LESSON 2

10/02/2020

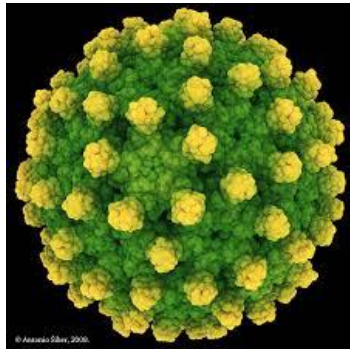Prof. Danilo Spasiano

Disinfection

Escherichia coli: gastroenteritis

Salmonelle: salmonellosis, typhoid fever.

Hapatitis a virus: infectious hepatitis

Tenia saginata egg: taeniasis.

Disinfection: Why?

organismo	Concentration in wastewater, MPN/100ml	Number of microorganisms causing the infection
Bacteria:		
Bacterioides	10^7-10^{10}	
Coliform, total	10^7-10^9	
Coliform, fecal[d]	10^6-10^8	10^6-10^{10}
Clostridium perfringens	10^3-10^5	$1-10^{10}$
Enterococci	10^4-10^5	
Fecal streptococci	10^4-10^7	
Pseudomonas aeruginosa	10^3-10^6	
Shigella	10^0-10^3	10–20
Salmonella	10^2-10^4	10^1-10^8
Protozoa:		
Cryptosporidium parvum oocysts	10^1-10^3	1–10
Entamoeba histolytica cysts	$10^{-1}-10^1$	10–20
Giardia lamblia cysts	10^3-10^4	<20
Helminth:		
Ova	10^1-10^3	
Ascaris lumbricoides	$10^{-2}-10^0$	1–10
Viruses:		
Enteric virus	10^3-10^4	1–10
Coliphage	10^3-10^4	

MNP: most probable number

Disinfection: how?

Chimical

- chlorine gas and hypochlorites (Cl_2, NaOCl)

- Chlorine dioxide (ClO_2);

- Peracetic acid;

- Ozone (O_3);

Physical

- UV radiation (UV_{254});
- Solar UV radiation ($UV_{300-400}$);

Chemical/Physical

- $UV_{254} + H_2O_2$;
- $UV_{254} + O_3$;
- …

Disinfection: comparison

Characteristic[a]	Cl$_2$ Chlorine	NaOCl Sodium hypochlorite	Ca(OCl)$_2$ Calcium hypochlorite	ClO$_2$ Chlorine dioxide	O$_3$ Ozone	UV$_{254}$ UV radiation
Availability/cost	Low cost	Moderately low cost	Moderately low cost	Moderately low cost	Moderately high cost	Moderately high cost
Deodorizing ability	High	Moderate	Moderate	High	High	na
Homogeneity	Homogeneous	Homogeneous	Homogeneous	Homogeneous	Homogeneous	na
Interaction with extraneous material	Oxidizes organic matter	Active oxidizer	Active oxidizer	High	Oxidizes organic matter	Absorbance of UV radiation
Noncorrosive and nonstaining	Highly corrosive	Corrosive	Corrosive	Highly corrosive	Highly corrosive	na
Nontoxic to higher forms of life	Highly toxic to higher life forms	Toxic	Toxic	Toxic	Toxic	Toxic
Penetration	High	High	High	High	High	Moderate
Safety concern	High	Moderate	Moderate	High	Moderate	Low
Solubility	Moderately	High	High	High	High	na
Stability	Stable	Slightly unstable	Relatively stable	Unstable, must be generated as used	Unstable, must be generated as used	na
Toxicity to microorganisms	High	High	High	High	High	High
Toxicity at ambient temperatures	High	High	High	High	High	High

[a] See Table 12-1 for a description of each characteristic.
[b] na = not applicable.

Disinfection: Cl_2

1) Chlorine gas kills pathogens such as bacteria and viruses by breaking the chemical bonds of their molecules.
2) When enzymes come into contact with chlorine gas, one or more atoms of their hydrogen molecules are replaced by chlorine. This involves deformation or deterioration of the enzymes. When enzymes don't work properly, microorganisms starve.
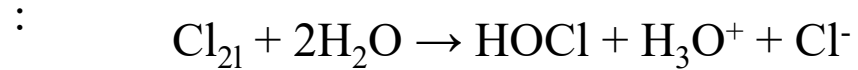
1)

Cl_2

2)

Cl_2

It does not eat and starves

substrato

enzima

complesso
enzima-substrato

prodotti

enzima
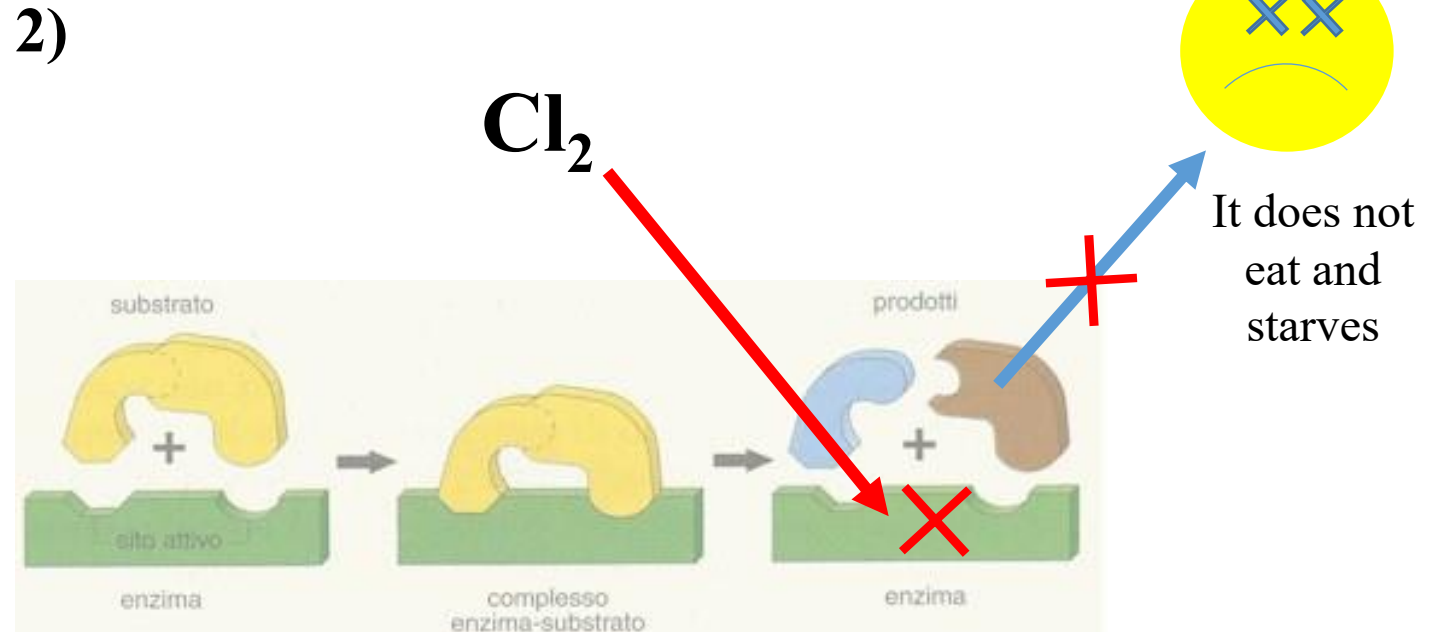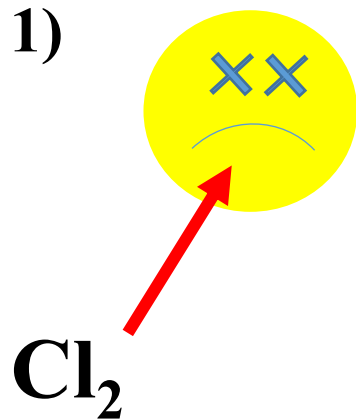
Disinfezione: Cl_2

Cl_2 is a gas: to dissolve the chlorine in solution we must make it bubble (like O_2 during the activated sludge treatment)
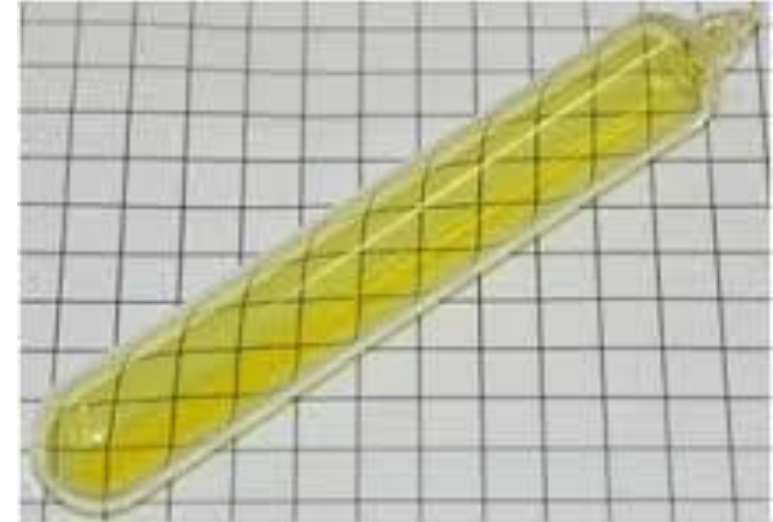
$$Cl_{2g} \leftrightarrow Cl_{2l}$$
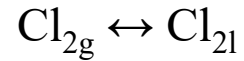
Once it is dissolved in water, hypochlorous acid is produced:

$$Cl_{2l} + 2H_2O \rightarrow HOCl + H_3O^+ + Cl^-$$

Depending on the pH, hypochlorous acid can dissociate, forming the hypochlorite ion:

$$HOCl + H_2O \leftrightarrow OCl^- + H_3O^+$$
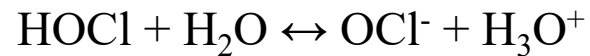
$$K_{eq} = 2.9 \ 10^{-8} \ M \ (25 \ °C)$$

HOCl	OCl⁻

Disinfection: hypochlorites

Problems related to the transport, storage and dosage of chlorine gas can be overcome by using sodium or calcium hypochlorites

NaOCl

Sodium hypochlorite

-It is purchased in aqueous solutions with a concentration of available chlorine varying between 12 and 15%
-A 16.7% solution stored at 26.7 °C will lose 10% of the available chlorine in 10 days (20% in 25 days)

Ca(OCl)$_2$

Calcium hypochlorite

-It is purchased in an aqueous solution with available chlorine concentration of up to 70%
- It is also purchased in powder, granules or tablets
-Due to its tendency to crystallize, calcium hypochlorite can lead to occlusion ... it is not good in a purifier or in a WWTP!

