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

Aim

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

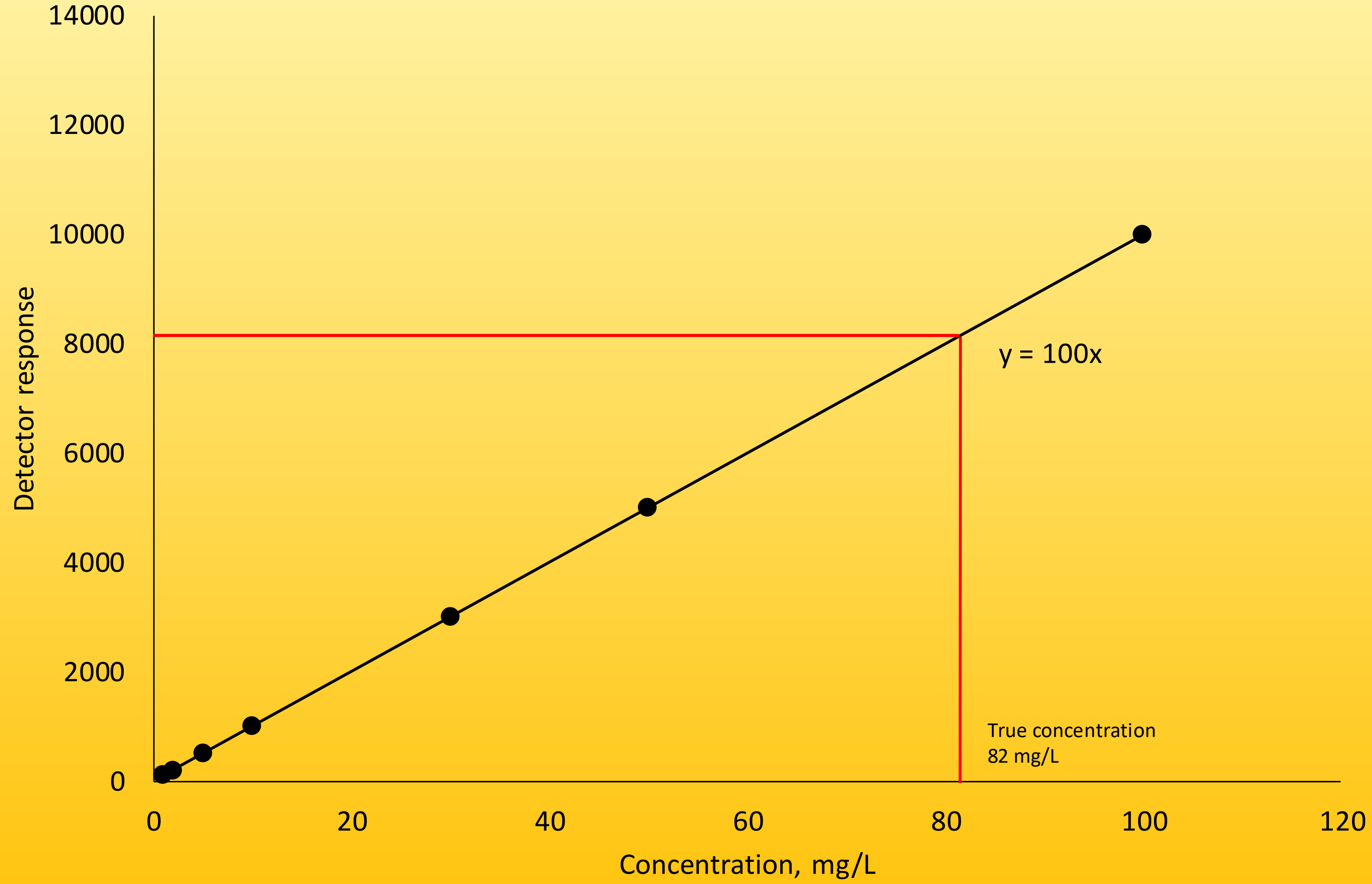
Importance

- Preparation of calibration samples (standards)
- Conducting chemical reactions in gas phase
- Production of commercial gases (LPG, etc.)
- Conducting research experiments

