Gravimetric methods of analysis

Why learning gravimetry

Most accurate analytical method (theoretically)

Does not require complex equipment

Often used in analytical laboratories

Gravimetry

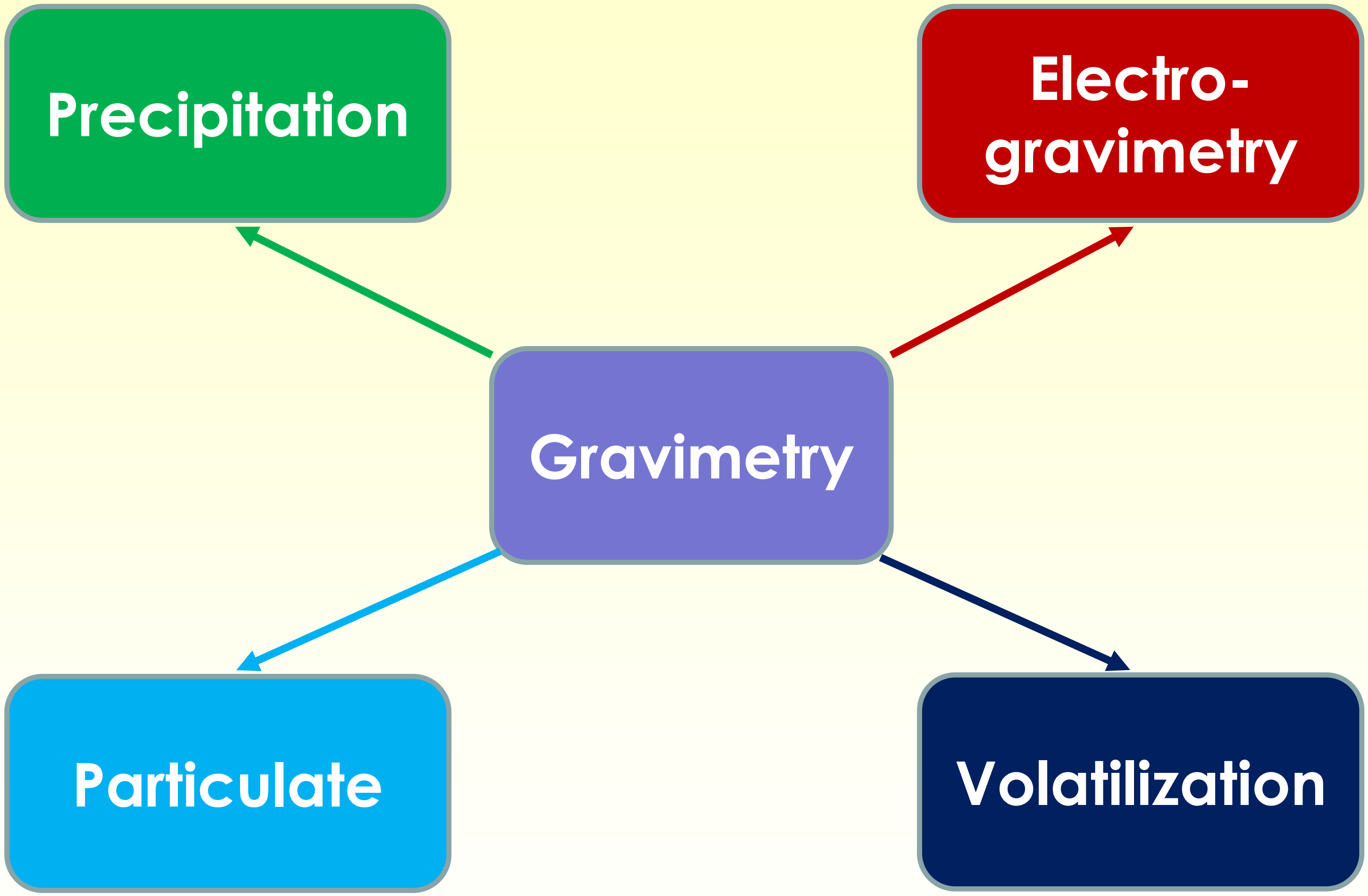
A method based on measurement of mass or change of mass

The oldest analytical technique

Very precise

Very reliable

Gravimetry


Precipitation
Electro-gravimetry
Gravimetry
Particulate
Volatilization

Precipitation gravimetry

Formed precipitate must have low solubility in water (high K_{sp}).
Question: what is K_{sp} and where can it be found?

Crystalline precipitates are preferred over **amorphous**

Reagent should be selective to analyte

Solubility product (K_{sp})

- multiplied concentrations of ions of poorly soluble electrolyte in it's saturated solution

Describes equilibrium between solution and precipitate:

$$A_nB_m \text{ (precipitate)} \leftrightarrow nA^+ + mB^-$$

$$K_{sp}\ (A_nB_m) = [A^+]^n \cdot [B^-]^m = \text{const}$$

Multiplied ion concentrations cannot be higher than K_{sp}.
A remaining part will be present as a precipitate.