NaOCl is generally preferred!
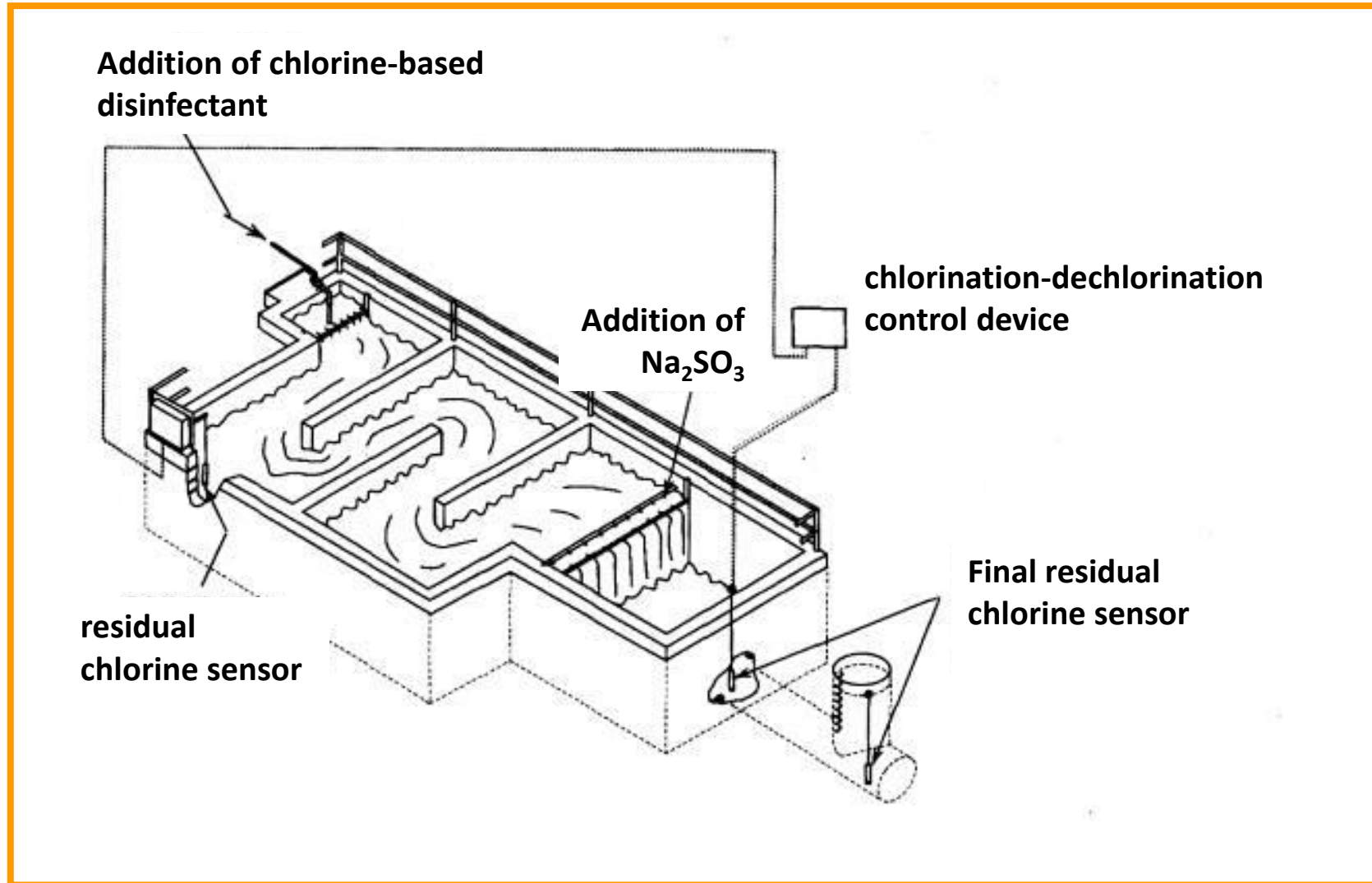
Disinfection: hypochlorites

Blanqueador

5% NaOCl

1.5% NaOCl

They act in this way:

$$NaOCl + H_2O \rightarrow \boxed{HOCl} + NaOH$$

$$Ca(OCl)_2 + 2H_2O \rightarrow \boxed{2HOCl} + Ca(OH)_2$$
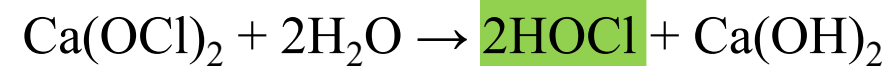
Disinfection: Chlorination tanks

Addition of chlorine-based disinfectant

chlorination-dechlorination control device

Addition of Na_2SO_3

residual chlorine sensor

Final residual chlorine sensor

Sulphite (Na_2SO_3) is typically used to remove excess residual chlorine

Chlorination disadvantage

The use of chlorine gas or hypochlorites leads to the formation of "organo-chlorinated" compounds
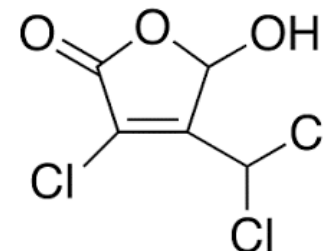
Trialomethanes: chloroform, dichloromethane …
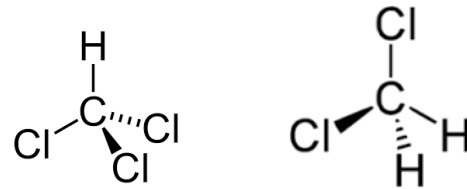
Alloacetic acids: mono-/di-/tri-chloroacetic acid
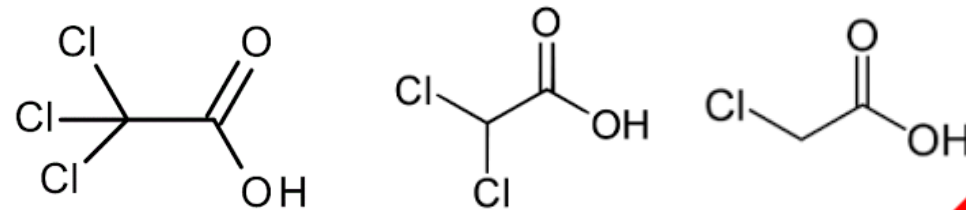
Chlorophenols: 2-chlorophenol, 2,4- dichlorophenol…
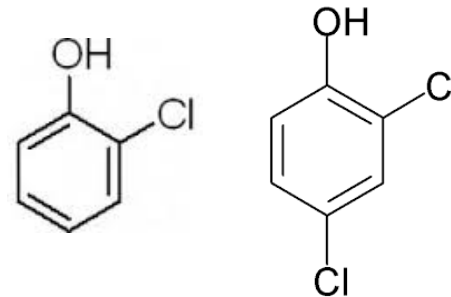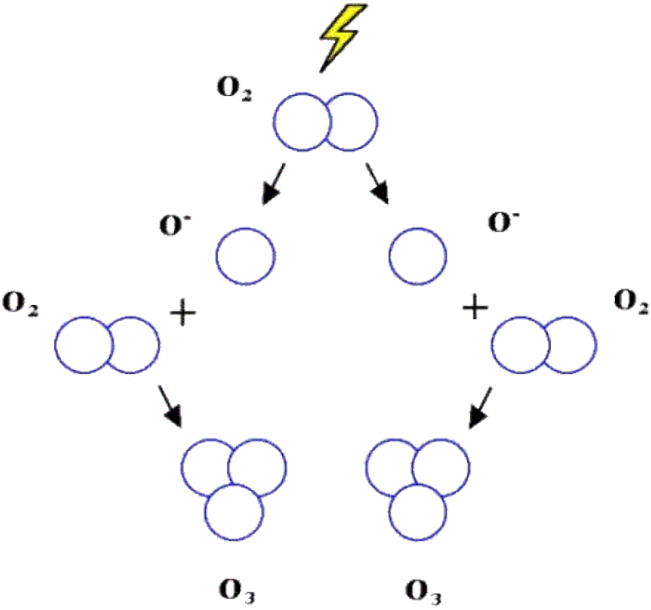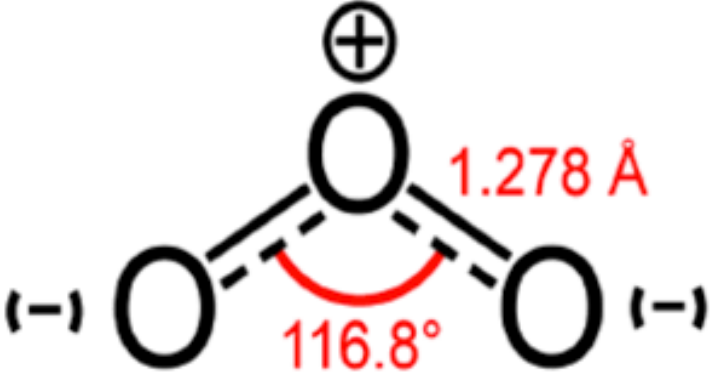
3-chloro-4(dichlorometyl)-5-hydroxy-2(5H)-furanone

…..Or Mutagen X (MX)

**they are all dangerous to human health**

Disinfection: peracetic acid

It is widely used in hospitals as a bactericide and fungicide, but has recently been suggested as a disinfectant in water purification because it does not lead to the formation of any toxic by-products.

hydrogen
peroxide

$$CH_3COOH + H_2O_2 \leftrightarrow CH_3CO_3H + H_2O$$

Acetic acid   Peracetic acid

Disinfection: Ozone (O$_3$)

$$3O_2 + \longrightarrow 2O_3$$

It is a very reactive compound, therefore it cannot be stored

It must be produced *in situ*

Disinfection: Ozone (O₃)

