystals that filter easily and adsorb fewer impurities.
- Precipitation (argentometric) titrations — titrant is standard silver nitrate. Learn the four methods as a comparison:

Method	Approach	Indicator	Endpoint	Key condition
Mohr's	Direct titration of Cl^-/Br^-	Potassium chromate	Red silver chromate (Ag_2CrO_4) after all AgCl has precipitated	Neutral pH — in acid the chromate dissolves, in alkali AgOH precipitates

Method	Approach	Indicator	Endpoint	Key condition
Volhard's	Back titration: excess AgNO_3 added, remainder titrated with thiocyanate	Ferric alum	Red $\text{Fe}(\text{SCN})^{2+}$ complex	Acidic medium (nitric acid)
Modified Volhard's	For chloride specifically	Same as Volhard's	Same	AgCl is filtered off before back-titration — AgCl reacts with thiocyanate and spoils the endpoint
Fajans	Direct titration	Adsorption indicator (fluorescein, eosin)	Indicator adsorbs on the precipitate surface with a colour change	Dextrin may be added to keep the precipitate colloidal

Remember: Mohr's reactions — $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow$ (white); at the endpoint $2\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4 \downarrow$ (red). Volhard's — $\text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN} \downarrow$; endpoint $\text{Fe}^{3+} + \text{SCN}^- \rightarrow [\text{Fe}(\text{SCN})]^{2+}$ (red).

Complexometric titrations

- Types (classification): direct titration (metal ion titrated directly, e.g. MgSO_4), back titration (excess EDTA added, remainder back-titrated), displacement/substitution titration, and indirect (alkalimetric) titration.
- EDTA (used as disodium EDTA) forms stable 1:1 complexes with metal ions regardless of valency — the basis of complexometry.
- Metal ion indicators (e.g. Eriochrome Black T, murexide): form a coloured complex with the metal (EBT: wine red). At the endpoint EDTA strips the metal from the indicator — EBT changes wine red $\rightarrow$ blue.
- Masking and demasking: masking agents (cyanide for heavy metals, fluoride for aluminium, triethanolamine for iron) tie up interfering ions so they don't consume EDTA; demasking releases a specific ion later for titration.
- Preparation and standardisation of EDTA: standardised against a primary standard such as zinc oxide or calcium carbonate (dissolved in acid, buffered to pH 10, EBT indicator).
- Estimation of magnesium sulphate: direct titration with EDTA at pH 10 (ammonia buffer), EBT indicator, wine red $\rightarrow$ blue endpoint.
- Estimation of calcium gluconate*: same principle — Ca^{2+} titrated with EDTA (murexide indicator is typical for calcium).

Remember: Complexometry runs at pH 10 (ammonia buffer) and EBT goes wine red to blue. If an exam question mentions "masking", quote cyanide or fluoride with the ion it masks.

Very short questions (2 marks)

- 1 State Ostwald's theory of acid-base indicators.
- 2 Why can a weak acid vs weak base titration not be done visually?
- 3 Name the titrant and indicator used in the acidimetric non-aqueous titration.
- 4 What is the endpoint colour change with Eriochrome Black T, and at what pH?
- 5 Why is AgCl filtered off in the modified Volhard's method?

Short questions (5 marks)

- 1 Compare Mohr's, Volhard's and Fajans methods of precipitation titration.
- 2 Explain masking and demasking in complexometry with one example each.
- 3 Describe the preparation and standardisation of hydrochloric acid and sodium hydroxide.

Long questions (10 marks)

- 1 Explain the classification of acid-base titrations with indicator choice for each type, supported by the theory of neutralisation curves.
- 2 Discuss non-aqueous titrations: types of solvents, acidimetric and alkalimetric titrations with titrant preparation, and the estimation of sodium benzoate.