A precipitate will not form if a product of ion concentrations will be lower than K_{sp}.

The law of mass action

Increase of concentrations of reagents results in the increase of a probability of their collision and interaction.

$$W = [A^{+}]^{n} \cdot [B^{-}]^{m}$$

Exercise

To 10 mL of solution containing chloride ions at C=0.0010 mol/L, 10 mL of $AgNO_3$ (C = 0.0020 mol/L) were added. Calculate concentration of chloride ions in the solution after formation of the precipitate (AgCl with a K_{sp} = 1.78E-10).

How many percents of chloride ions will remain in the solution?

Typical steps

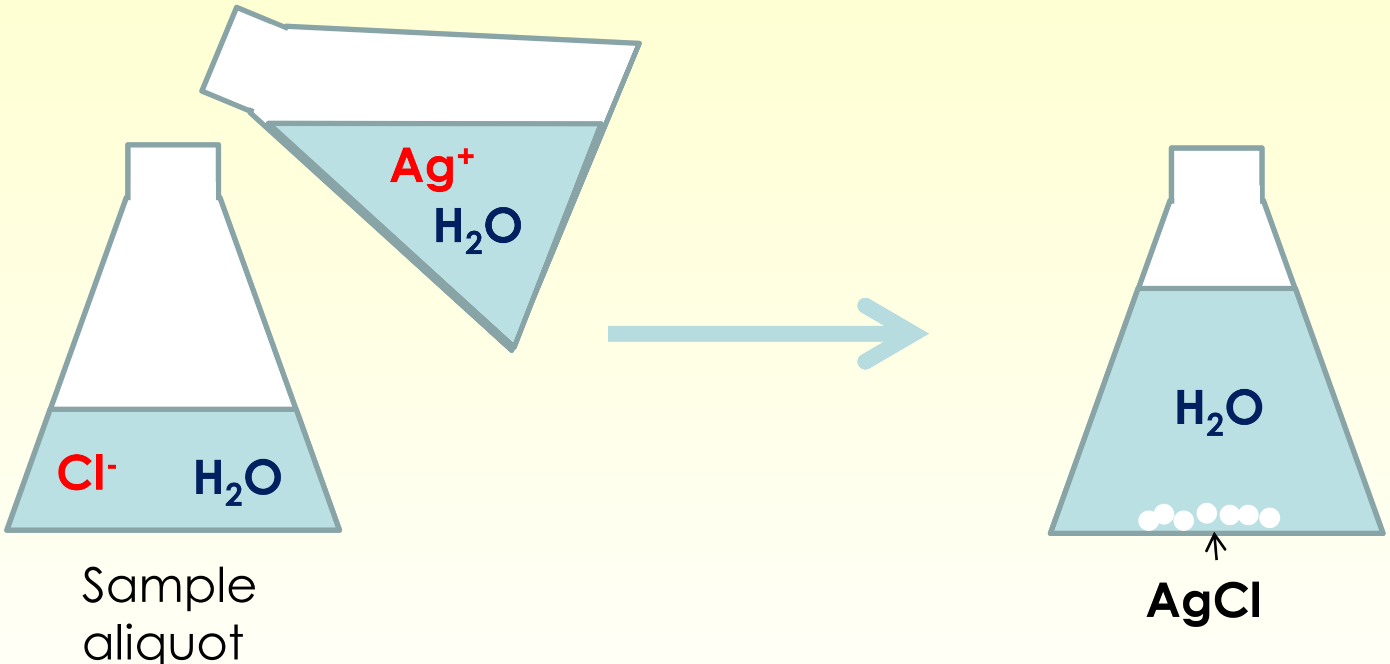
Take sample aliquot,
add reagent, wait for precipitate to be formed

Carefully filter

Put the filter with precipitate into the crucible;
dry it in desiccator, separate filter and precipitate or
burn filter in muffle furnace

Measure the weight of crucible with precipitate, wait until the mass becomes constant