As always, we try to copy what happens in nature …


Ozone Production from Corona Discharge
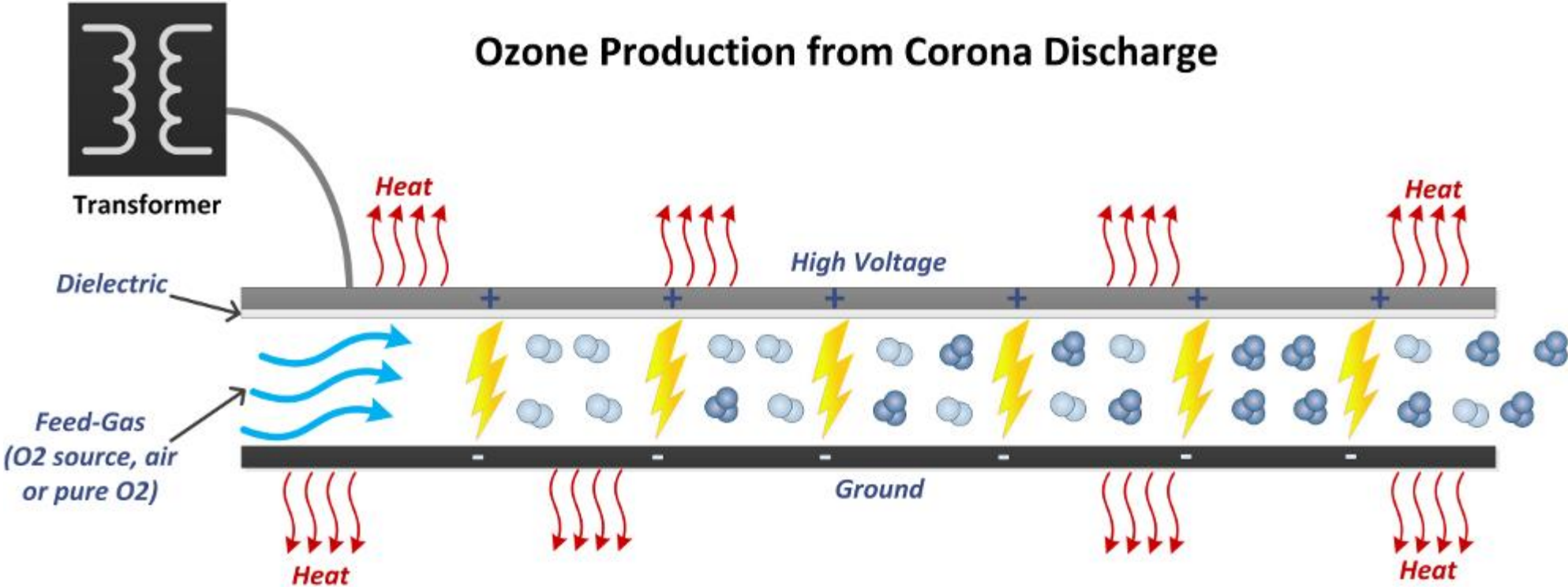
Ozone is formed via an electrical discharge that is diffused over an area using a dielectric to create a corona discharge. Oxygen passed through this corona discharge is converted to ozone.
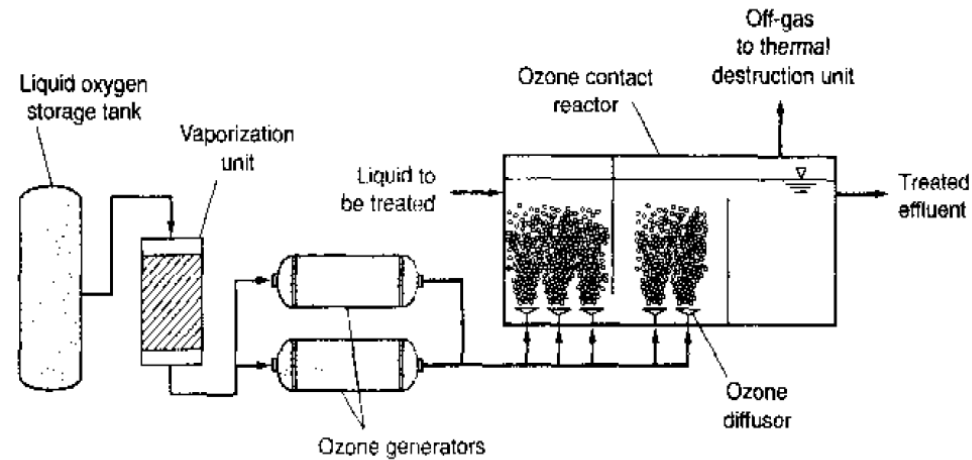
Disinfection: Ozone (O$_3$)
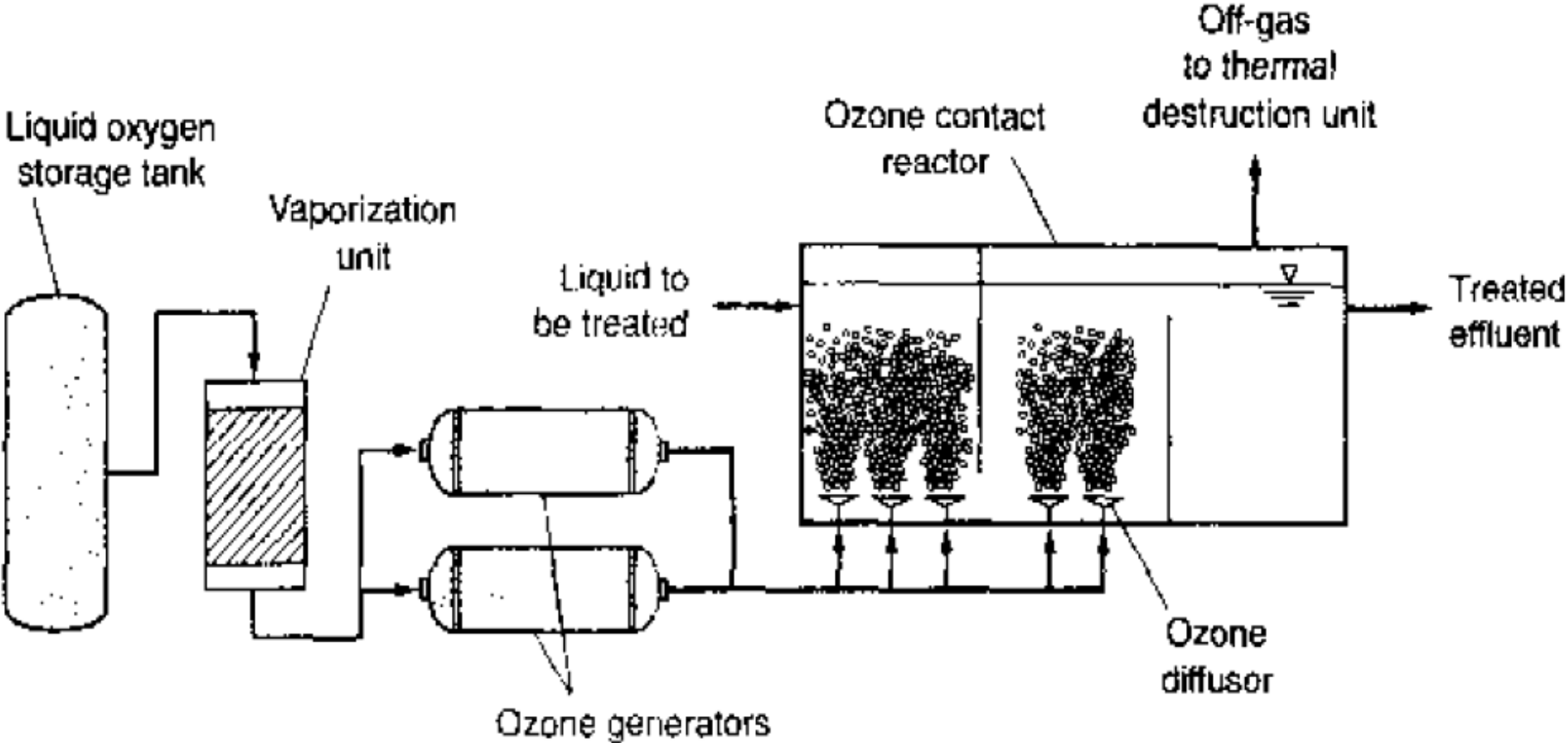
Disinfection: Ozone (O₃)

Ozone is a very powerful oxidant. For example, it is able to react with the molecules that make up the cell walls of microorganisms (algae, bacteria, viruses, fungi, spores... It has no mercy!
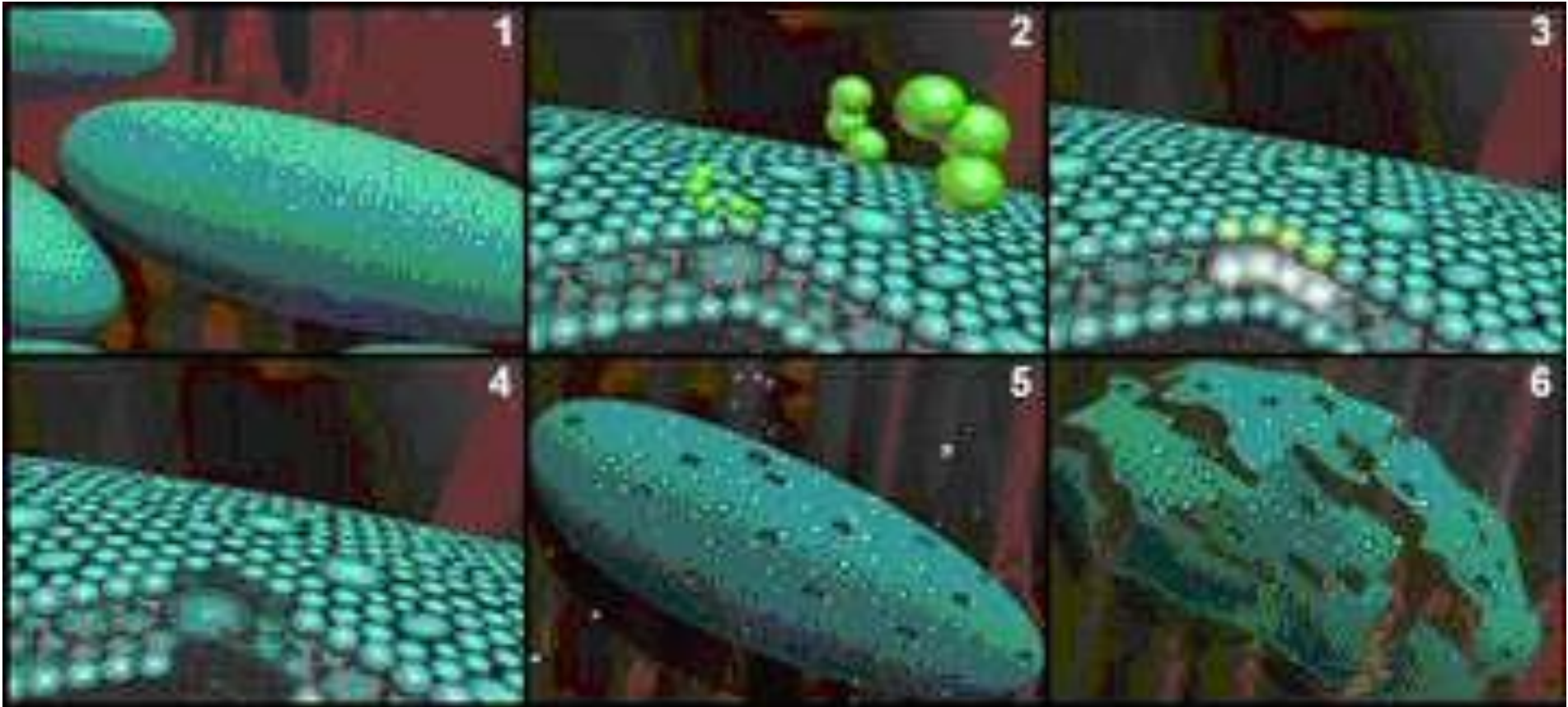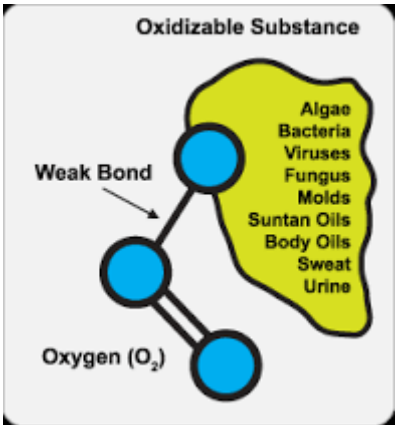
Disinfection: Ozone (O$_3$)

What if we used dry air instead of pure oxygen?

1) If we use pure oxygen, we find an ozone concentration equal to 3-10%, while with air (79% is N$_2$) the gaseous mixture would only have 1-3% ozone

