Techniques for preparation of liquid samples with a desired concentration of analyte

Aim

- Learn **to prepare liquid samples with desired concentration of a solute**

Importance

- Preparation of calibration samples (standards)
- Conducting chemical reactions
- Production of commercial liquids (gasoline, solvents, etc.)
- Conducting research experiments

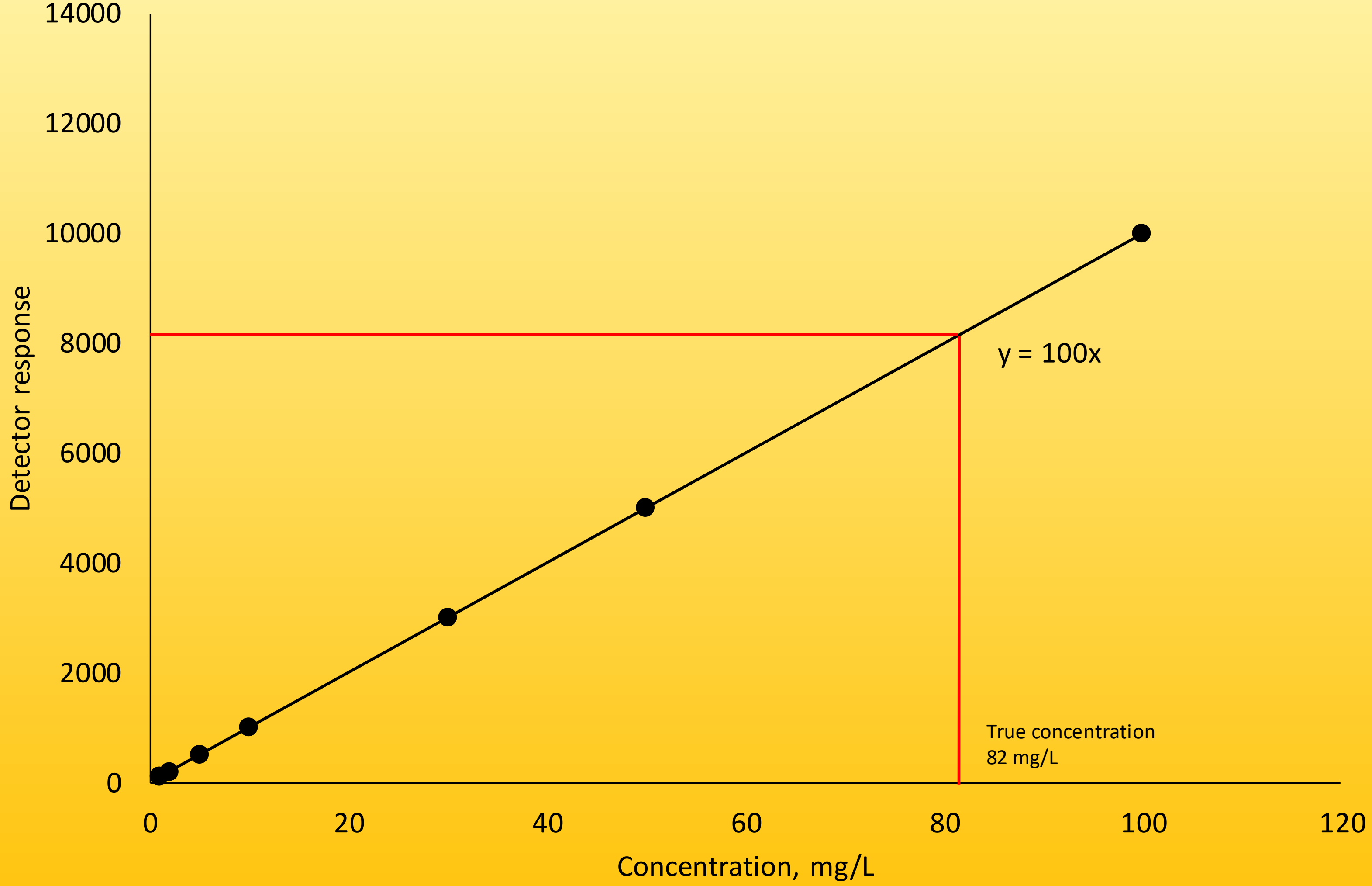
Advantages of having the skill

- More accurate analytical measurements
- Lower consumption of expensive materials (solvents)
- More accurate and reliable experimental research
- Higher quality of manufactured products
- ***Greater satisfaction of the employer / salary***