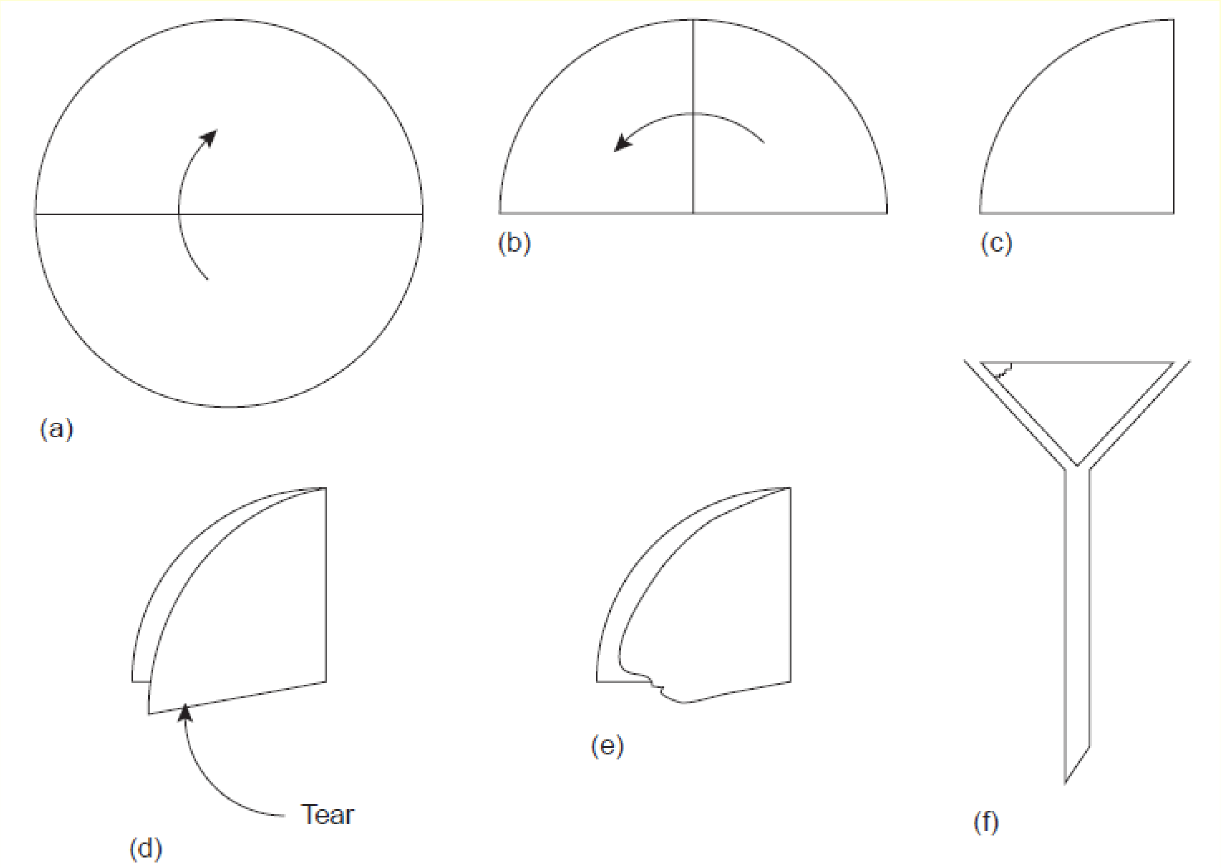
Precipitation gravimetry



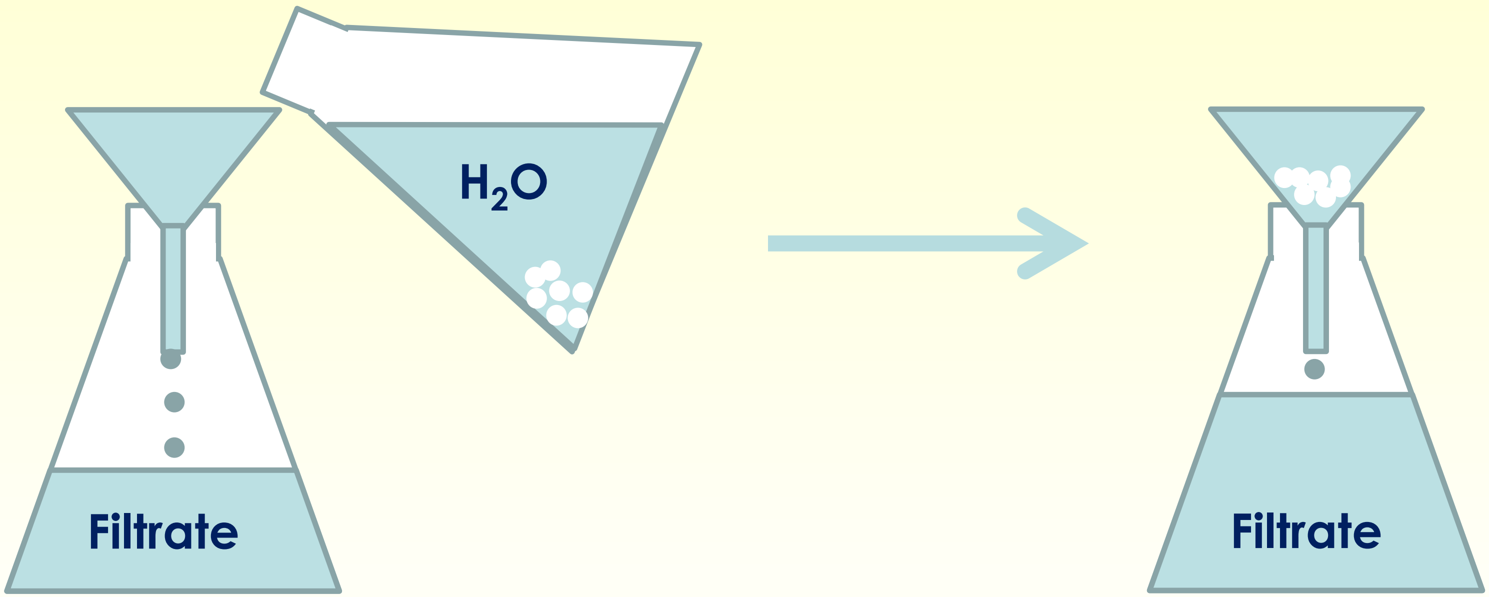
$$Cl^- + Ag^+ \rightarrow AgCl$$

If 0.125 Mole of AgCl was formed, how many moles of Cl^- were present in the sample?