2) Part of the nitrogen present in the air could be oxidized to form nitrogen monoxide: N$_2$ + O$_2$ → 2NO
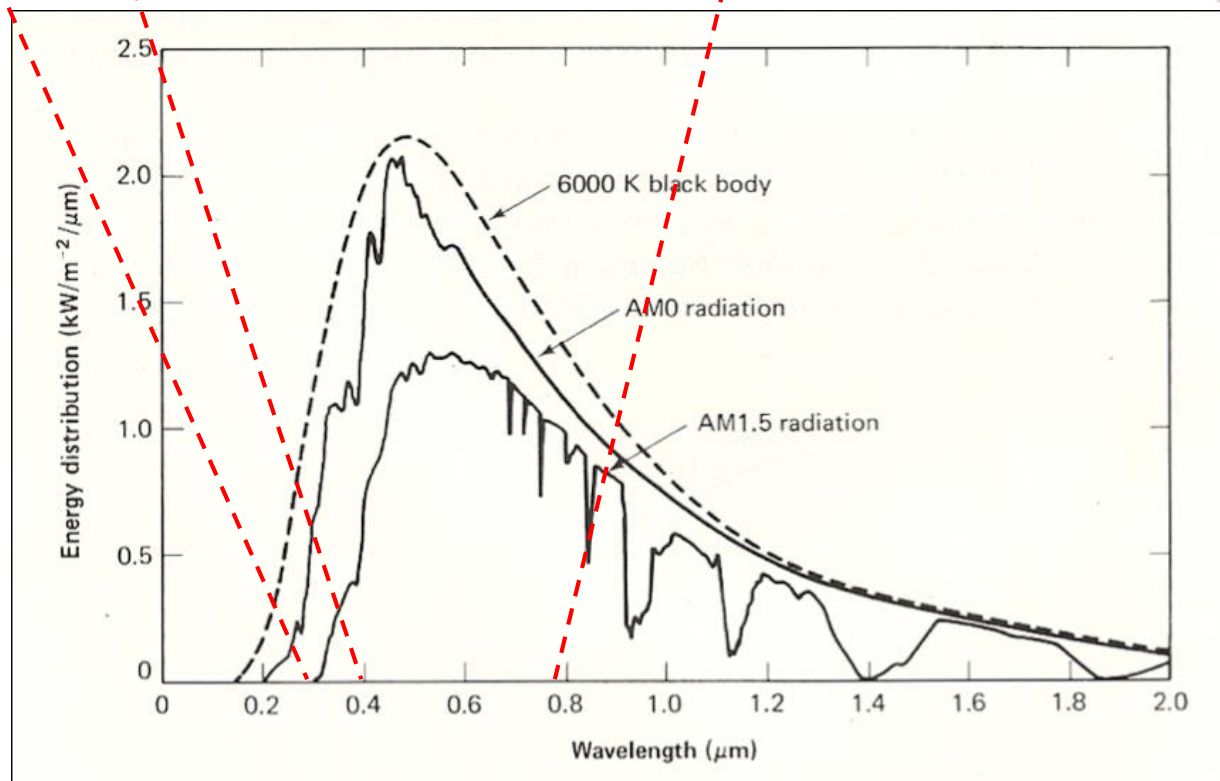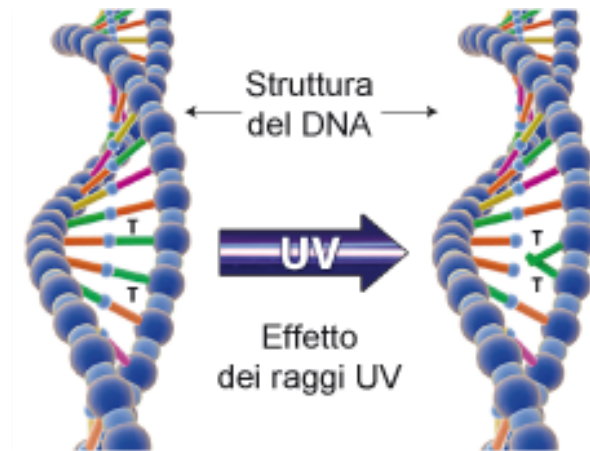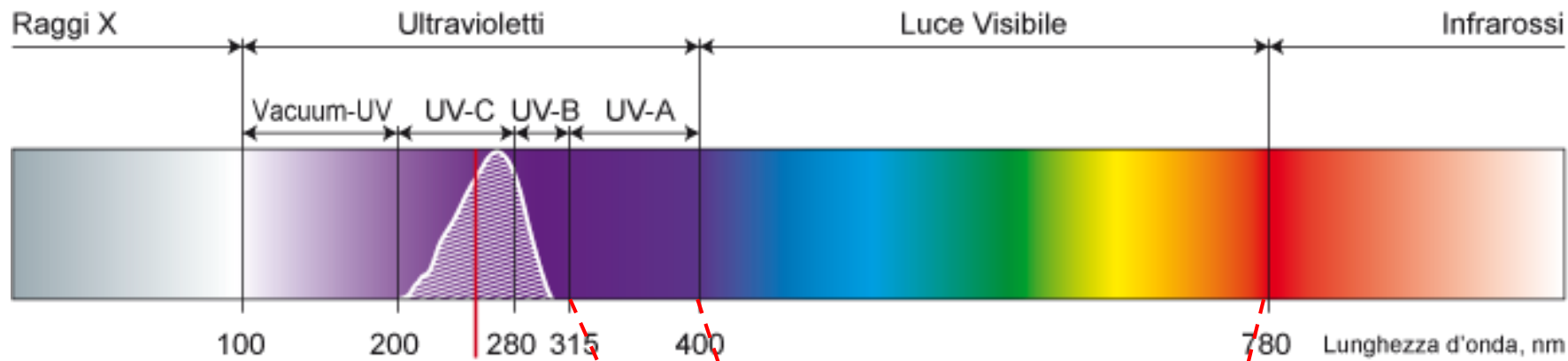Nitrogen monoxide can react (by consuming it) with ozone and form nitrogen dioxide: NO + O$_3$ → NO$_2$ + O$_2$

In addition to wasting ozone, we also produce the infamous NOx
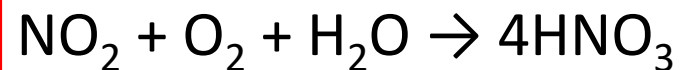
NO$_2$ + O$_2$ + H$_2$O → 4HNO$_3$ Now we know why dry air should be used! ;)

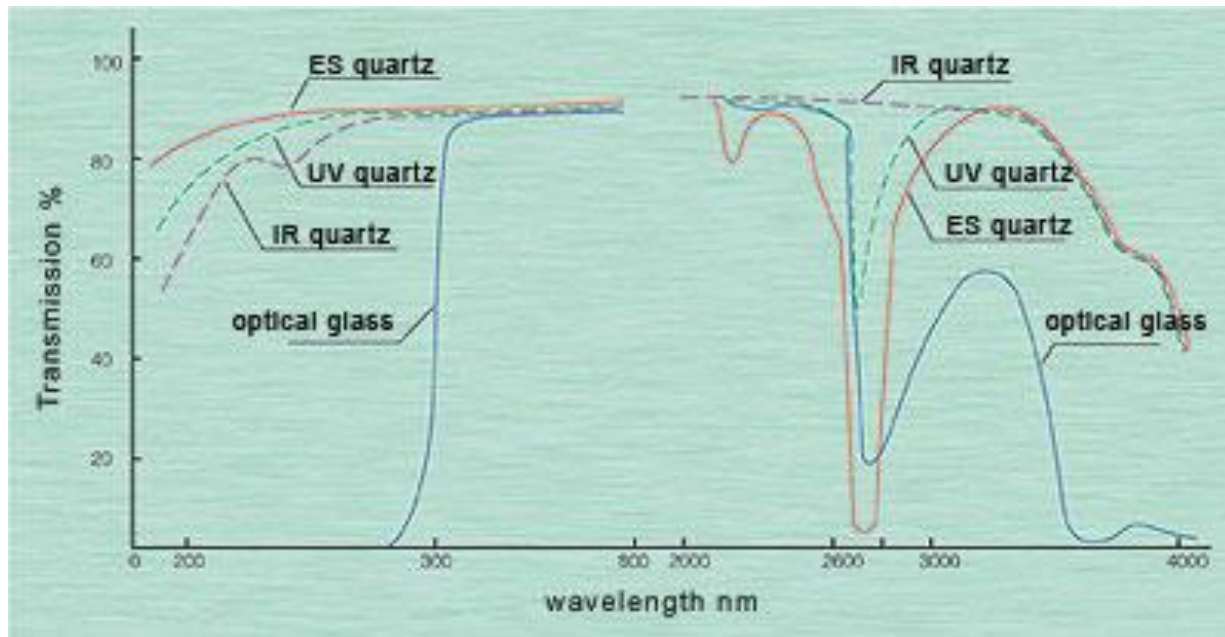# Disinfection: UVC radiation (UV$_{254\text{ nm}}$)

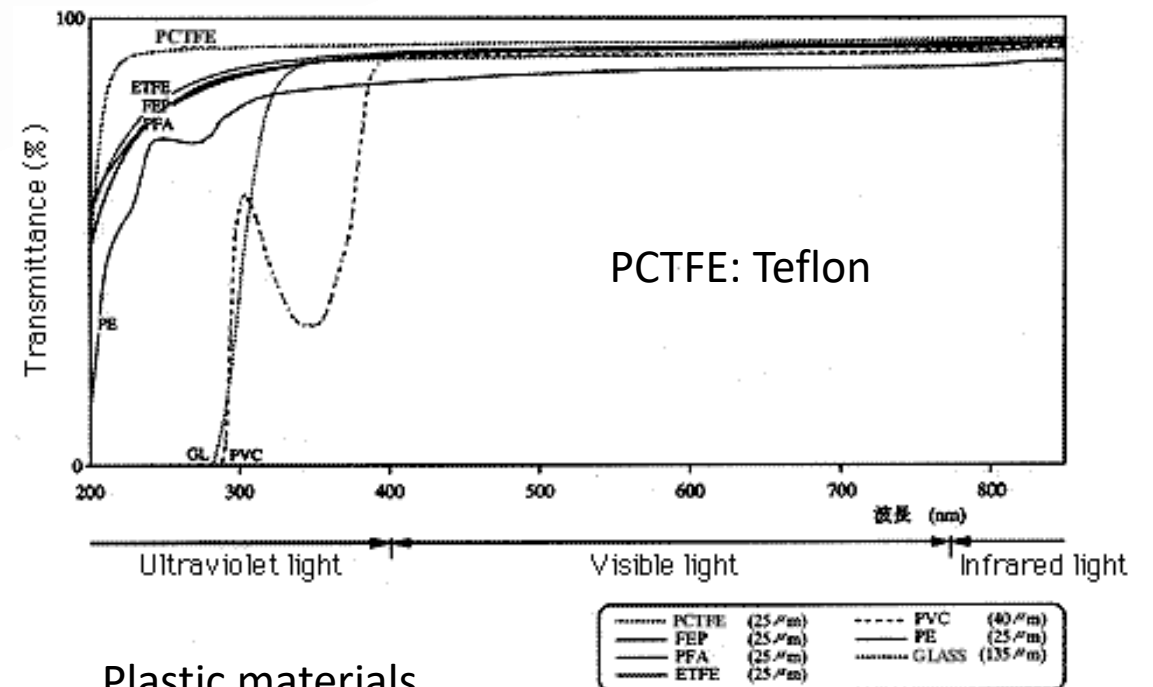# Disinfection: UVC radiation (UV$_{254\,nm}$)

UVC radiation can be produced with low pressure Hg vapor lamps equipped with a quartz sleeve.

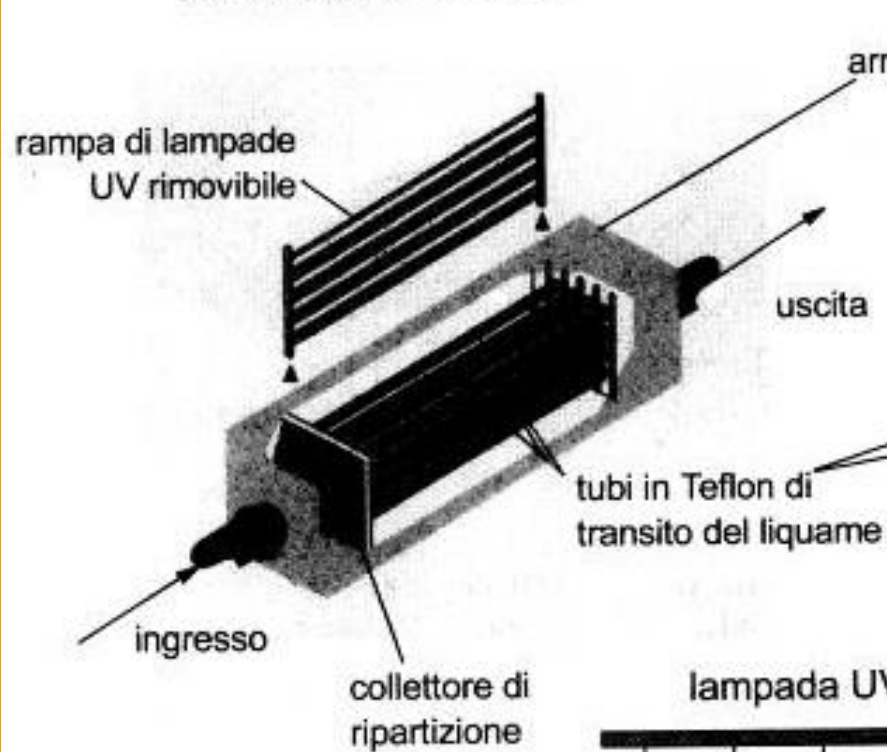Since quartz is expensive, why don't we use glass sleeves?