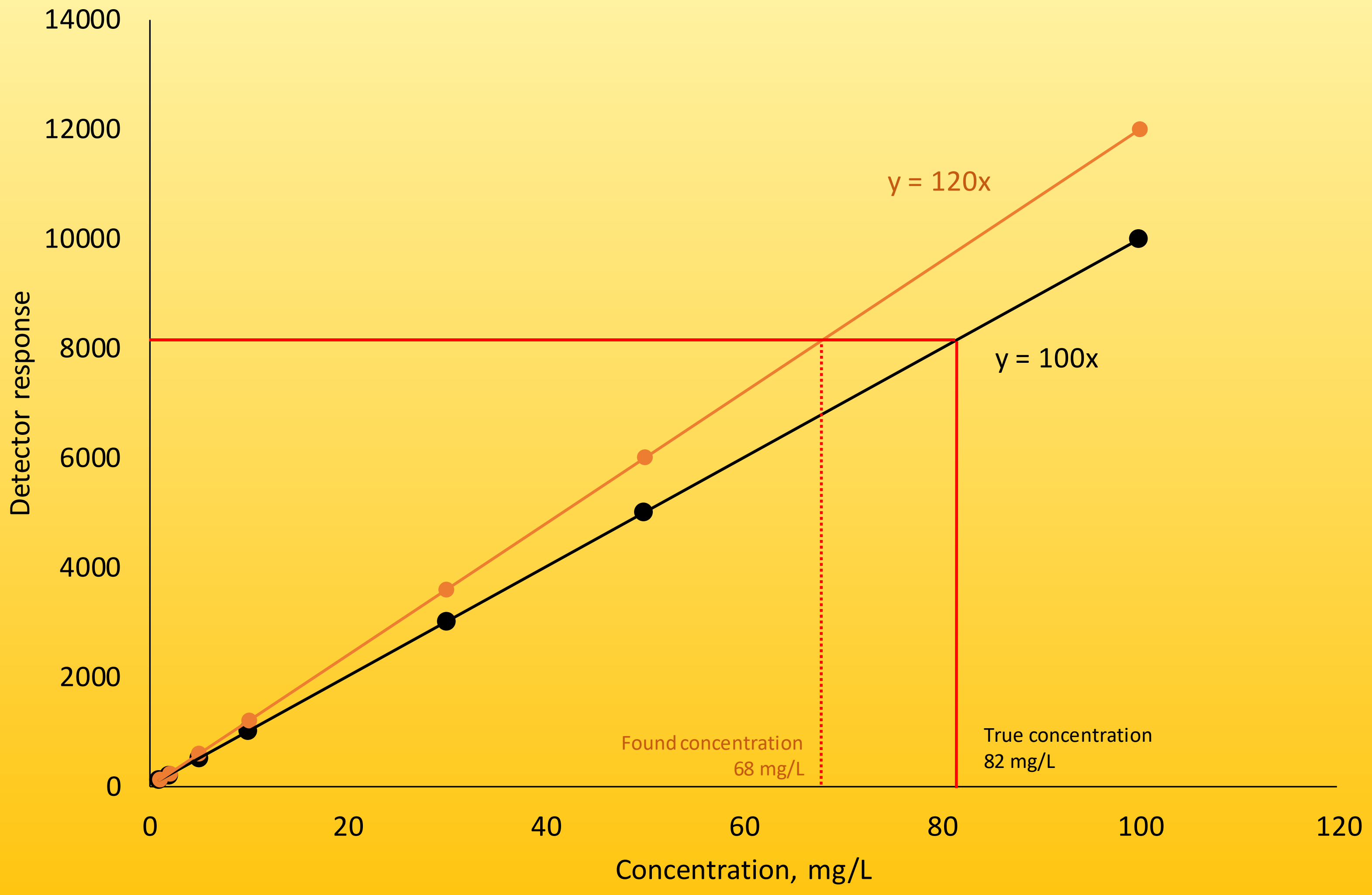
Problems for student without the skill

- Poor accuracy and precision of measurements
- Greater consumption of materials
- Extra time consumption for repeating experiments
- Poor quality of products
- ***Lower satisfaction of the employer / salary***