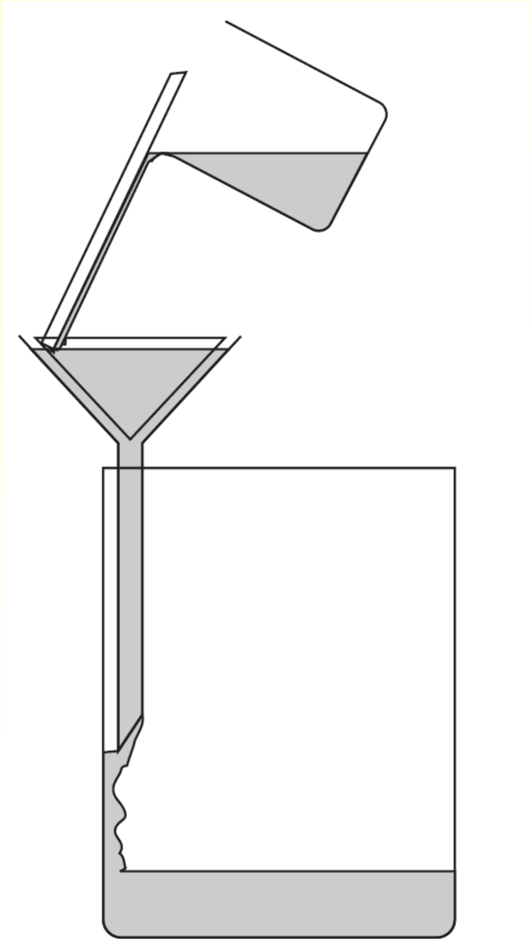
Preparing filter



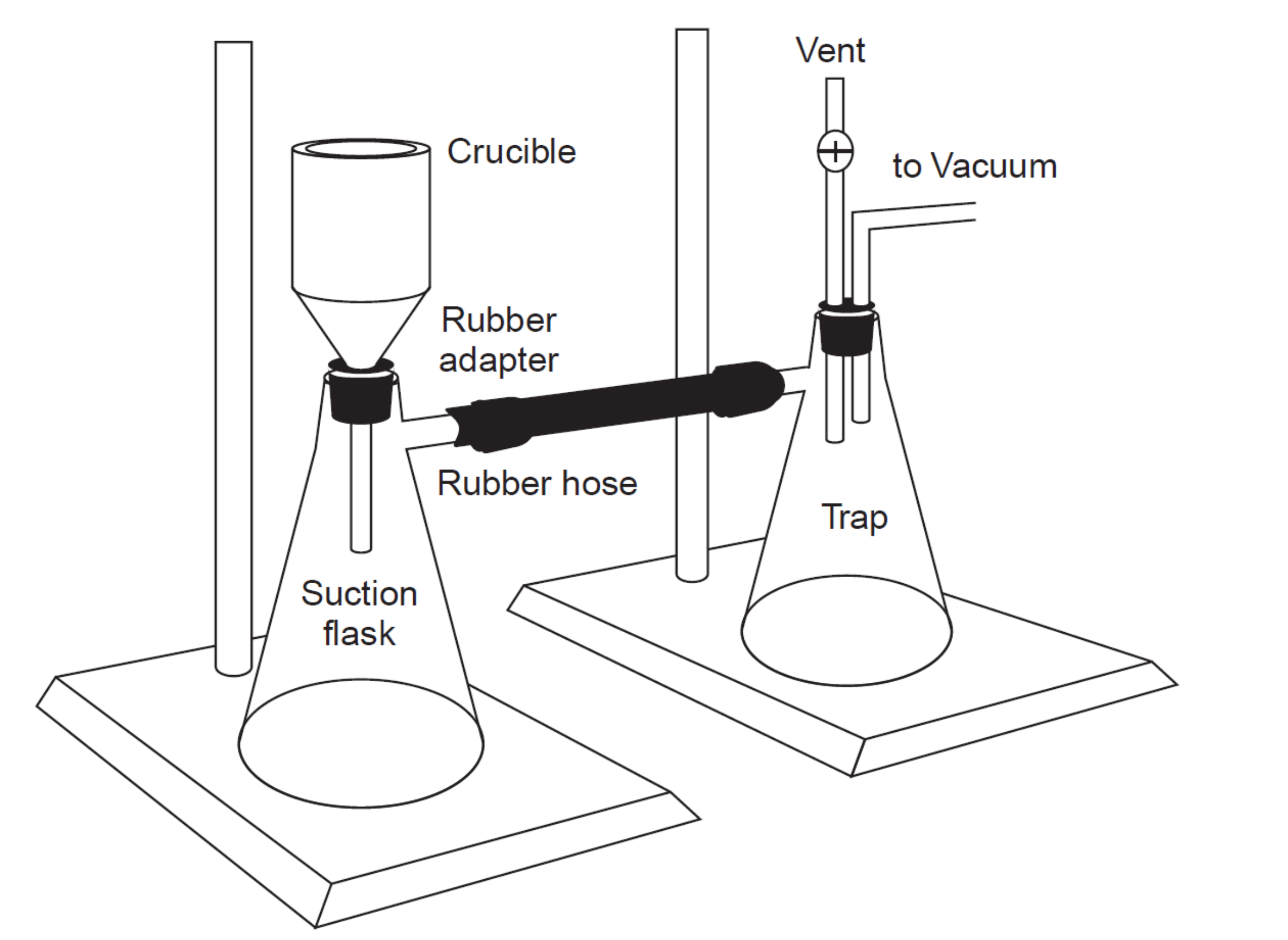
Filtration



Correct filtration



Vacuum filtration



Reaching constant mass: repeat until the mass does not change

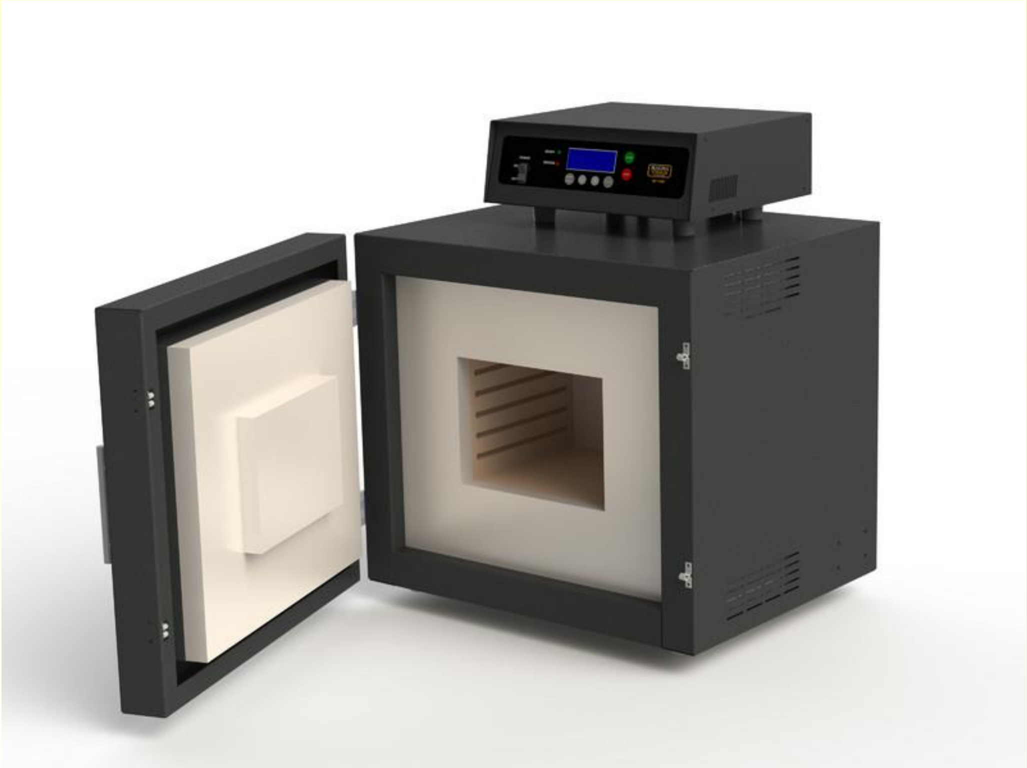
Crucible

Drying chamber

Desiccator

Muffle furnace

OR



Species analyzed	Precipitated form	Form weighed	Interfering species
K^+	$KB(C_6H_5)_4$	$KB(C_6H_5)_4$	NH_4^+, Ag^+, Hg^{2+}, Tl^+, Rb^+, Cs^+
Mg^{2+}	$Mg(NH_4)PO_4 \cdot 6H_2O$	$Mg_2P_2O_7$	Many metals except Na^+ and K^+
Ca^{2+}	$CaC_2O_4 \cdot H_2O$	$CaCO_3$ or CaO	Many metals except Mg^{2+}, Na^+, K^+
Ba^{2+}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-
Ti^{4+}	TiO (5,7-dibromo-8-hydroxyquinoline)$_2$	Same	Fe^{3+}, Zr^{4+}, Cu^{2+}, $C_2O_4^{2-}$, citrate, HF
VO_4^{3-}	Hg_3VO_4	V_2O_5	Cl^-, Br^-, I^-, SO_4^{2-}, CrO_4^{2-}, AsO_4^{3-}, PO_4^{3-}
Cr^{3+}	$PbCrO_4$	$PbCrO_4$	Ag^+, NH_4^+
Mn^{2+}	$Mn(NH_4)PO_4 \cdot H_2O$	$Mn_2P_2O_7$	Many metals
Fe^{3+}	$Fe(HCO_2)_3$	Fe_2O_3	Many metals
Co^{2+}	Co(1-nitroso-2-naphtholate)$_2$	$CoSO_4$ (by reaction with H_2SO_4)	Fe^{3+}, Pd^{2+}, Zr^{4+}
Ni^{2+}	Ni(dimethylglyoximate)$_2$	Same	Pd^{2+}, Pt^{2+}, Bi^{3+}, Au^{3+}