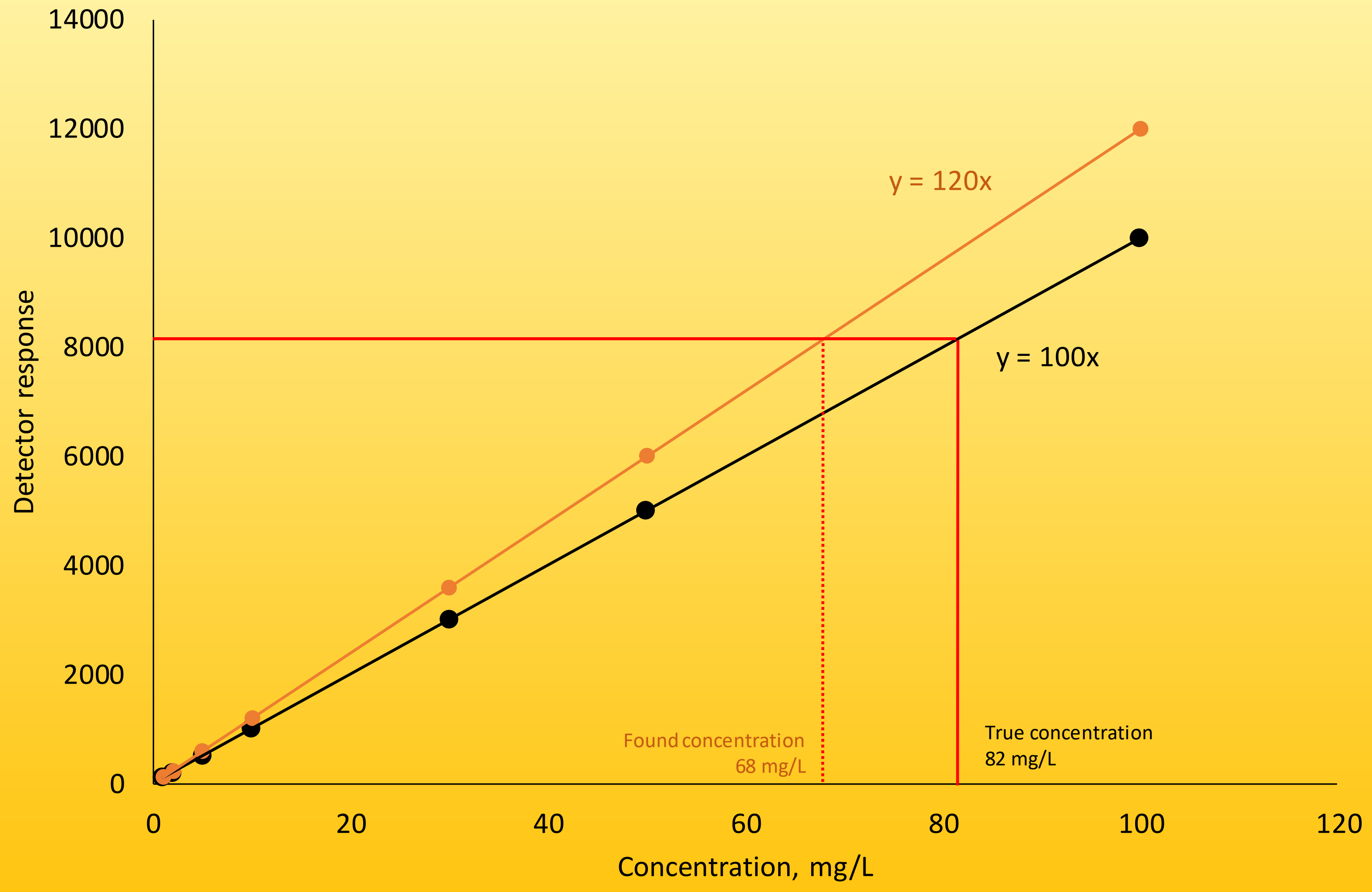
Advantages of having the skill

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

Example - quantification



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



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

Units of concentrations of gases

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) – milligrams of gaseous compound in 1 m^3 of gas mixture
- mg/m^3, $µg/m^3$, ng/m^3

Types of concentrations

- Volume/volume – does not change with T and P
- Mass / volume – depends on T and P

- atm (or bar) – (partial) pressure units

Main formula for conversions

$$pV = \frac{mRT}{M}$$

- p – pressure (ambient or partial), kPa
- V – volume, L
- m – mass, g; M – molar mass, g/mol
- R – gas constant, 8.31 L · kPa / (mol · K)

