

Unit 3 Chemistry - Gravimetric Analysis

Gravimetric analysis is a quantitative chemical analysis used to determine the unknown concentration of one reactant [the analyte] by measuring the mass of precipitate formed when an excess of a second reactant [the precipitant] is added to it.

For a successful gravimetric analysis ...

- the analyte must be in a solution when the precipitant is added
- an excess of precipitant must be added
- only the analyte ions in the sample should form a precipitate with the precipitant
- the precipitate must be very insoluble
- the chemical composition of the precipitate must be known
- the precipitate must be able to be collected, washed and dried

Glossary of Terms – Gravimetric Analysis

analyte	substance of unknown concentration that is being determined by the analysis
precipitant	reactant added to analyte solution resulting in the formation of an insoluble product in a precipitation reaction
precipitate	the insoluble product of a precipitation reaction
constant weight	when successive drying and weighing results in a mass that is within about 0.005 g of the previous mass
desiccator	container loaded with desiccant which keeps objects dry as they are cooling

A Typical Gravimetric Analysis

- an exact amount of sample is measured out [weighed or pipetted]
- if the sample is a solid, it is dispersed in distilled water to dissolve the analyte and if solid remains in this mixture, it must be filtered and washed ... the filtrate and washings, which contain the analyte, collected in a beaker for analysis
- an excess of precipitant solution is then added to the analyte solution
- to check for excess, the precipitate is allowed to settle and a drop of precipitant added to see if any extra precipitate forms
- the mixture is then filtered through a dry, weighed filter crucible under vacuum
- the glassware and precipitate are washed in small portions of distilled water
- the crucible and collected precipitate are dried in an oven at 102°C for several hours
- the dried crucible and precipitate are cooled in a desiccator
- the dried crucible and precipitate are weighed accurately
- the dried crucible and precipitate are returned to the oven for ½ hour, cooled in a desiccator and reweighed
- the heating, cooling and weighing is continued until a constant weight is obtained
- the mass of precipitate and stoichiometry are used to determine the concentration of the unknown analyte

Empirical Formula

- Chemical analysis enables us to determine the **empirical formula** of a compound.
- The empirical formula is the simplest whole-number ratio of atoms found in a pure compound ... eg. the empirical formula of propene [C₃H₆] is **CH₂**
- The empirical formula is established from the masses of elements found in the compound, which are usually determined experimentally.

Finding the Empirical Formula

Example: A factory produced waste gas, an oxide of sulfur, is isolated and analysed chemically. It is found to contain 50.1% sulfur.

What is the empirical formula of the compound?

50.1% S and [100 – 50.1 = 49.9% O]

S	:	O	
50.1	:	49.9	[mass ratio]
50.1/32.1	:	49.9/16.0	[mole ratio]
1.56	:	3.12	
1	:	2	[mole ratio in whole number terms]

Determining the Molecular Formula

Example: A 1.20 g mass of a hydrocarbon [containing C, H and O] is burned completely in air and yields 0.982 g of water and 1.22 L of CO₂ gas @ STP. In another analysis, an approximate molecular mass of 88 was found for the compound. What is the molecular formula of the compound?

mass of H₂O = 0.982 g ... mole H₂O = 0.982/18.0 = 0.054555..
mole of H = 2(0.054555..) = 0.10911..
mass of H = nM = 0.10911(1.01) ≈ 0.1102 g

mol CO₂ = V/22.4 = 1.22/22.4 = 0.05446..
mole of C = 0.05446..
mass of C = nM = 0.05446..(12.0) ≈ 0.6536 g

so, 1.20 g sample contains 0.110 g H, 0.654 g C and therefore ...
[1.20 – 0.110 – 0.654] ≈ 0.436 g of O

empirical formula ...	C	:	H	:	O	
	0.654		0.110		0.436	→ mass ratio
	0.654/12		0.110/1		0.436/16	
	0.0545	:	0.110	:	0.0273	→ mole ratio
	2	:	4	:	1	→ simplest mol ratio

empirical formula is C₂H₄O₁

empirical formula has a mass = 2(12) + 4(1) + 16 = 44 [half of 88]
the molecular formula is whole number multiple of empirical formula ...
molecular formula is C₄H₈O₂

Example of Gravimetric Analysis #1

The %Calcium in limestone

The amount of calcium in a limestone sample can be determined by gravimetric analysis. The limestone is reacted with dilute hydrochloric ...



The $\text{Ca}^{2+}_{(aq)}$ ions in solution are precipitated by the addition of ammonium oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4]$ precipitant ... $\text{Ca}^{2+}_{(aq)} + \text{C}_2\text{O}_4^{2-}_{(aq)} \rightarrow \text{CaC}_2\text{O}_{4(s)}$

The $\text{CaC}_2\text{O}_{4(s)}$ precipitate is then filtered off, washed, dried and weighed.