Cu^{2+}	CuSCN (after reduction of Cu^{2+} to Cu^+ with HSO_3^-)	CuSCN	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
Zn^{2+}	$Zn(NH_4)PO_4 \cdot H_2O$	$Zn_2P_2O_7$	Many metals
Ce^{4+}	$Ce(IO_3)_4$	CeO_2	Th^{4+}, Ti^{4+}, Zr^{4+}
Al^{3+}	Al(8-hydroxyquinolate)$_3$	Same	Many metals
Sn^{4+}	Sn(cupferron)$_4$	SnO_2	Cu^{2+}, Pb^{2+}, As(III)
Pb^{2+}	$PbSO_4$	$PbSO_4$	Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Ag^+, HCl, HNO_3
NH_4^+	$NH_4B(C_6H_5)_4$	$NH_4B(C_6H_5)_4$	K^+, Rb^+, Cs^+
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
Br^-	AgBr	AgBr	Cl^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
I^-	AgI	AgI	Cl^-, Br^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
SCN^-	CuSCN	CuSCN	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
CN^-	AgCN	AgCN	Cl^-, Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$
F^-	$(C_6H_5)_3SnF$	$(C_6H_5)_3SnF$	Many metals (except alkali metals), SiO_4^{4-}, CO_3^{2-}
ClO_4^-	$KClO_4$	$KClO_4$	
SO_4^{2-}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-
PO_4^{3-}	$Mg(NH_4)PO_4 \cdot 6H_2O$	$Mg_2P_2O_7$	Many metals except Na^+, K^+