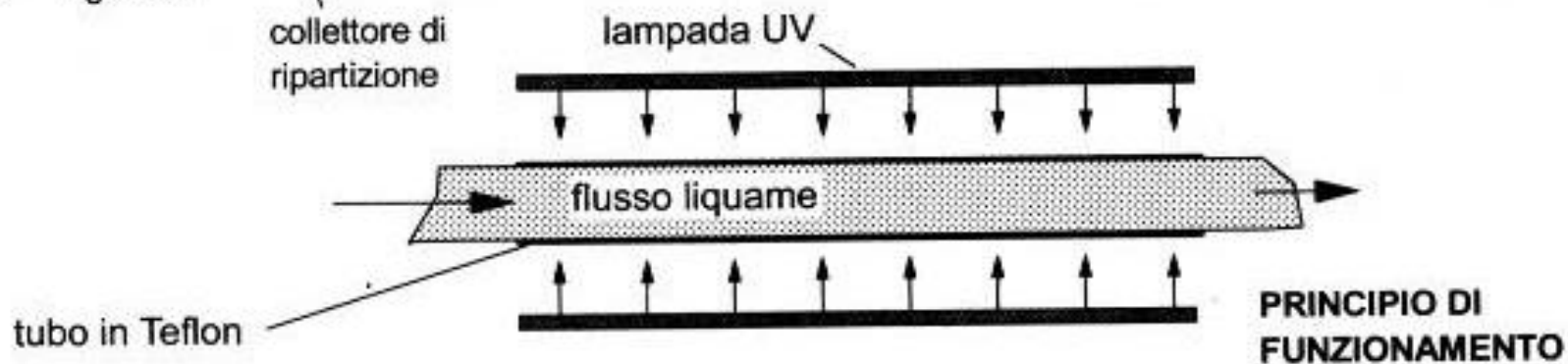SiO2 based materilas

PCTFE: Teflon

Plastic materials

VISTA PROSPETTICA

SEZIONE TRASVERSALE

rampa di lampade UV rimovibile

armadio in lamiera

rampe lampade UV

percorso dell'aria

alettatura raffreddamento aria

uscita

tubi in Teflon di transito del liquame

sostegno

ingresso

collettore di ripartizione

lampada UV

tubo in Teflon

flusso liquame

PRINCIPIO DI FUNZIONAMENTO

Ci=20-80 L/(min·lamp)

pannello di controllo

modulo UV estratto per manutenzione e pulizia

moduli UV

direzione del flusso

moduli UV

stramazzo per mantenimento del livello dell'acqua

vasca di contenimento

lampade

Disinfection: UVC radiation (UV$_{254\,nm}$)

During disinfection with UVC raradiation we not only break down the microbial load: we can also oxidize (and remove) some compounds. This phenomenon proceeds in two steps: 1) the compound absorbs UVC radiation and excites; 2) the excited molecule photolizes. This process is called direct photolysis.

$$S + h\nu \rightarrow S^*$$
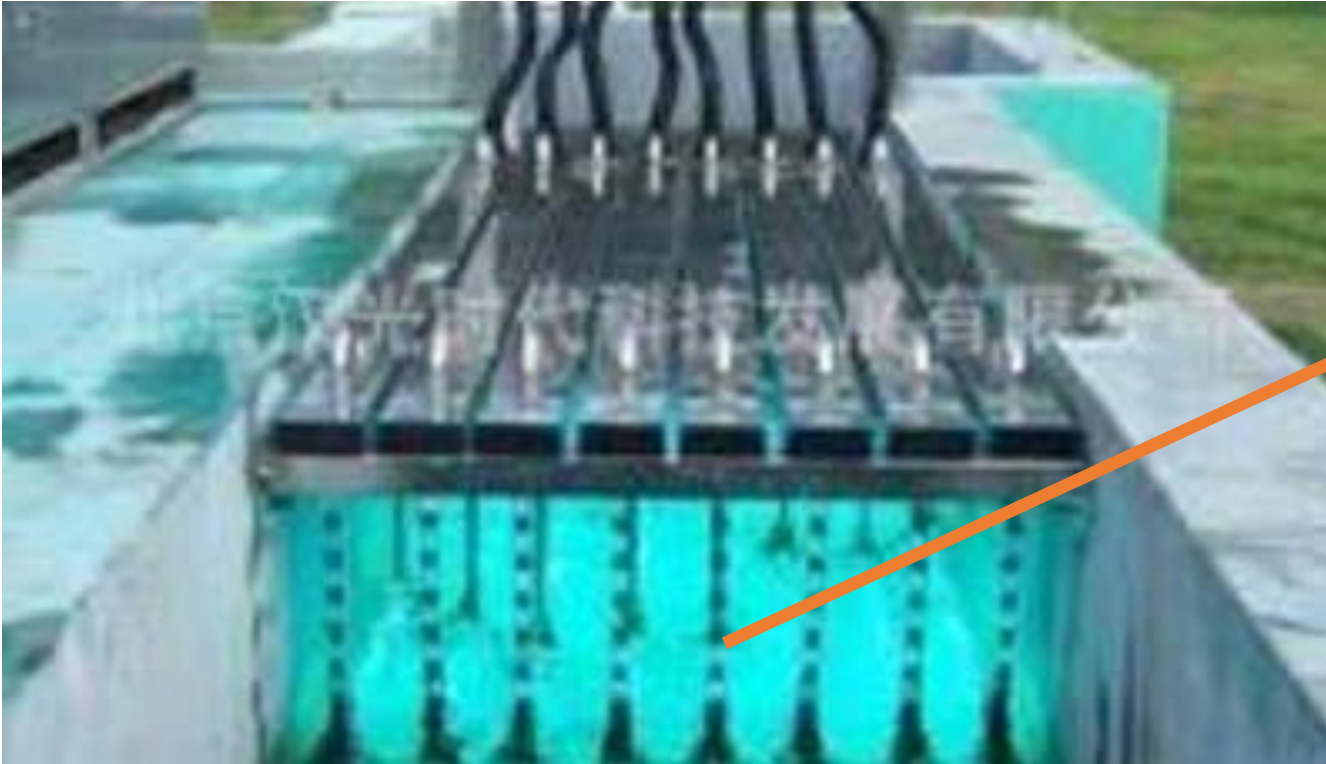
$$S^* \rightarrow \text{by-products}$$

WARNING: by-products are not necessarily less harmful than S ...

Absorbance: Lambert & Beer law
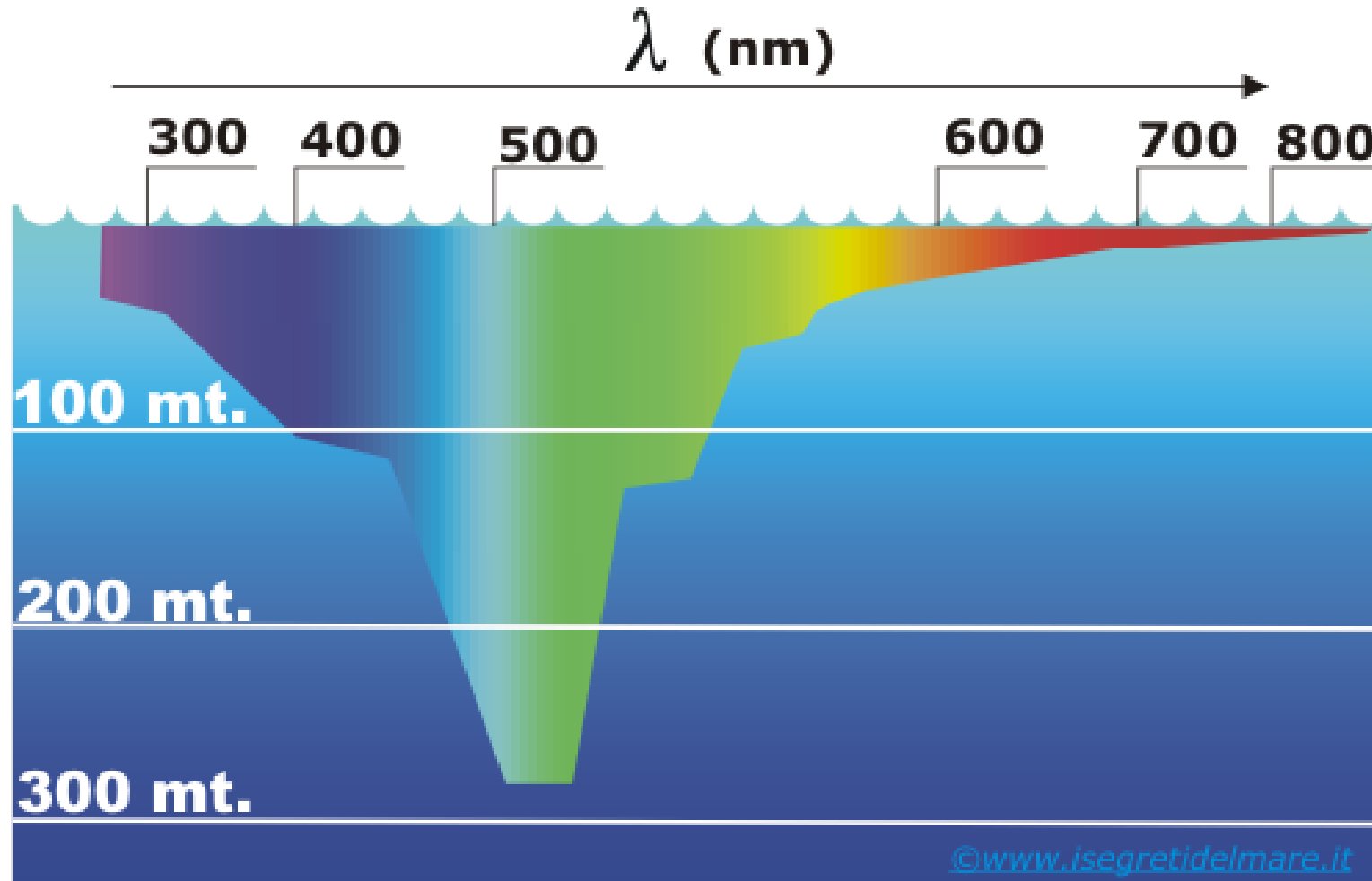
How do we explain this phenomenon?
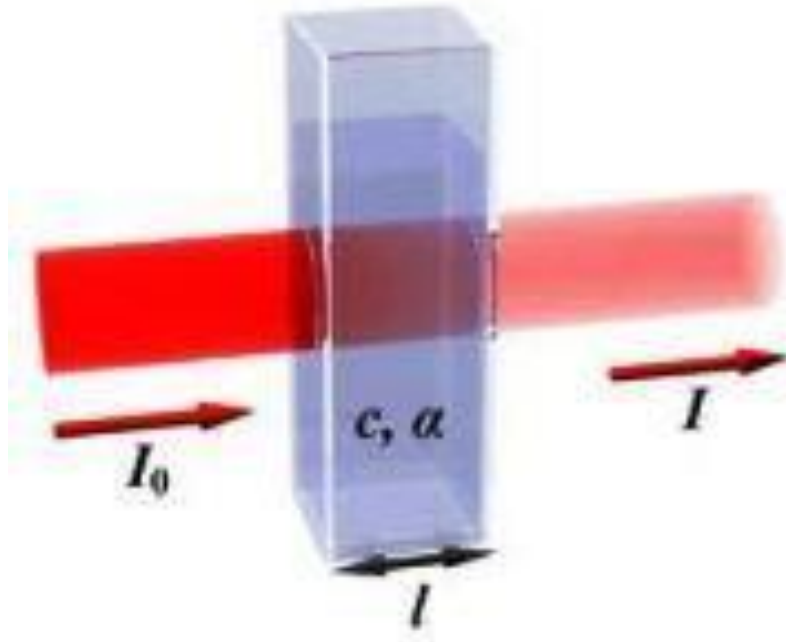
Absorbance: Lambert & Beer law

1760 - According to Lambert, the absorption of a light radiation I_0 by a solution depends on its "average optical path", i.e. on its thickness l.

1852 - According to Beer, the absorption of a light radiation I_0 by a solution depends on the concentration of compounds C able to absorb it.