The Gravimetric analysis:

- a 2.00 g sample of limestone is weighed into a 250 ml beaker
- 20 ml of 1M hydrochloric acid is added to dissolve the limestone
- an excess of ammonium oxalate solution is added to the beaker ... excess is checked by allowing the $\text{CaC}_2\text{O}_{4(s)}$ precipitate to settle and adding a further drop of precipitant to see if new precipitate is formed
- the precipitate is filtered through a weighed filter crucible [22.225 g] and washed with small portions of distilled water
- the crucible and precipitate are dried in an oven at 102°C for 2 hours, cooled in a desiccator and weighed [24.658 g]
- the crucible is returned to the oven at 102°C for ½ hour, cooled in a desiccator and reweighed ... this step is repeated until constant weight is obtained ... [final constant mass = 24.655 g]

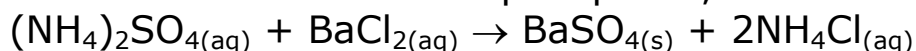
The Calculation:

- mass of $\text{CaC}_2\text{O}_{4(s)}$ precipitate = $24.655 - 22.225 = 2.430 \text{ g}$
- $M_r \text{ CaC}_2\text{O}_{4(s)} = 40.1 + 2(12.0) + 4(16.0) = 128.1$
- amt. of $\text{CaC}_2\text{O}_{4(s)}$ precipitate $n = m/M_r = 2.430/128.1 = 0.018969 \text{ mole}$
- amt. of Ca = 0.018969 mole [1 Ca atom in 1 $\text{CaC}_2\text{O}_{4(s)}$ formula]
- mass of Ca $m = nM_r = 0.018969(40.1) = 0.760677 \text{ g}$
- % Ca [w/w] = $[0.760677/2.00] \times 100 \approx 38.0\%$

Example of Gravimetric Analysis #2

The Sulfate Content [as $(\text{NH}_4)_2\text{SO}_4$] in Plant Food

The amount of sulfate, calculated as ammonium sulfate, in a plant food can be determined by gravimetric analysis. The plant food sample is dispersed in distilled water to dissolve the soluble sulfate compounds. The dispersed sample is then filtered and the insoluble residue washed with distilled water. The filtrate and washings, containing the dissolved sulfate ions, are reacted with an excess of precipitant, barium chloride solution ...



The $\text{BaSO}_{4(\text{s})}$ precipitate can be filtered off, washed, dried and weighed.

The Gravimetric analysis:

- 5.86 g sample of the plant food is dispersed in 100 ml of distilled water
- the dispersion is then filtered and the residue washed
- the filtrate and washings are collected in a 250 ml beaker
- an excess of barium chloride solution is added to the beaker
- the precipitate formed is allowed to settle and the supernatant liquid above the precipitate tested for completeness of precipitation
- the precipitate is collected on a weighed filter crucible [27.844 g] under vacuum and washed with several small portions of distilled water
- the crucible and precipitate are then repeatedly dried in an oven at 102°C , desiccator cooled and weighed to constant mass [28.350 g]

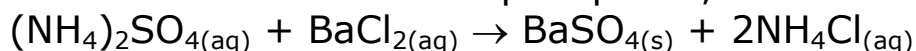
The Calculation:

- mass of $\text{BaSO}_{4(\text{s})}$ precipitate = $28.350 - 27.844 = 0.506 \text{ g}$
- $M_r \text{ BaSO}_{4(\text{s})} = 137.3 + 32.1 + 4(16.0) = 233.4$
 $M_r (\text{NH}_4)_2\text{SO}_4 = 2(14.0 + 4[1.01]) + 32.1 + 4(16.0) = 132.2$
- amt. of BaSO_4 $n = m/M_r = 0.506/233.4 = 0.0021679 \text{ mole}$
- amt. of $(\text{NH}_4)_2\text{SO}_4 = 0.0021679 \text{ mole}$ [equal moles of sulfate]
- mass of $(\text{NH}_4)_2\text{SO}_4$ $m = nM_r = 0.0021679(132.2) = 0.286596 \text{ g}$
- $\% (\text{NH}_4)_2\text{SO}_4 \text{ [w/w]} = [0.286596/5.86] \times 100 \approx 4.89\%$

Example of Gravimetric Analysis #2

The Sulfate Content [as $(\text{NH}_4)_2\text{SO}_4$] in Plant Food

The amount of sulfate, calculated as ammonium sulfate, in a plant food can be determined by gravimetric analysis. The plant food sample is dispersed in distilled water to dissolve the soluble sulfate compounds. The dispersed sample is then filtered and the insoluble residue washed with distilled water. The filtrate and washings, containing the dissolved sulfate ions, are reacted with an excess of precipitant, barium chloride solution ...



The $\text{BaSO}_{4(\text{s})}$ precipitate can be filtered off, washed, dried and weighed.

The Analysis:

In a particular analysis, 5.860 g sample of the plant food was dispersed in distilled water. Insoluble material in the plant food was then filtered off and washed. The filtrate and washings [containing dissolved sulfate] were collected in a beaker and an excess of barium chloride solution added. The precipitate was then collected in a weighed [27.844 g] filter crucible, washed and air dried to constant weight [28.350 g].

Questions:

1. Why was the dispersion of plant food in water, filtered before the precipitant was added?
2. What chemical is the precipitant in this gravimetric analysis?
3. What is the chemical formula of the precipitate formed?
4. What mass of precipitate was collected?
5. What amount of barium sulfate [in mole] was filtered off?
6. What amount [in mole] of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ must have been in the beaker before the precipitant was added?
7. What mass of $(\text{NH}_4)_2\text{SO}_4$ was in the 5.860 g of sample?
8. What is the %[w/w] $(\text{NH}_4)_2\text{SO}_4$ in the plant food?