How to approach these answers

- Very-short Q3: name perchloric acid in glacial acetic acid + crystal violet; add the violet-to-green endpoint for the extra mark.
- Short Q1: open with the principle of argentometry, then the comparison table (approach, indicator, endpoint, condition), close with one line on when each is preferred.
- Long Q2: structure — intro (levelling effect of water), main body under 3 subheads (solvents, acidimetry/alkalimetry, sodium benzoate estimation), conclusion on why the method matters for drugs.

Unit IV — Redox Titrations, Gastrointestinal Agents and Radiopharmaceuticals

Redox titrations — concepts

- Oxidation is loss of electrons, reduction is gain — they always occur together. The oxidising agent gets reduced; the reducing agent gets oxidised.

- Redox titrations need a visible endpoint: some titrants are self-indicators (KMnO_4), others need an external/specific indicator (starch for iodine, ferroin or diphenylamine for cerimetry).

◆ **Mnemonic: the five types — "Please Come In In Kerala"**

Permanganometry, Cerimetry, Iodimetry, Iodometry, (potassium) Iodate.

- Permanganometry:** titrant KMnO_4 , a self-indicator (purple colour persists at the endpoint). Done in acidic medium with sulphuric acid — never HCl, which gets oxidised to chlorine and gives a falsely high result. Key half-reaction: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$. Standardised against oxalic acid or sodium oxalate (heated to $\sim 70^\circ\text{C}$). Used to estimate Fe^{2+} , hydrogen peroxide, oxalates.
- Cerimetry:** titrant ceric sulphate, $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ — a single-electron change, so calculations are simple and the solution is very stable. Indicator ferroin or diphenylamine. Used for Fe^{2+} where permanganate's side reactions are a problem.
- Iodimetry vs iodometry** — the pair examiners love to confuse:

	Iodimetry	Iodometry
Type	Direct titration with standard iodine	Indirect — analyte liberates I_2 from KI first
Analyte is a...	Reducing agent (e.g. arsenious oxide, sodium thiosulphate)	Oxidising agent (e.g. copper sulphate, KMnO_4)
Titrated with	Standard iodine directly	Liberated iodine titrated with standard sodium thiosulphate

- Key reaction: $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$. Starch is added near the endpoint (deep blue starch-iodine complex disappears) — adding it early traps iodine and blurs the endpoint.
- Titration with potassium iodate: KIO_3 is a stable, primary-standard-grade oxidant (Andrews titration — iodine monochloride endpoint in strong HCl), used where iodine titrations are unsuitable.

Gastrointestinal agents

Acidifiers

Given when stomach acid is deficient (achlorhydria).

- Dilute hydrochloric acid — supplements gastric HCl to aid digestion.
- Sodium acid phosphate — also used as a urinary acidifier.

Antacids

Bases that neutralise excess gastric acid in hyperacidity.

- Ideal properties: rapid onset and reasonably sustained action; should not cause systemic alkalosis; should not be constipating or laxative on its own; palatable; cheap.
- Why antacids are combined: aluminium salts constipate while magnesium salts are laxative — combining them (e.g. aluminium hydroxide + magnesium hydroxide/trisilicate) balances the bowel effect and broadens the action. This "why combine" point is a favourite short question.
- Sodium bicarbonate* — systemic antacid, very rapid, but releases CO₂ (belching, flatulence) and absorbed sodium can cause systemic alkalosis — caution in hypertension and cardiac patients.
- Aluminium hydroxide gel* — non-systemic, slow-acting, constipating; also adsorbs phosphate (used in chronic kidney disease to control phosphate).

Agents that promote bowel movement

- Magnesium hydroxide (milk of magnesia) — osmotic laxative that also acts as an antacid.
- Sodium orthophosphate — saline purgative; draws water into the bowel osmotically.
- Sodium potassium tartrate (Rochelle salt) — saline purgative.
- Magnesium trisilicate — antacid with adsorbent action; also mildly laxative, which is why it pairs well with aluminium hydroxide.