Example - quantification



Concentrations of calibration standards are 20% greater than they should be



Example - manufacture

Blending gasoline with octane booster

- Higher concentration = higher cost of production
- Lower concentration = lower octane number
- Much higher concentration = lower quality
- Much lower concentration = damage of engines

Concentration

- general measurement unit stating the amount of solute present in a known amount of solution

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}}$$

- Amount – mass, volume or amount of substance

Concentrations

- Molar (M/L)
- Normal (moles of equivalent / L)
- Percentage (mass, volumetric or molar)
- Many other
- Whatever you wish to use

Molarity

- **Molarity** - number of moles per 1 L of solution

- 1 Mole = 6.02×10^{23} molecules
- 1 Mole of ions = 6.02×10^{23} ions

- 1 mol/L of methanol in water = 6.02×10^{23} methanol molecules per 1 L of water

- 1 mol/L of Cl^- (chloride) ions in water = 6.02×10^{23} of Cl^- (chloride) ions per 1 L of water

Exercise

- How many moles of NaCl are present in 100 mL of NaCl solution in water having concentration 0.123 moL/L?

Answer

- How many moles of Na^+ ions are present in 100 mL of NaCl solution in water having concentration 0.123 moL/L?

- Answer: 0.0123 moL or 12.3 mmoL

Quiz 1/2

How many SO_4^{2-} ions are present in 1.00 mL of Na_2SO_4 solution in water having concentration 0.921 moL/L?

1 – 6.02×10^{23}

2 – 5.54×10^{20}

3 – 8.55×10^{21}

4 – 1.66×10^{22}

Quiz 2/2

How many milligrams of Ag^{+} ions are present in 15.4 mL of $AgNO_3$ solution in water having concentration 0.0213 moL/L?

- 1 – 35
- 2 – 250
- 3 – 14.2
- 4 - 130

Normality

- **Normality** – a number of equivalents of chemical compound per 1 L of sample

- Equivalent is a number of moles of chemical compound or ion that reacts with or supply:

- 1 mole of hydrogen (H^+) or hydroxyl (OH^-) ions in acid-base reactions
- 1 mole of electrons in redox reactions

- Normality is obsolete and rarely used in modern laboratories

Example of normality

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

or

$$2H^+ + SO_4^{2-} + 2Na^+ + 2OH^- \rightarrow 2Na^+ + SO_4^{2-} + 2H_2O$$

or

$$H_2SO_4 + 2OH^- \rightarrow SO_4^{2-} + 2H_2O$$

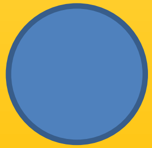
or

$$\mathbf{\tfrac{1}{2}\, H_2SO_4 + OH^- \rightarrow \tfrac{1}{2}\, SO_4^{2-} + H_2O}$$

1 ion of OH^- ions corresponds to ½ molecule of H_2SO_4

1 equivalent of H_2SO_4 in acid-base reactions = ½ mol of H_2SO_4

or 3.01×10^{23} molecules of H_2SO_4



1 mole H_2SO_4

6.02×10^{23} molecules

1 equivalent H_2SO_4

3.01×10^{23} molecules

(1/2 mole H_2SO_4)

Percentage

Percentage – is the concentration of compound (%) in solution

$$\text{Weight \%} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Example: 1.00 kg of solution contains 22.5 g of NaCl. What is the weight % of NaCl in the solution?

Concentration of NaCl in the solution= $\frac{22.5\text{ g}}{1000\text{ g}} \times 100\% = 2.25\ \%$

Volume %

$$\text{Volume \%} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

Example: 1 L of gasoline contains 11.4 mL of benzene. What is the volume % of benzene in gasoline?

$$\text{Volume \% of benzene in gasoline} = \frac{11.4\ \text{mL}}{1000\ \text{mL}} \times 100\% = 1.14\ \%$$