Exercise

Convert 50 ppm (v/v) of hydrogen sulfide in air to mg/m^3

$$50\,ppm\,\left(\frac{v}{v}\right) = \frac{50\,\mu L}{L} = \frac{50\,mL}{m^3}$$

Now we need to find the weight of 50 mL of hydrogen sulfide. For that purpose, we can use ideal gas law:

$$pV = \frac{mRT}{M}$$

Solution (continued)

$$m = \frac{pVM}{RT}$$

V = 50 mL; R=8.31 L· kPa / (moL K); M (H_2S) = 34 g/moL

Pressure and temperature are not given. But let's imagine that we are in Almaty now. The pressure is 680 mmHg, temperature 10°C

- We need to convert temperature to K: T = 273 + 10 = 283 K
- The pressure must be converted to kPa. We know that 760 mmHg = 101.325 kPa. P = 101.325 kPa x 680 mmHg / 760 mmHg = 90.66 kPa

Solution (continued)

$$m = \frac{90.66\, kPa \times 50\, mL \times 34\, g\, K\, moL}{8.31\, L\, kPa \times 283\, K\, moL} \times \frac{1\, L}{1000\, mL}$$

$$m = 0.0655\, g = 65.5\, mg$$

$$C\left(\frac{mg}{m^3}\right) = \frac{65.5\, mg}{m^3} = 65.5\ \frac{mg}{m^3}$$

Q: will the C increase if temperature is increased to 30 ^oC?

Question

- What is the partial pressure of H_2S at this concentr.?
- m = 0.0655 g; V = 1000 L

$$p = \frac{mRT}{MV} = \frac{0.0655\ g\ \times 8.31\ L\ kPa \times 283K\ mol}{34\ g\ 1000\ L\ mol\ K}$$

p = 0.00453 kPa = 4.53 Pa

Q: will the partial pressure increase if temperature is increased to 30 ^{o}C?

Quiz 1/2

Sulfur dioxide concentration in Almaty air now is 37 μg/m^3. Convert this concentration to ppbV. Atmospheric pressure is 740 mmHg, temperature 25^{o}C.

1 – 37

2 – 55

3 – 25

4 - 43

5 – 15

Quiz 2/2

Sample bag (V = 1.00 L) was filled with 0.70 L of air having benzene concentration 56 µg/m^3. Sampling was done at a temperature -10^{o}C. Then, the bag was transported to the laboratory where the temperature was 25^{o}C. What is the benzene concentration in the air inside a sampling bag stored in the lab?

1 – 49 µg/m^3

2 – 56 µg/m^3

3 – 64 µg/m^3

4 - 51 µg/m^3

5 – 61 µg/m^3

Question

- What equipment and glassware is used for preparing liquid solutions?

Calibrated gas sampling bulb

To prepare gas standard, inject small amount (<10 uL) of analyte to bulb

Exercise

- How many nanograms of naphthalene should be injected into a 500-mL bulb filled with "zero" air to prepare air with naphthalene concentration 50 ng/L

$$m = C\,V = 50\,\frac{ng}{L} \times 0.5\,L = 25\,ng$$

Exercise (continued)

- What concentration should the injected solution have if the injected volume is 5.0 µL?

$$C = \frac{25\,ng}{5.0\,\mu L} = 5.0\ \frac{ng}{\mu L}$$

Exercise

Solution of benzene (5.00 µL) in methanol with concentration 10 mg/mL was injected to calibrated bulb having volume 250 mL and filled with air. All injected solution were evaporated. What is the concentration of benzene in the air inside bulb (in µg/L)

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{5.00\ \mu L \times 10\ \frac{\mu g}{\mu L}}{250\ mL} = \frac{50\ \mu g}{250\ mL} = 0.200\ \frac{\mu g}{mL} = 200\ \frac{mg}{L}$$

Task

- Convert this concentration to ppmV
- Convert this concentration to Pa

Question

- How many microliters of water can be introduced to a 250-mL flask containing dry air at 25^{o}C?