NO_3^-	Nitron nitrate	Nitron nitrate	ClO_4^-, I^-, SCN^-, CrO_4^{2-}, ClO_3^-, NO_2^-, Br^-, $C_2O_4^{2-}$
CO_3^{2-}	CO_2 (by acidification)	CO_2	(The liberated CO_2 is trapped with Ascarite and weighed.)

Calculation of analyte concentration

$$xA^- + yB^+ \rightarrow zAB$$

$$C\ (A^-) = \frac{m_{AB} \times x}{M_{AB} \times V_0 \times z}$$

m_{AB} – mass of precipitate, g;
M_{AB} – molar mass of AB precipitate; g/mol;
V_0 – volume of initial solution of analyte, L;
$C\ (A^-)$ – molar concentration of initial solution of analyte, mol/L;
x, y and z - stoichiometric coefficients of chemical reaction

Calculation of analyte concentration

$$\mathbf{Cl^- + Ag^+ \rightarrow AgCl}$$

$$C\,(Cl^-) = \frac{m_{AgCl}}{M_{AgCl} \times V_0}$$

m_{AgCl} – mass of AgCl precipitate, g;
M_{AgCl} – molar mass of AgCl; g/mol;
V_0 – volume of initial solution of Cl^-, L;
C (Cl^-) – molar concentration of initial solution of Cl^-, mol/L

Exercise

To 10 mL of water sample containing chloride ions, 10 mL of $AgNO_3$ (C = 0.020 mol/L) were added. After separation of the precipitate and burning-out the filter in a muffle furnace, its measured mass was 132.0 mg. Calculate concentration of chloride ions in the analyzed sample.