Concentrations as ratios

In modern analytical chemistry, trace concentrations are often expressed as parts-per-million (ppm), parts-per-billion (ppb), parts-per-trillion (ppt) or parts-per-quadrillion (ppq)

$$1\text{ ppm}\left(\frac{\text{w}}{\text{w}}\right) = \frac{1\text{ mg of solute}}{1\text{ kg of solution}} = \frac{1\text{ µg of solute}}{1\text{ g of solution}} = \frac{mass\ of\ solute\ (g)}{mass\ of\ solution\ (g)} \times 10^6$$

$$1\text{ ppm}\left(\frac{\text{v}}{\text{v}}\right) = \frac{1\text{ mL of solute}}{1\text{ m}^3\text{ of solution}} = \frac{1\text{ µL of solute}}{1\text{ L of solution}} = \frac{vol\ of\ solute\ (g)}{vol\ of\ solution\ (g)} \times 10^6$$

$$1\text{ ppm}\left(\frac{\text{m}}{\text{v}}\right) = \frac{1\text{ mg of solute}}{1\text{ m}^3\text{ of solution}} = \frac{1\text{ µg of solute}}{1\text{ L of solution}} = \frac{mass\ of\ solute\ (g)}{vol\ of\ solution\ (mL)} \times 10^6$$

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$$1\ \text{ppb}\ \left(\frac{\text{w}}{\text{w}}\right) = \frac{1\ \mu\text{g of solute}}{1\ \text{kg of solution}} = \frac{1\ \text{ng of solute}}{1\ \text{g of solution}} = \frac{mass\ of\ solute\ (g)}{mass\ of\ solution\ (g)} \times 10^9$$

$$1\ \text{ppb}\ \left(\frac{\text{v}}{\text{v}}\right) = \frac{1\ \mu\text{L of solute}}{1\ \text{m}^3\ \text{of solution}} = \frac{1\ \text{nL of solute}}{1\ \text{L of solution}} = \frac{vol\ of\ solute\ (nL)}{vol\ of\ solution\ (L)} \times 10^9$$

$$1\ \text{ppb}\ \left(\frac{\text{m}}{\text{v}}\right) = \frac{1\ \mu\text{g of solute}}{1\ \text{m}^3\ \text{of solution}} = \frac{1\ \text{ng of solute}}{1\ \text{L of solution}} = \frac{mass\ of\ solute\ (g)}{vol\ of\ solution\ (mL)} \times 10^9$$

Typical units of concentrations

Liquid samples:

- volume %;
- mol/L;
- g/L;
- ppm (w/v); ppb (w/v); ppt (w/v)

Solid samples:

- weight %;
- g/kg;
- ppm (mg/kg or µg/g); ppb (µg/kg); ppt (ng/kg)

Gaseous samples:

- volume %;
- ppm (v/v) – milliliters of gaseous compound in 1 m^3 of gas mixture;
- ppm (w/v)

Exercise

Concentration of N-methyl aniline in gasoline is 13.5 mg/mL. Convert this concentration to volumetric % (v/v). Density of N-methyl aniline is 0.99 g/mL.

$$1\% \left(\frac{v}{v}\right) = \frac{10\ \mu L}{mL} = 0.01$$

From this formula, it is clear that we need to convert 13.5 mg to µL (mass to volume). To do this, we can use formula: m = V ρ or V = m/ρ

$$V = \frac{13.5\ mg\ mL}{0.99\ g} \times \frac{1\ g}{1000\ mg} = 0.0136\ mL$$

$$C = \frac{0.013.6\ mL}{mL} = 0.0136 \times 100\% = 1.36\%$$

Measurement of weight

Analytical precision:

- 0.000001 g (1 µg);
- 0.00001 g (0.01 mg);
- 0.0001 g (0.1 mg).

Technical balances:

- 0.001 g;
- 0.01 g;
- 0.1 g, etc.

Balances also differ by weight range.

Some (most modern) models can be connected to PC.

Measurement of volume

Volumetric flasks: precise measurement of final volume of solution being prepared (10-1000 mL)

Pipettes (hand-operated or automated): precise injection of volumes (microliters to 5 mL)

Analytical syringes: precise injection of small volumes (0.1 to 1000 μL)

Graduated cylinders, beakers, flasks: used for non-precise fast measurements of volumes

Volume measurement

Pipettes

Volumetric flasks

Glass pipettes

Graduated cylinders

Exercise

How many microliters of MTBE (density 0.74 g/mL) must be added to 1 mL of gasoline having MTBE concentration 50 mg/mL to increase MTBE concentration in gasoline to 70 mg/mL? Density of gasoline before and after addition of MTBE will remain unchanged (0.74 g/mL).