Antimicrobials (inorganic)

- Mechanism: inorganic antimicrobials act by oxidation, protein precipitation, or halogenation — a broader, less selective attack than organic antibiotics, which is why most are for external/antiseptic use.
- Potassium permanganate — strong oxidising agent; gargle/mouthwash and wound wash in very dilute solution (around 1:10000). Stains skin brown.
- Boric acid — weak antiseptic; eye washes and dusting powders. Toxic if absorbed in large amounts, especially in infants.
- Hydrogen peroxide* — 3% solution releases nascent oxygen with effervescence ($2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$), which mechanically cleans wounds. Decomposes on storage — kept in light-resistant, cool containers.
- Chlorinated lime* (bleaching powder) — releases chlorine on exposure to air/moisture; disinfectant for water and surfaces.
- Iodine and its preparations — tincture of iodine, povidone-iodine (less staining, sustained release), Lugol's solution. Broad-spectrum antiseptic; the brown colour itself shows where it has been applied.

Radiopharmaceuticals

- Basics of radioactivity: unstable nuclei decay by emitting alpha, beta or gamma radiation. Half-life ($t_{1/2}$) — time for half the atoms to decay — decides whether an isotope suits diagnosis (short $t_{1/2}$, hours) or therapy. Activity is measured in becquerel (Bq) and curie (Ci).

Radioisotope	Half-life	Use
Sodium iodide I-131	~8 days	Thyroid diagnosis and therapy (thyroid cancer, hyperthyroidism — thyroid selectively takes up iodine)
Technetium-99m	~6 hours	The workhorse of diagnostic imaging (bone, heart, kidney scans); from a molybdenum-99 generator; short $t_{1/2}$ keeps patient dose low
Cobalt-60	~5.27 years	External beam radiotherapy for cancer (gamma rays)
Phosphorus-32	~14.3 days	Therapy of polycythaemia vera and some bone conditions (beta emitter)

- Safe handling, storage and disposal: follow ALARA (As Low As Reasonably Achievable) — minimise time, maximise distance, use shielding (lead containers). Store in labelled, shielded areas; dispose through authorised radioactive-waste channels. In India this is regulated under AERB (Atomic Energy Regulatory Board) guidelines — the exam expects the safe-handling principles and regulatory adherence, not the full rulebook.

◆ **Mnemonic: the four isotopes — "I Treat Cancer Patients"**

I-131, Tc-99m, Co-60, P-32. Pair each with its half-life (8 d, 6 h, 5.27 y, 14.3 d).

Very short questions (2 marks)

- Why is sulphuric acid, and not hydrochloric acid, used in permanganometry?
- When is starch indicator added in an iodometric titration, and why?
- Give two ideal properties of an antacid.
- Name one therapeutic use each of I-131 and Tc-99m.
- What does ALARA stand for?

Short questions (5 marks)

- Distinguish between iodimetry and iodometry with one example each.
- Why are antacids combined instead of given singly? Illustrate with the aluminium-magnesium pair.
- Write short notes on: (a) hydrogen peroxide*, (b) chlorinated lime*.

Long questions (10 marks)

- 1 Describe the types of redox titrations — permanganometry, cerimetry, iodimetry, iodometry and titrations with potassium iodate — with titrant, indicator and endpoint for each.
- 2 Explain the basics of radioactivity and the applications of the radioisotopes of sodium iodide I-131, technetium-99m, cobalt-60 and phosphorus-32, including safe handling, storage and disposal.

How to approach these answers

- Very-short Q1: one line on HCl being oxidised to chlorine + one line on the consequence (extra KMnO_4 consumed, falsely high result).
- Short Q1: open with the one-line distinction (direct vs indirect), then the comparison table with examples, close with the starch point.
- Long Q2: structure — intro (radioactivity basics: radiation types, half-life), main body under 3 subheads (the four isotopes in a table; safe handling/storage/disposal; regulatory guidelines), conclusion on the diagnosis-vs-therapy logic.

Unit V — Miscellaneous Compounds

Short unit, but every compound here is a direct "write a short note" question. Learn each as: use → key property → one caution.