Gravimetric determination of total petroleum hydrocarbons in soil

Extraction of petroleum hydrocarbons from soil by chloroform

↓

Solvent change to hexane (after evaporation of chloroform)

↓

Extract cleanup by passing through column packed with alumina (Al_2O_3)

↓

Full evaporation of hexane under nitrogen flow

↓

Weighing, reaching constant mass

Determination of carbon and hydrogen

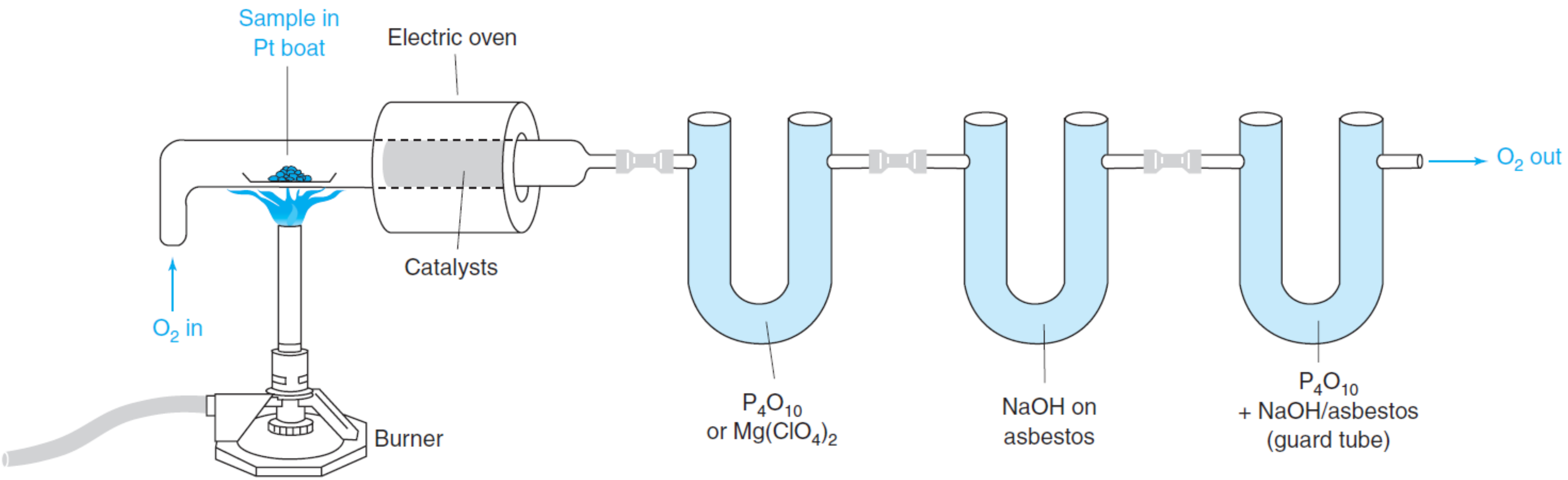


FIGURE 26-5 Gravimetric combustion analysis for carbon and hydrogen.

The combustion products are flushed through a chamber containing P_4O_{10} ("phosphorus pentoxide"), which absorbs water, and then through a chamber of Ascarite (NaOH on asbestos), which absorbs CO_2.

Task

A compound weighing 5.714 mg produced 14.414 mg of CO_2 and 2.529 mg of H_2O upon combustion. Find the wt% of C and H in the sample