- Answer: check vapor pressure of water at 25^{o}C (3.169 kPa)

$$pV = \frac{mRT}{M}$$

$$m = \frac{pVM}{RT} = \frac{3.169\ kPa \times\ 0.25\ L\ \times 18\ g\ mol\ K}{8.31\ L\ kPa\ mol \times 298K} = 5.8\ mg$$

Task 2

How many microliters of methanol can be introduced to a 250-mL flask containing air at 25^{o}C of a 20% humidity?

p = 16.9 kPa

$$m = \frac{pVM}{RT} = \frac{16.9\ kPa \times\ 0.25\ L\ \times 31\ g\ mol\ K}{8.31\ L\ kPa\ mol \times 298K} = 53\ mg$$

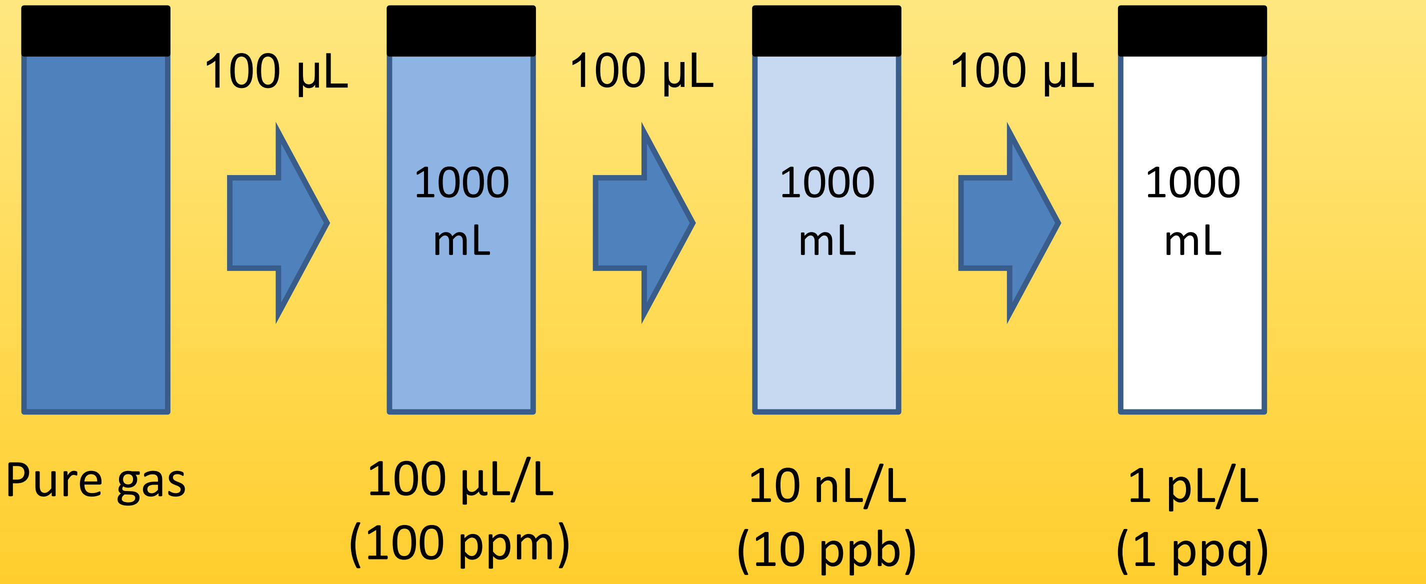
$$m = 53\ mg\ \times 80\% = 42.4\ mg$$

$$V = \frac{42.4\ mg\ \mu L}{0.792\ mg} = 53.5\ \mu L$$

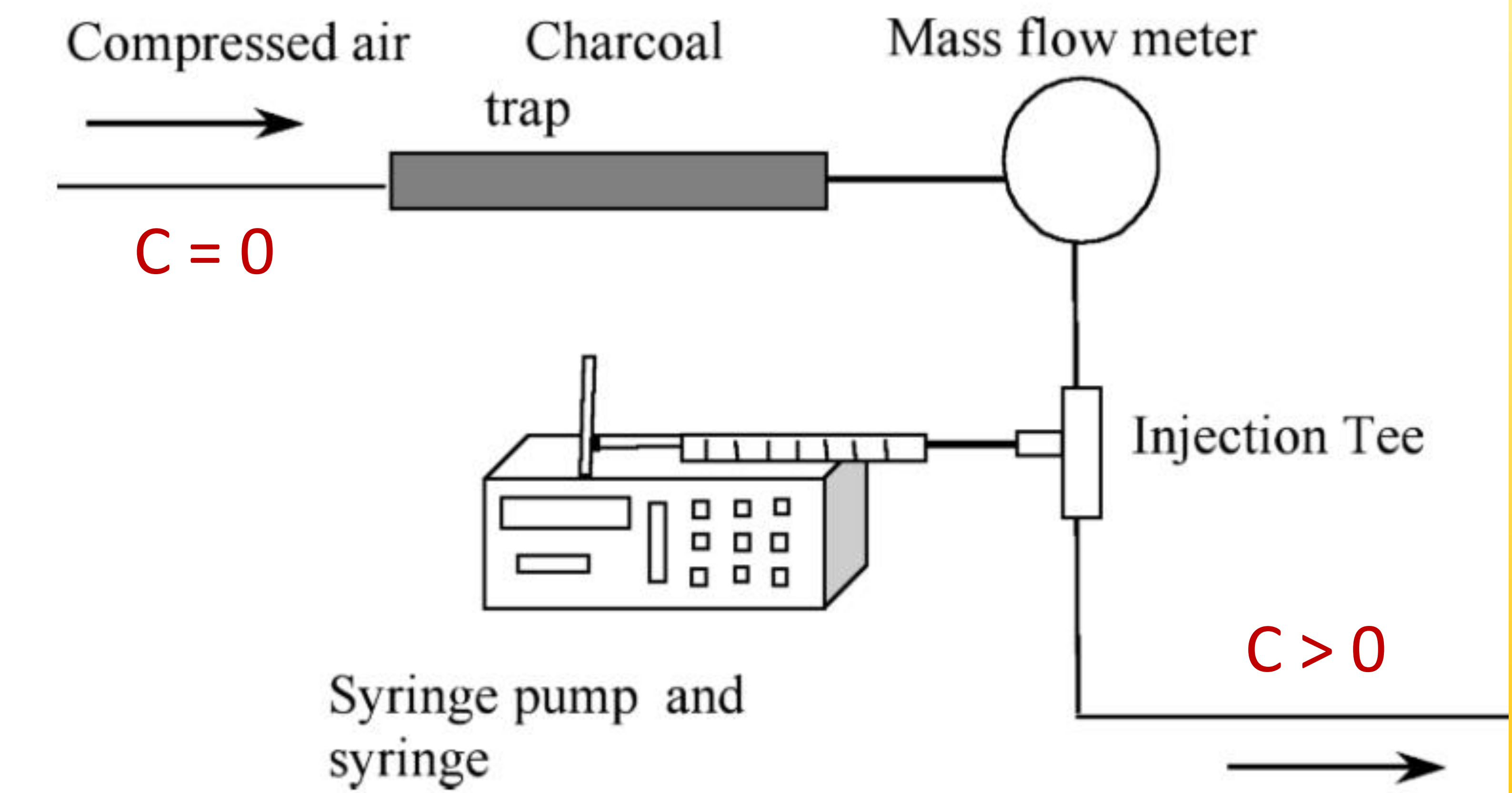
Gas tight syringes

PTFE plunger

Serial gas dilution (10000x)



Method 2



Tuduri et al., 2001

New Era NE-1002X

Example

- “Zero” air is supplied at 100 mL/min rate
- Benzene solution in methanol (C = 50 ng/μL) is supplied at 10 μL/h rate
- Calculate benzene concentration in produced air

Calculation

$$C = \frac{R_{analyte}}{R_{air}}$$

$$R_{analyte} = R_{sol} \times C_{sol} = 10\ \frac{\mu L}{h} \times 60\ \frac{ng}{\mu L} = 600\ \frac{ng}{h}$$

$$R_{air} = 100\frac{mL}{min} = 6000\frac{mL}{h} = 6\frac{L}{h}$$

$$C = \frac{600\frac{ng}{h}}{6\frac{L}{h}} = 100\frac{ng}{L} = 100\frac{\mu g}{m^3}$$

Task

- What concentration should toluene solution in methanol have for supplying to “zero” air flow at 200 mL/min and obtaining air with tolune concentration 50 ng/L? Syringe pump should operate at 5.0 µL/h rate
- What volume should syringe have to operate for 24 h?
- What will be the linear plunger rate for this syringe at the desired volumetric rate?