Absorbance: Lambert & Beer law

Absorbance (dimensionless)

$$A = \log(I_0) - \log(I)$$

$$A = \log\left(\frac{I_0}{I}\right)$$

l: **medium optical path**

If in the solution there is a compound S, at concentration [S], and which absorbs radiation characterized by a wavelength λ, the absorbance will be:

Lambert & Beer law: $\qquad A = \varepsilon_S^\lambda \cdot l \cdot [S]$ $\qquad\qquad \dfrac{I_0}{I} = e^{2,3 \cdot \varepsilon_S^\lambda \cdot l \cdot [S]}$

Lambert & Beer law: $A = \varepsilon_S^{\lambda} \cdot l \cdot [S]$

$$A = \log\left(\frac{I_0}{I}\right)$$

$$\frac{I_0}{I} = 10^{\varepsilon_S^{\lambda} \cdot l \cdot [S]}$$

$$\frac{I_0}{I} = e^{2,3 \cdot \varepsilon_S^{\lambda} \cdot l \cdot [S]}$$

$$I = I_0 \cdot e^{-2,3 \cdot \varepsilon_S^{\lambda} \cdot l \cdot [S]}$$

$I_a = I_0 - I$ = radiation absorbed by the solution

$$I_a = I_0 \cdot \left(1 - e^{\left(-2,3 \cdot \varepsilon_S^{\lambda} \cdot l \cdot [S]\right)}\right)$$

$$\varepsilon_S^\lambda : \text{molar extinction coefficient} \left(\frac{L}{moli \cdot cm}\right)$$

it is a constant that depends on the substance and the wavelength. It represents the ability of a compound to absorb radiation having a given wavelength λ.

It is measured with a spectrophotometer

light source

diffraction grating

detector

aperture

sample cuvette
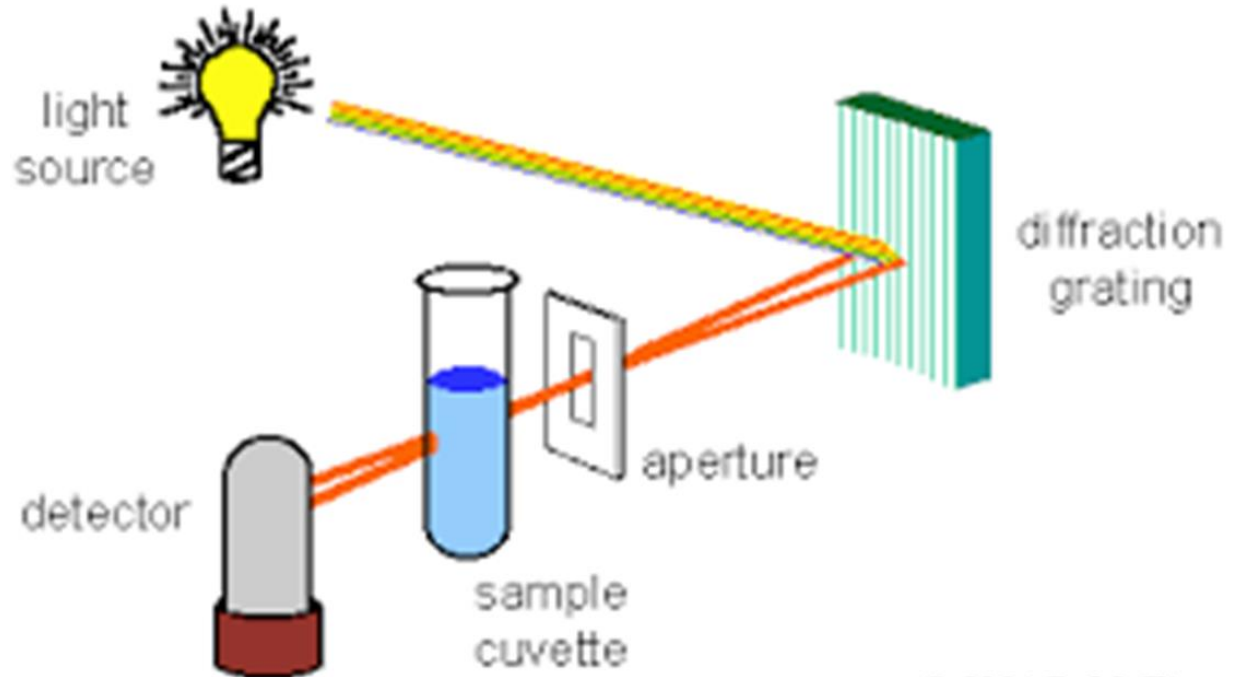
Absorption spectra of Methotrexate (MTX)
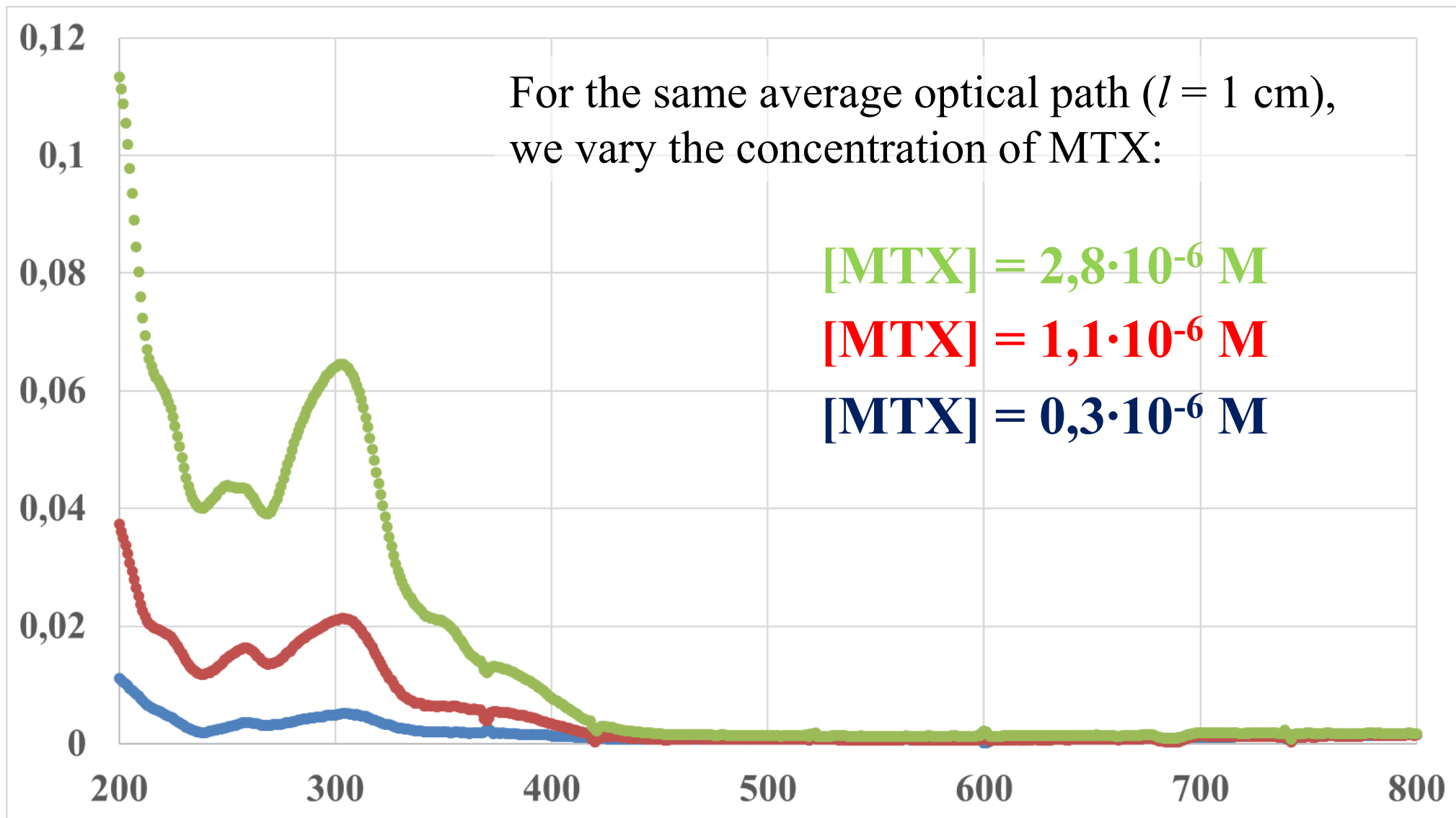
For the same average optical path ($l = 1$ cm), we vary the concentration of MTX:

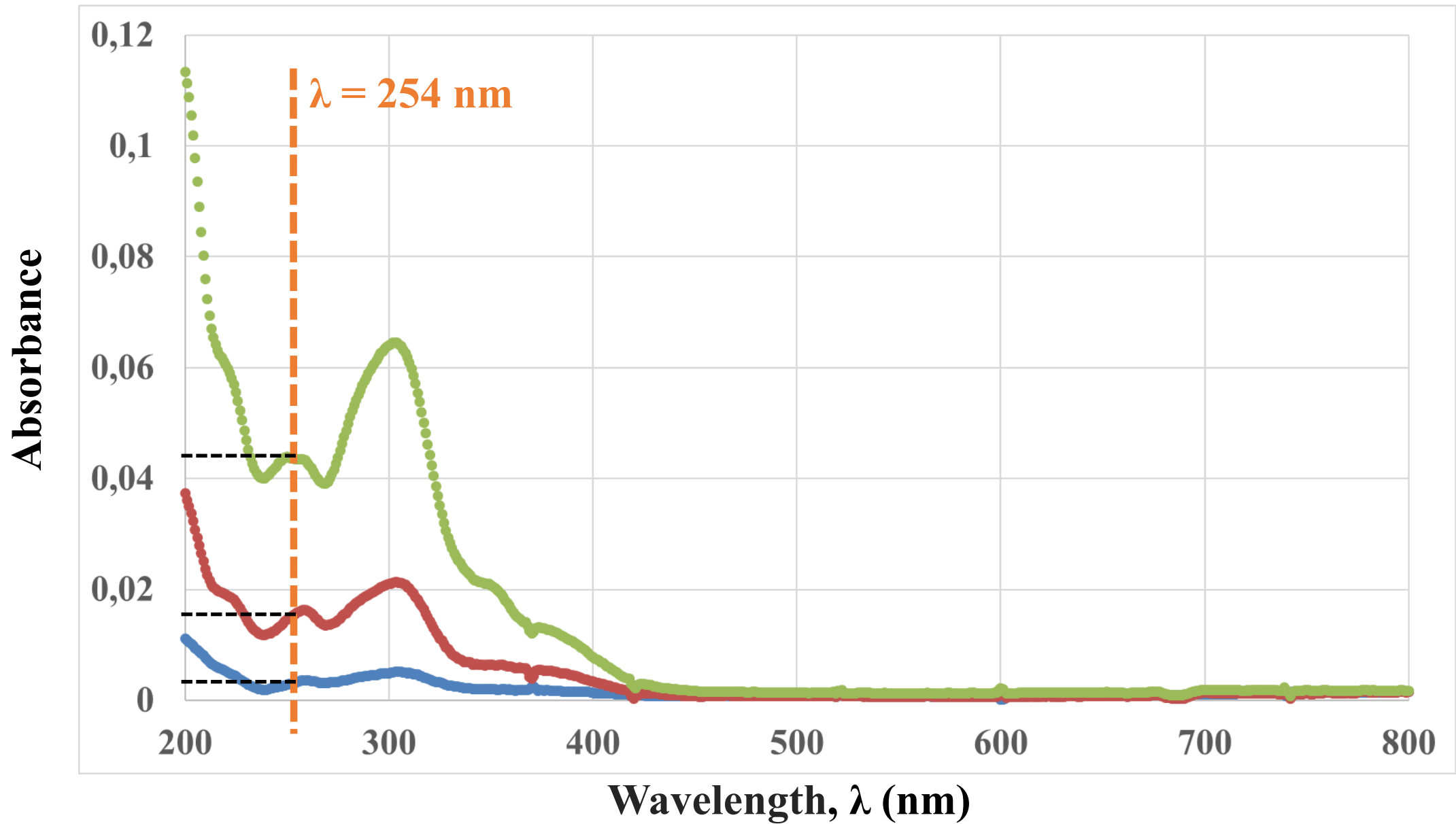$[MTX] = 2,8 \cdot 10^{-6}$ M

$[MTX] = 1,1 \cdot 10^{-6}$ M

$[MTX] = 0,3 \cdot 10^{-6}$ M

Evaluation of $\varepsilon_{MTX}^{\lambda=254nm}$
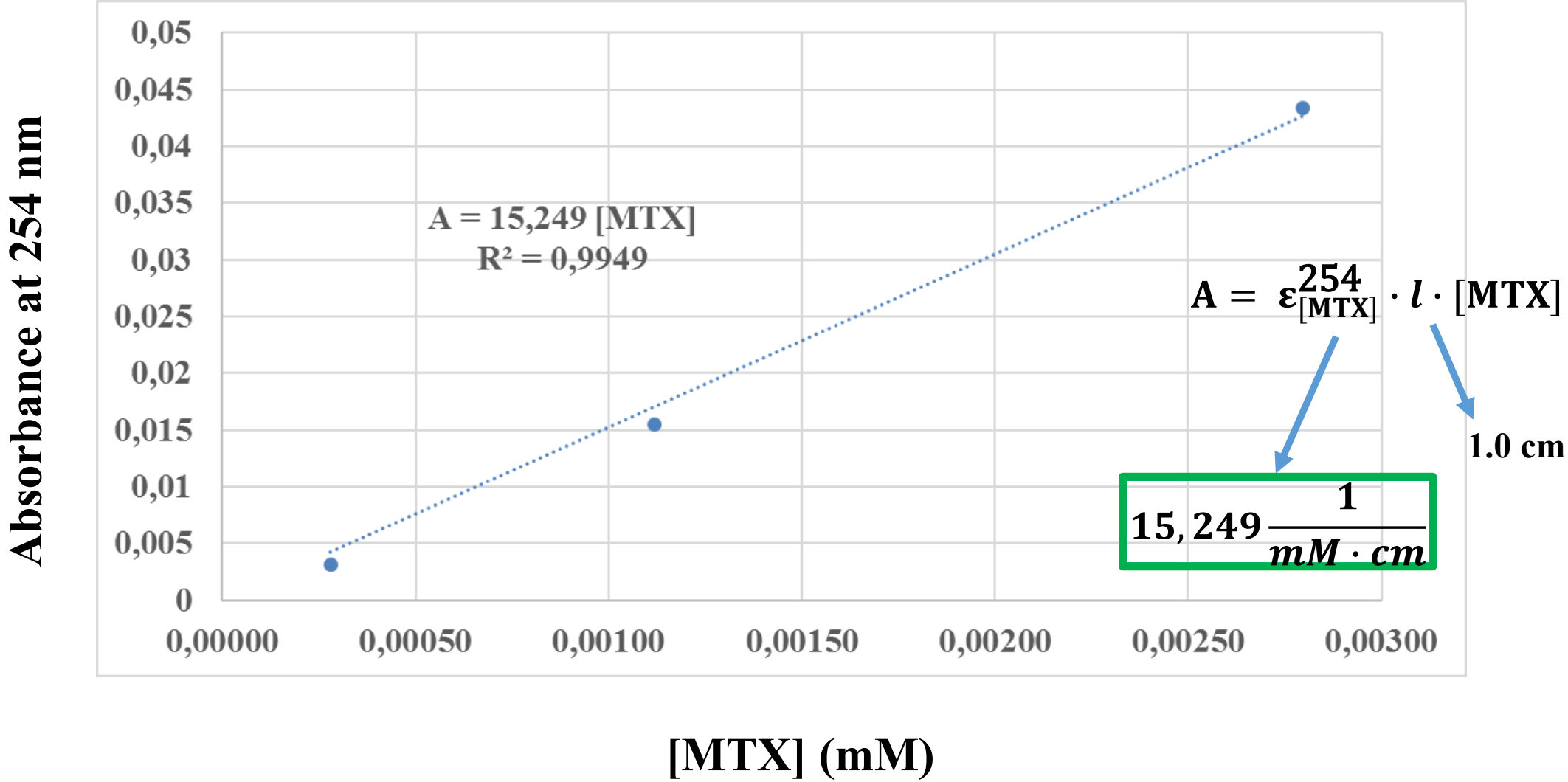
$\lambda = 254$ nm

Evaluation of $\varepsilon_{MTX}^{\lambda=254nm}$

$A = 15,249 \, [MTX]$
$R^2 = 0,9949$

$A = \varepsilon_{[MTX]}^{254} \cdot l \cdot [MTX]$

1.0 cm

$15,249 \, \dfrac{1}{mM \cdot cm}$

What happens if a compound S absorbs radiation?

The first thing he does is 'get excited'

$$S + h\nu \rightarrow S*$$

$$S* \rightarrow S + \text{heat}$$

$$S* + P \rightarrow S + P*$$

$$S* \rightarrow \text{by-products}$$
«direct photolysis»
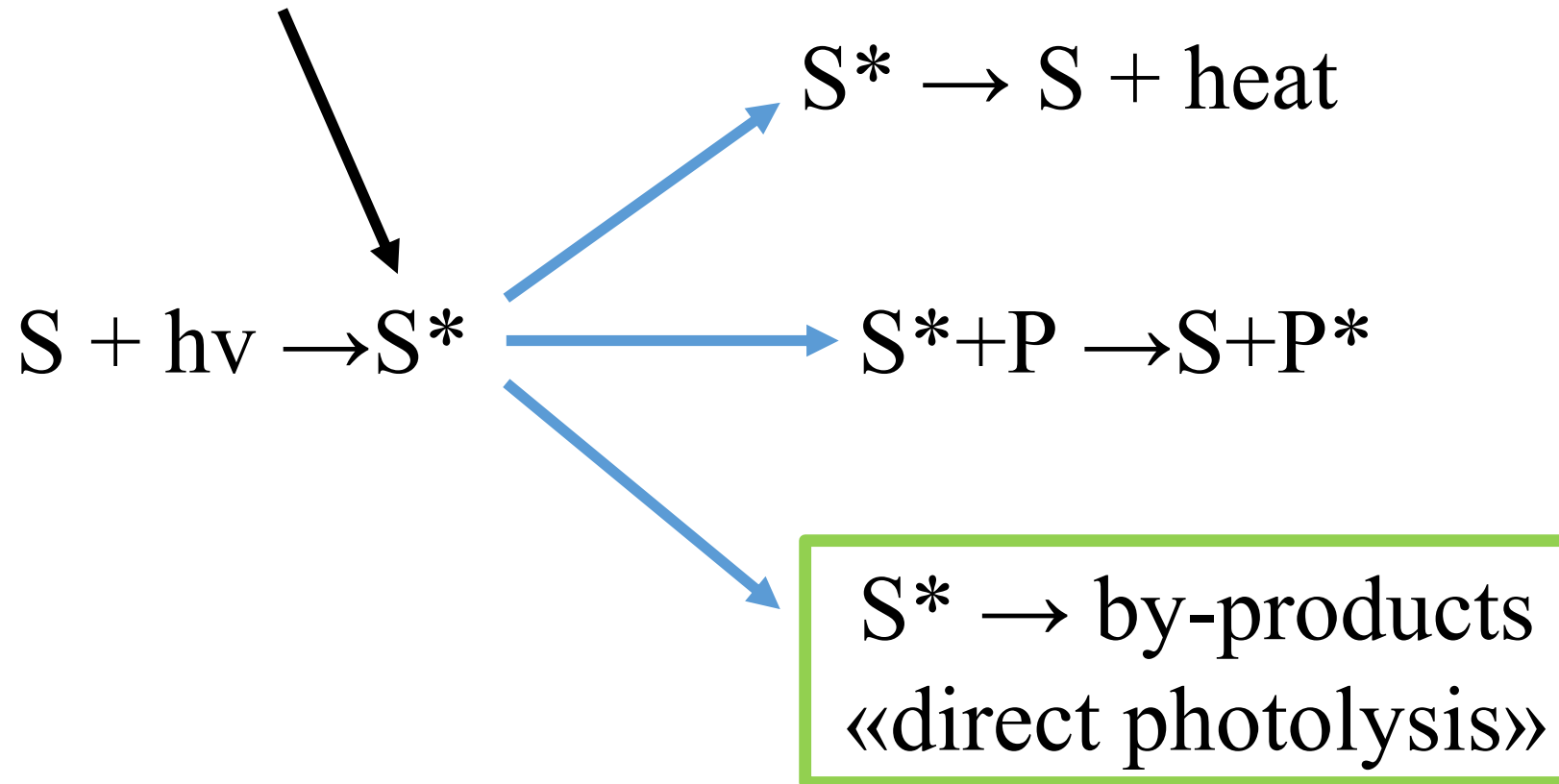
Direct photolysis

To photolize a substance under the effect of radiation with a wavelength λ, it is necessary it absorbs the radiation. Therefore, the following condition must occur:

$$\varepsilon_S^\lambda \neq 0$$

If this condition has occurred, then it is possible that S photolises, at a rate equal to:

$$\frac{d[S]}{dt} = -\frac{I_a^\lambda}{V} \cdot \Phi_S^\lambda$$

I_a^λ: represents the absorbed radiation and is expressed in (Ein are Einstein)

V: represents the solution volume(L)

Φ_S^λ: represents the 'quantum yield' and it is expressed in mol_S/Ein

To understand this, it is better to define this new unit of measurement: the Einstein

An Einstein represents the energy associated with a mole of photons

According to Einstein's equation, a photon carries an energy equal to: **h·v·c**

h: Plank constant. $6,6 \cdot 10^{-34}$ J·s

v: frequency (1/m). (is the inverse of λ: $v=1/\lambda$)

c: light speed. $3 \cdot 10^5$ Km/s

By representing Avogadro's number ($6.02 \cdot 10^{23}$) with NA, we can express an Ein as:

$$1Ein = \frac{NA \cdot h \cdot c}{\lambda} \quad (J)$$

Note: radiation with a lower wavelength is characterized by greater energy!

Returning to direct photolysis…

$$\frac{d[S]}{dt} = -\frac{I_a^\lambda}{V} \cdot \Phi_S^\lambda$$

$$I_a = I_0 \cdot \left(1 - e^{\left(-2,3 \cdot \varepsilon_S^\lambda \cdot l \cdot [S]\right)}\right)$$

$$\frac{d[S]}{dt} = -\frac{\Phi_S^\lambda}{V} \cdot I_0 \cdot \left(1 - e^{\left(-2,3 \cdot \varepsilon_S^\lambda \cdot l \cdot [S]\right)}\right)$$