Expectorants

Expectorants increase bronchial secretion or make sputum less viscous so it can be coughed out.

- Potassium iodide — stimulates bronchial glands to increase respiratory tract fluid, thinning mucus. Also the classic reagent for liberating iodine in iodometry (Unit IV crossover — examiners like linking these).
- Ammonium chloride* — reflex expectorant (irritates gastric mucosa → vagal reflex → increased bronchial secretion). Also a systemic acidifier and diuretic. Large doses can cause systemic acidosis — the caution to quote.

Emetics

Emetics induce vomiting, used in certain poisonings to empty the stomach (before safer methods like gastric lavage took over).

- Copper sulphate* — prompt emetic; also an astringent and fungicide. Excess is toxic (copper poisoning), so the dose window matters.

- Sodium potassium tartrate (Rochelle salt) — listed here as an emetic; better known as a saline purgative (you also met it in Unit IV). Know both roles.

Haematinics

Haematinics supply iron for haemoglobin synthesis in iron-deficiency anaemia.

- Ferrous sulphate* — the standard oral iron salt. Ferrous (Fe^{2+}) iron is absorbed far better than ferric (Fe^{3+}) — iron is absorbed in the ferrous state in the duodenum, and ferric must first be reduced. Given with vitamin C to keep iron reduced and improve absorption. Common side effects: constipation and black stools — warn the patient so they don't panic.
- Ferrous gluconate — milder on the stomach than ferrous sulphate, often preferred when the sulphate causes gastric irritation; slightly lower elemental iron content.

Poison and antidote

- Poison: any substance that causes injury, illness or death on entering the body in relatively small amounts.
- Antidote: a substance that counteracts a poison. Classification: (1) physiological/pharmacological antidotes — oppose the poison's action on the body (e.g. physostigmine for atropine poisoning); (2) chemical antidotes — react with the poison to form a harmless compound (e.g. sodium thiosulphate for cyanide); (3) mechanical antidotes — prevent absorption (e.g. activated charcoal adsorbing the poison, demulcents coating the gut).
- Sodium thiosulphate — the syllabus antidote: used in cyanide poisoning (given with sodium nitrite — it converts cyanide to non-toxic thiocyanate, which is excreted) and to neutralise excess iodine/chlorine. Reaction to remember: it reduces iodine to iodide — the same chemistry as the iodometric titration endpoint ($\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$).

◆ Mnemonic: antidote classes — PCM

Physiological, Chemical, Mechanical. And remember that sodium thiosulphate does double duty: cyanide antidote in Unit V and the iodometry titrant in Unit IV.

Very short questions (2 marks)

- 1 How does ammonium chloride act as an expectorant?
- 2 Why are ferrous salts preferred over ferric salts as haematinics?
- 3 Classify antidotes with one example each.
- 4 Give the reaction by which sodium thiosulphate neutralises iodine.
- 5 Name the two roles of sodium potassium tartrate in this syllabus.

Short questions (5 marks)

- 1 Write short notes on: (a) ferrous sulphate*, (b) ferrous gluconate.
- 2 Explain the classification of antidotes with examples.
- 3 Describe the mechanism of action of sodium thiosulphate in cyanide poisoning.

Long questions (10 marks)

- 1 Define poison and antidote. Classify antidotes with examples and describe sodium thiosulphate as an antidote in detail.
- 2 Write detailed notes on the expectorants, emetics and haematinics of the syllabus, covering uses, key properties and cautions for each.

How to approach these answers

- Very-short Q2: one line on Fe^{2+} being the absorbed form in the duodenum + one line on ferric needing reduction first.
- Short Q2: open with the one-line definition of antidote, then the three classes as numbered points with one example each, close with one line on sodium thiosulphate as the chemical type.
- Long Q2: structure — intro (what each class does), main body under 3 subheads (expectorants, emetics, haematinics — one line of use, property and caution per compound), conclusion comparing the asterisked compounds.