$$C\left(\frac{\mu g}{mL}\right) = \frac{m_{MTBE}}{V_{gasoline}}$$

After addition of MTBE, mass of MTBE in gasoline, volume of gasoline and concentration of MTBE will increase. Final concentration of MTBE in gasoline will be equal to:

$$C\left(\frac{\mu g}{mL}\right) = \frac{m_{MTBE\ initial} + m_{MTBE\ added}}{V_{total}}$$

Solution (continued)

$$m_{MTBE\ initial} = C_{MTBE\ initial} \times V_{gasoline\ initial} = \frac{50\ mg \times 1\ mL}{mL} = 50\ mg$$

Lets express volume of MTBE added as "X" µL. Then the mass of MTBE added is equal to:

$$m_{MTBE\ added} = \frac{X\ \mu L \times 0.74\ g}{mL} \times \frac{1\ mL}{1000\ \mu L} = 0.00074\ X\ g = 0.74\ X\ mg$$

Lets find the total volume of gasoline after addition of MTBE:

$$V = \frac{m_{gasoline} + m_{MTBE\ added}}{\rho_{gasoline}} = \frac{1\ mL \times 0.74 \frac{g}{mL} + 0.74\ X\ mg}{0.74}$$

$$= \frac{740\ mg + 0.74\ X\ mg}{0.74 \frac{g}{mL}} = \frac{0.74\ (1000 + X)\ mg\ mL}{0.74\ g} = (1 + 0.001X)\ mL$$

$$70 \frac{mg}{mL} = \frac{(50 + 0.74X)\ mg}{(1 + 0.001X)\ mL}$$

Solution (continued)

$$70 + 0.070X = 50 + 0.74X$$

$$X = \frac{70 - 50}{0.74 - 0.07} = \frac{20}{0.67} = 29.9\ \mu L$$

Answer: 29.9 µL of MTBE should be added

Question

- Propose method to prepare solution of ethanol in water with C = 1.00 mg/mL

Options

- Inject 100 mg of methanol into 50 mL of water in 100-mL volumetric flask, add water to the mark
- Dissolve 50 mg of methanol in water (50-mL flask)
- Dissolve 25 mg of methanol in water (25-mL flask)
- Dissolve 1.0 mg of methanol in 1.00 mL of water

Question

- Propose method to prepare solution of NaCl in water with C = 5.0% (w/w)

- Density of 5% solution of NaCl in water – 1.034 g/mL

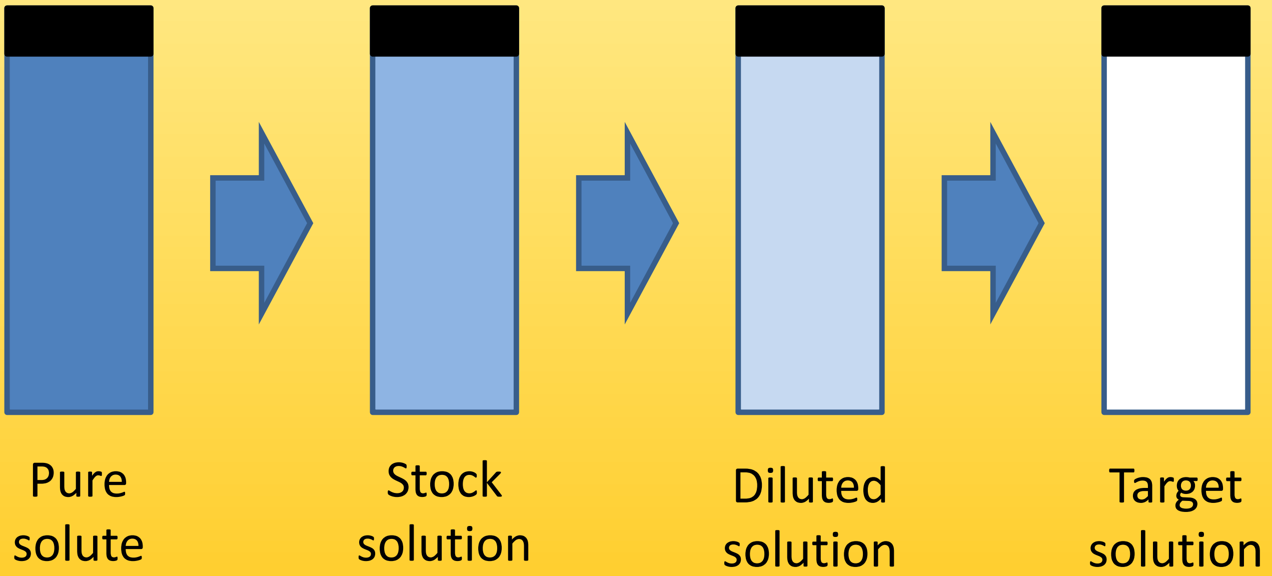
Options

- Add 95 g of water to 5.00 g of NaCl
- Accurately weight around 5 g of NaCl and add corresponding mass of water
- ???