Modern CHNS analyzer

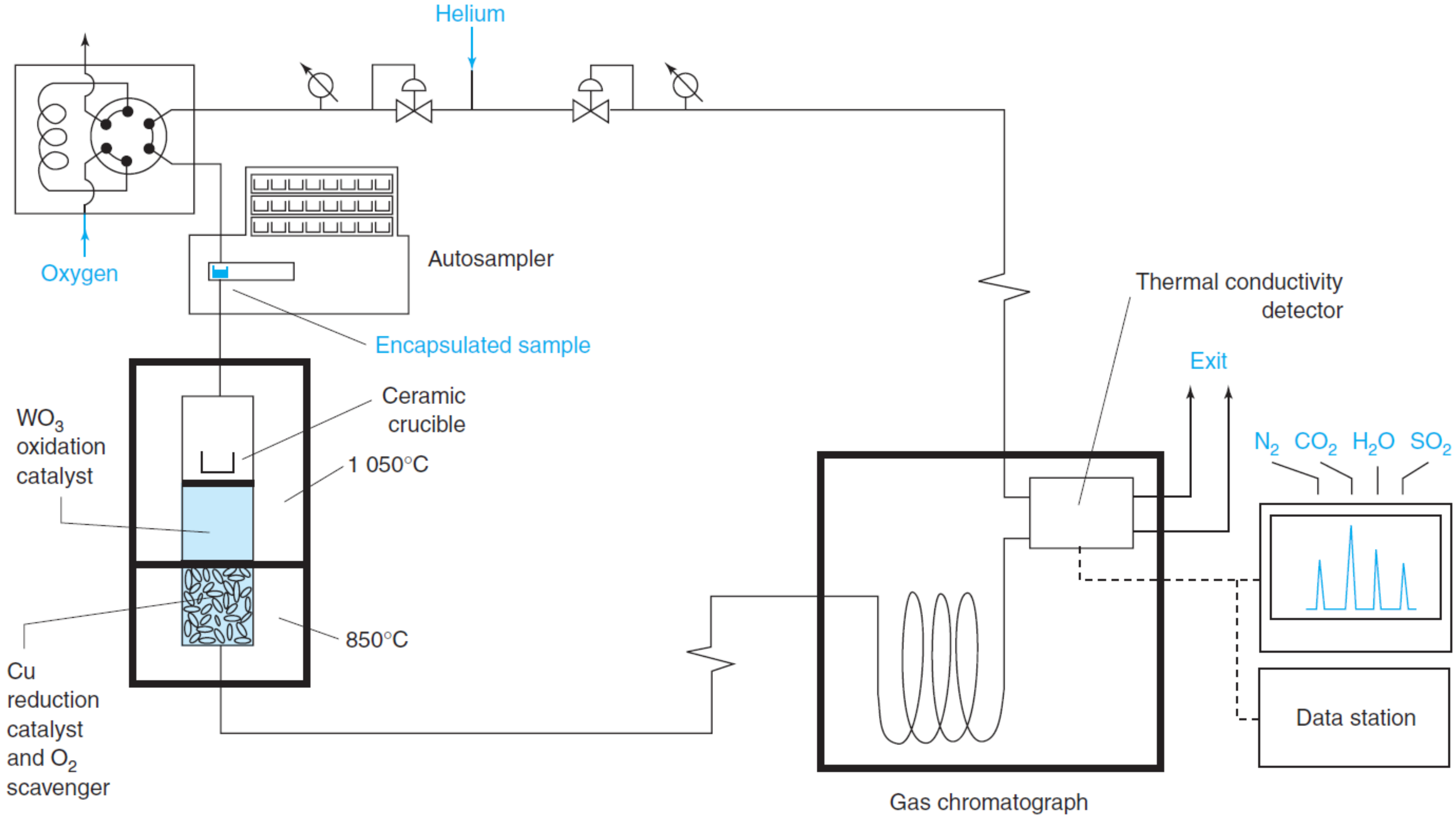


FIGURE 26-6 C,H,N,S elemental analyzer uses gas chromatography with thermal conductivity detection to measure N_2, CO_2, H_2O, and SO_2 combustion products. [Adapted from E. Pella, "Elemental Organic Analysis. 2. State of the Art," *Am. Lab.*, August 1990, p. 28.]

Quiz 1/5

What is the main equipment in gravimetry?

1 – pipette

2 – syringe

3 – technical balances

4 – analytical balances

Quiz 2/5

What parameter shows efficiency of precipitation?

1 – Henry's Law constant

2 – vapor pressure

3 – solubility product

4 – temperature

Quiz 3/5

When AgCl starts precipitating?

1 – $[Ag^+]\ [Cl^-] > K_{sp}$

2 – $[Ag^+]\ [Cl^-] < K_{sp}$

3 – $[Ag^+]\ [Cl^-] = K_{sp}$

4 – it is water soluble

Quiz 4/5

What type of gravimetry determines concentration of particulate matter in water?

1 – volatilization

2 – precipitation

3 – particulate

4 – electrogravimetry

Quiz 5/5

Why do you need desiccator during gravimetry?

1 – to evaporate sample

2 – to form precipitate

3 – to cool crucible with sample

4 – to remove moisture from precipitate

26-12. Marie Curie dissolved 0.091 92 g of $RaCl_2$ and treated it with excess $AgNO_3$ to precipitate 0.088 90 g of AgCl. In her time (1900), the atomic mass of Ag was known to be 107.8 and that of Cl was 35.4. From these values, find the atomic mass of Ra that Marie Curie would have calculated.

26-13. A 0.050 02-g sample of impure piperazine contained 71.29 wt% piperazine (FM 86.136). How many grams of product (FM 206.240) will be formed when this sample is analyzed by Reaction 26-6?

26-14. A 1.000-g sample of unknown gave 2.500 g of bis(dimethylglyoximate)nickel(II) (FM 288.91) when analyzed by Reaction 26-7. Find the weight percent of Ni in the unknown.