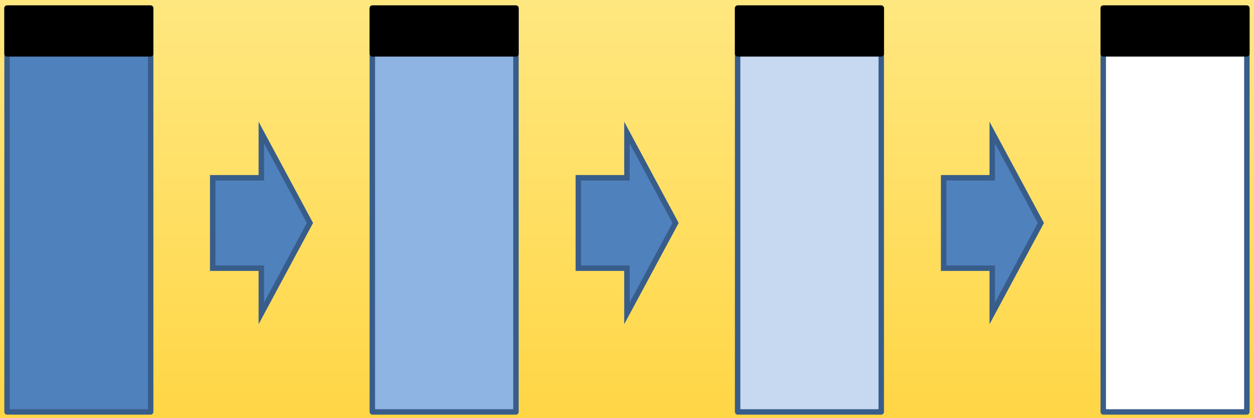
Question

- Propose method to prepare solution of methanol in water with C = 1.00 µg/L

Serial dilution

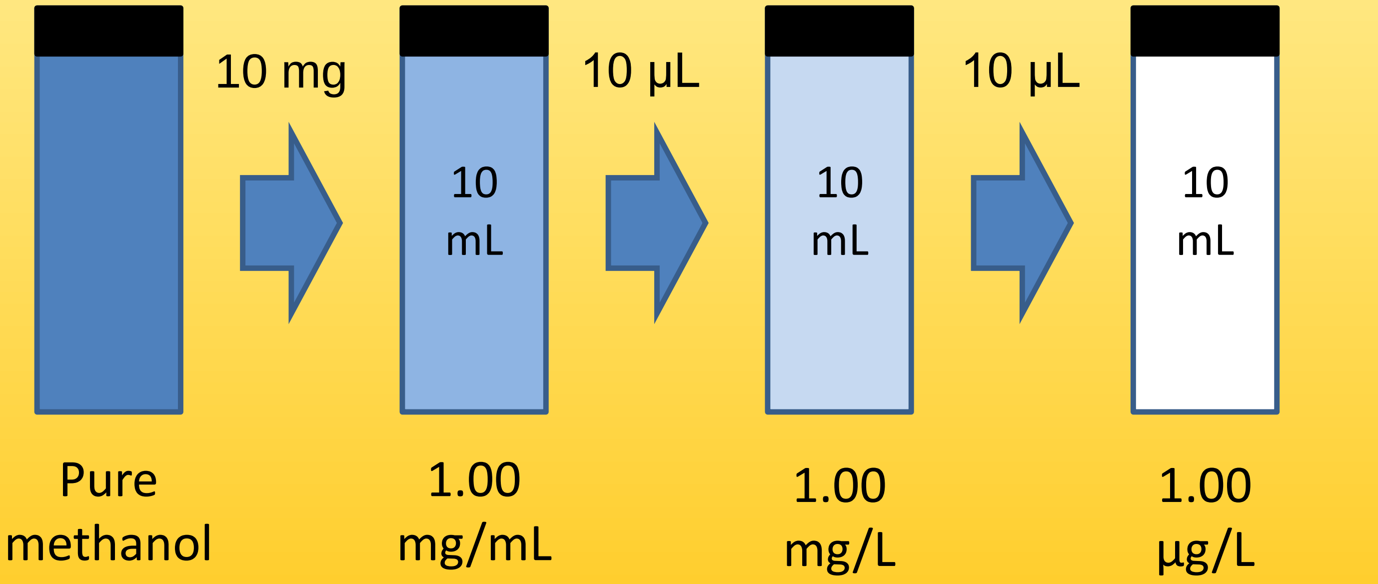


Serial dilution (100x)

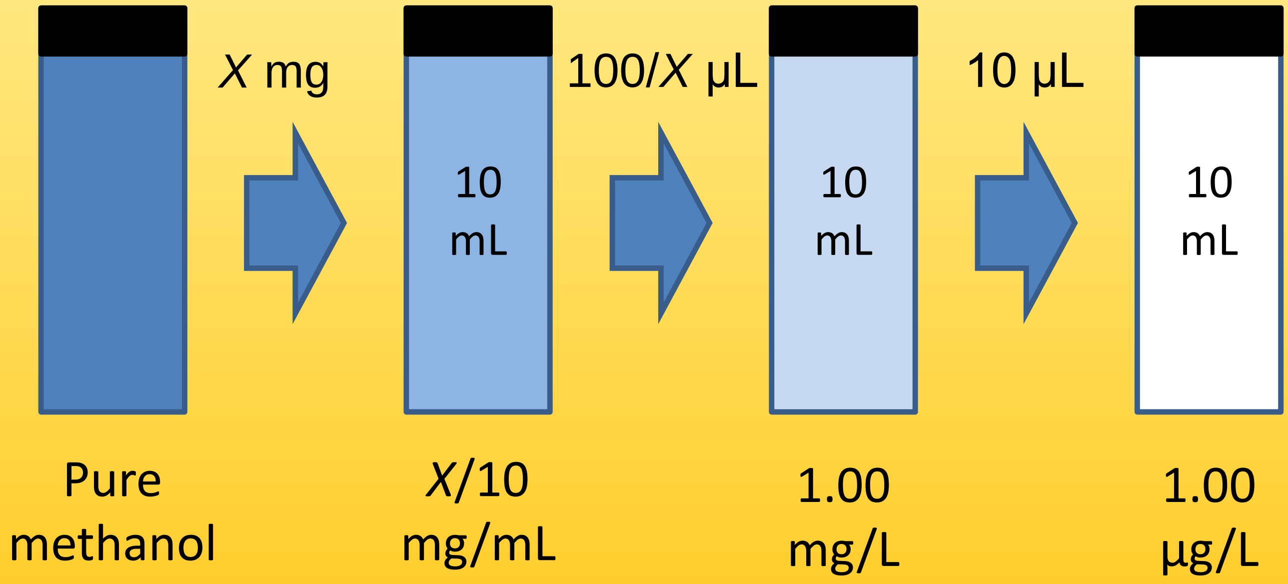


Pure methanol | 10.0 mg/mL | 100 mg/L | 1.00 mg/L

Serial dilution (1000x)



Serial dilution



Preparation of stock solution

$$\text{m (pure substance)} = \frac{\text{m}(solute)}{\text{Purity}} = \frac{\text{C x V}}{\text{Purity}}$$

Preparation of stock solution

Task: to prepare 100 mL of stock solution of 1M NaCl in water

Substances needed:

1) NaCl, >99%
2) Distilled water

$$m\,(NaCl) = \frac{C \text{ x } V \text{ x } MW}{Purity}$$

$$m\,(NaCl) = \frac{1\ \frac{mol}{L} \text{ x } 0.1\ L \text{ x } 58.44\ \frac{g}{mol}}{0.99} = \frac{5.844\ g}{0.99} = 5.903\ g$$

Recommendations for dilution

- Max 1000x dilution for aqueous solutions
- Max 100x dilution for organic solutions

Selection of volumes

- Depends on what volume is needed
- Higher volumes are required for higher accuracy
- Lower volumes are preferred for lower cost
- Lower volumes are mandatory for expensive materials

Tasks

- Propose method to prepare solution of toluene in methanol with a concentration 100 μg/L
- Propose method to prepare solution of naphthalene in methanol with a concentration 10 μg/L