To observe the photolysis of S under a radiation λ, these two conditions must occur:

$$\varepsilon_S^\lambda \neq 0 \qquad \Phi_S^\lambda \neq 0$$

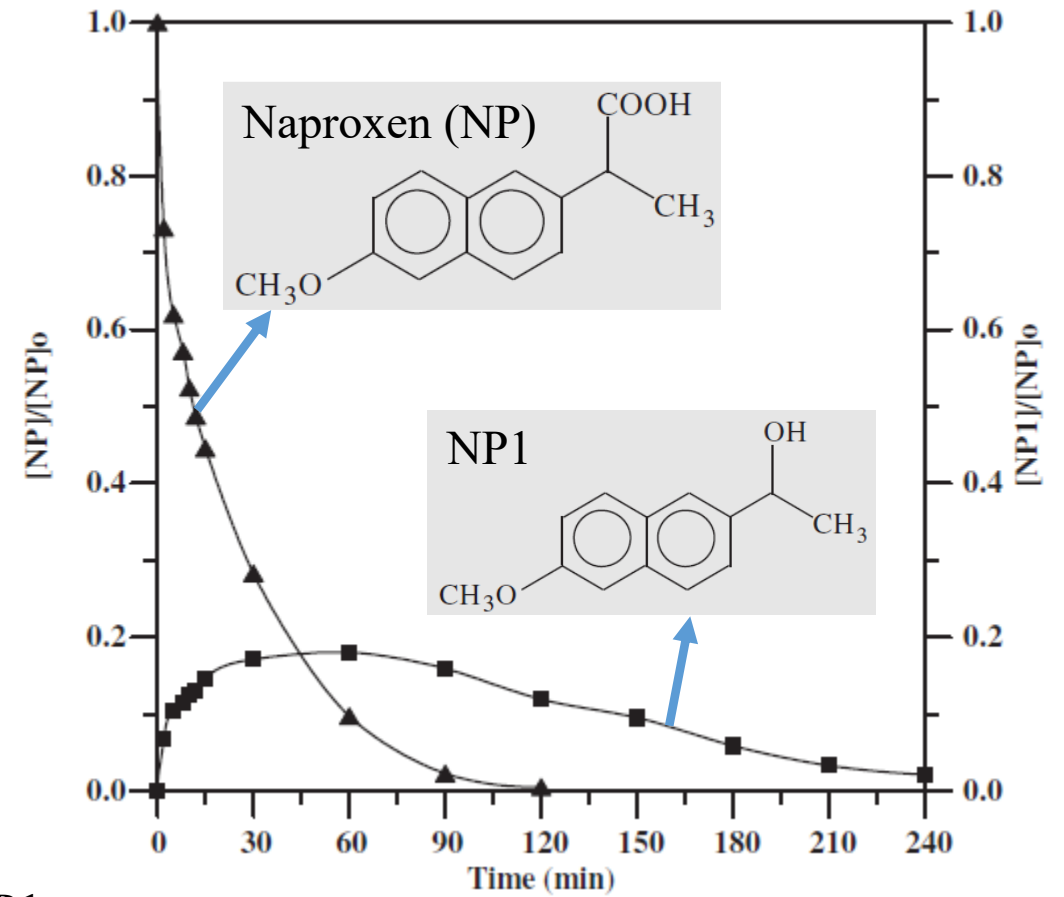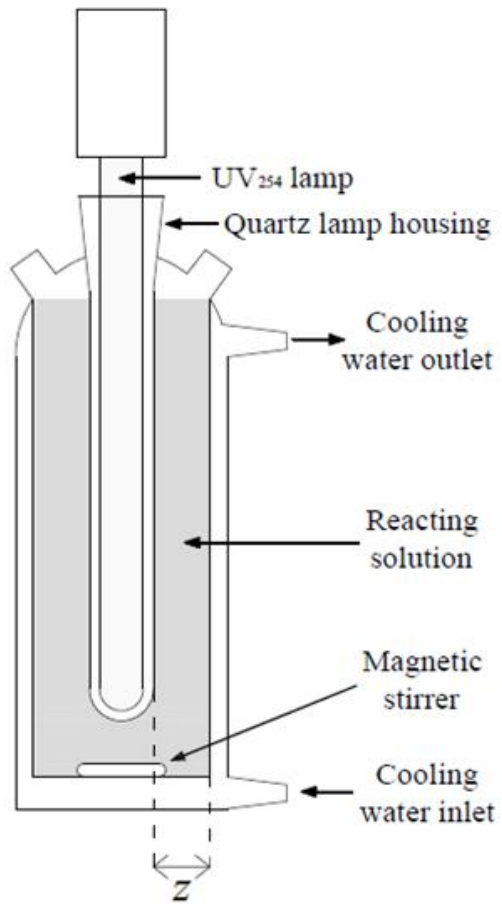# Meaning of the quantum yield Φ_S^{λ}

Φ_S^{λ} has units of measurement equal to mol/Ein.

It makes us understand how many moles of S photolize for each Eistein of radiation at the wavelength λ absorbed by S

Example 1: in solution there are other compounds;
Example 2: effect of by-products;

Example: Direct photolysis of Naproxen

$$NP + h\nu \rightarrow NP1$$

$$\varepsilon_{NP}^{254} = 4{,}18 \cdot 10^3 \ M^{-1}cm^{-1}$$

$$\Phi_{NP}^{254} = 1{,}29 \cdot 10^{-2} \ moli \cdot E^{-1}$$

Esempio: Fotolisi diretta del Naproxene

ORIGINAL PAPER

M. DellaGreca · M. Brigante · M. Isidori · A. Nardelli ·
L. Previtera · M. Rubino · F. Temussi

Phototransformation and ecotoxicity of the drug Naproxen-Na

Conclusion

Naproxen Na was found to be light sensitive in biomimetic conditions affording several photoproducts. Toxicity data indicate that exposure of bacteria and crustaceans to the parental drug and its photoderivatives caused effects at the order of mg/L. These concentrations do not represent the amounts expected in aquatic environment, but they might be found in sewage treatment plants where the daily load of naproxen is in the order of grams (Ternes 1998). These results underscore the importance of identifying reaction products in environmental systems. Furthermore, it would be very important to also evaluate the chronic toxicity of these compounds for aquatic organisms.

BISOGNA TROVARE UNA SOLUZIONE!

Simplified photolysis rate

$$\frac{d[S]}{dt} = -\frac{\Phi_S^\lambda}{V} \cdot I_0 \cdot \left(1 - e^{\left(-2,3 \cdot \varepsilon_S^\lambda \cdot l \cdot [S]\right)}\right)$$

If $2,3 \cdot \varepsilon_S^\lambda \cdot l \cdot [S]$ is close to zero (this case occurs when the solutions are very diluted), the photolysis rate of S can be expressed as:

$$\frac{d[S]}{dt} = -\frac{\Phi_S^\lambda}{V} \cdot I_0 \cdot 2,3 \cdot \varepsilon_S^\lambda \cdot l \cdot [S]$$
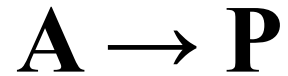
It is a constant

$$\frac{d[S]}{dt} = -k_S^\lambda \cdot [S]$$

It is a pseudo-first order kinetic: the photolysis rate of S is a function of only k and [S]

Kinetics of reactions

Let us consider a generic reaction

$$\mathbf{A \rightarrow P}$$

The speed with which A is consumed is given by:

$$\mathbf{\frac{d[A]}{dt} = -k \cdot [A]^n}$$

n: order of the reaction (in the case of a direct photolysis reaction in dilute solutions we have seen that the reaction is pseudo-first order)

k: kinetic constant ... depends temperature.

kinetic constant expression according to Arrhenius

$$k = k_0 \cdot e^{\left(-\frac{Ea}{R \cdot T}\right)}$$

k_0: pre-exponential constant. It is a parameter depending on the reaction type: it represents the the maximum value of the kinetic constant

Ea: Activation energy. It is a parameter depending on the reaction type.

R: universal gas constant.

T: temperature

Reaction kinetics

$$\frac{d[A]}{dt} = -k_0 \cdot e^{\left(-\frac{Ea}{R \cdot T}\right)} \cdot [A]^n$$

The reaction rate depends on 3 kinetic parameters: k_0, T and n

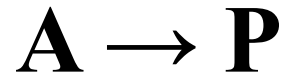Let's make a hypothesis that simplifies the problem: T=cost.
Consequently, $\frac{Ea}{R \cdot T} = \text{cost}$

$$k = -k_0 \cdot e^{\left(-\frac{Ea}{R \cdot T}\right)}$$

$$\frac{d[A]}{dt} = -k \cdot [A]^n$$

The reaction rate depends on 2 kinetic parameters: k and n.

Zero order kinetics

$$A \rightarrow P$$

$$\frac{d[A]}{dt} = -k \cdot [A]^0 = -k$$

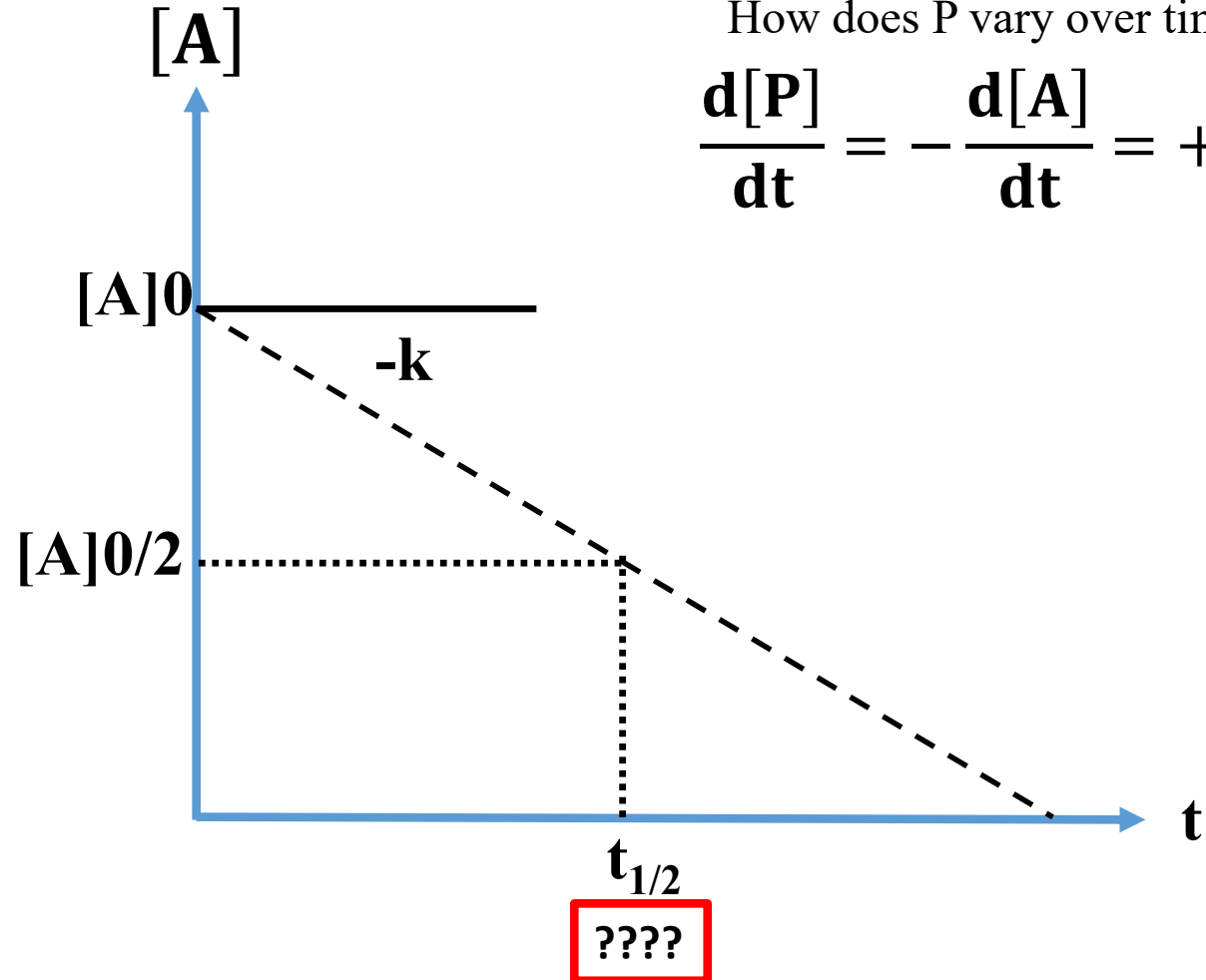$$d[A] = -kdt$$

after integrating the equation, we obtain:

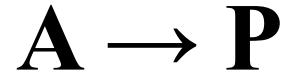$$[A] = -kt + \textbf{cost}$$

At t=0, $[A]=[A]_0$

$$[A] = -kt + [A]0$$

How does P vary over time?

$$\frac{d[P]}{dt} = -\frac{d[A]}{dt} = +k$$

[A]

[A]0

-k

[A]0/2

$t_{1/2}$

????

t

In this case k has a unit of measurement equal to M / t (if the concentration of A is expressed in M)

First order kinetics

$$A \rightarrow P$$

$$\frac{d[A]}{dt} = -k \cdot [A]^1$$
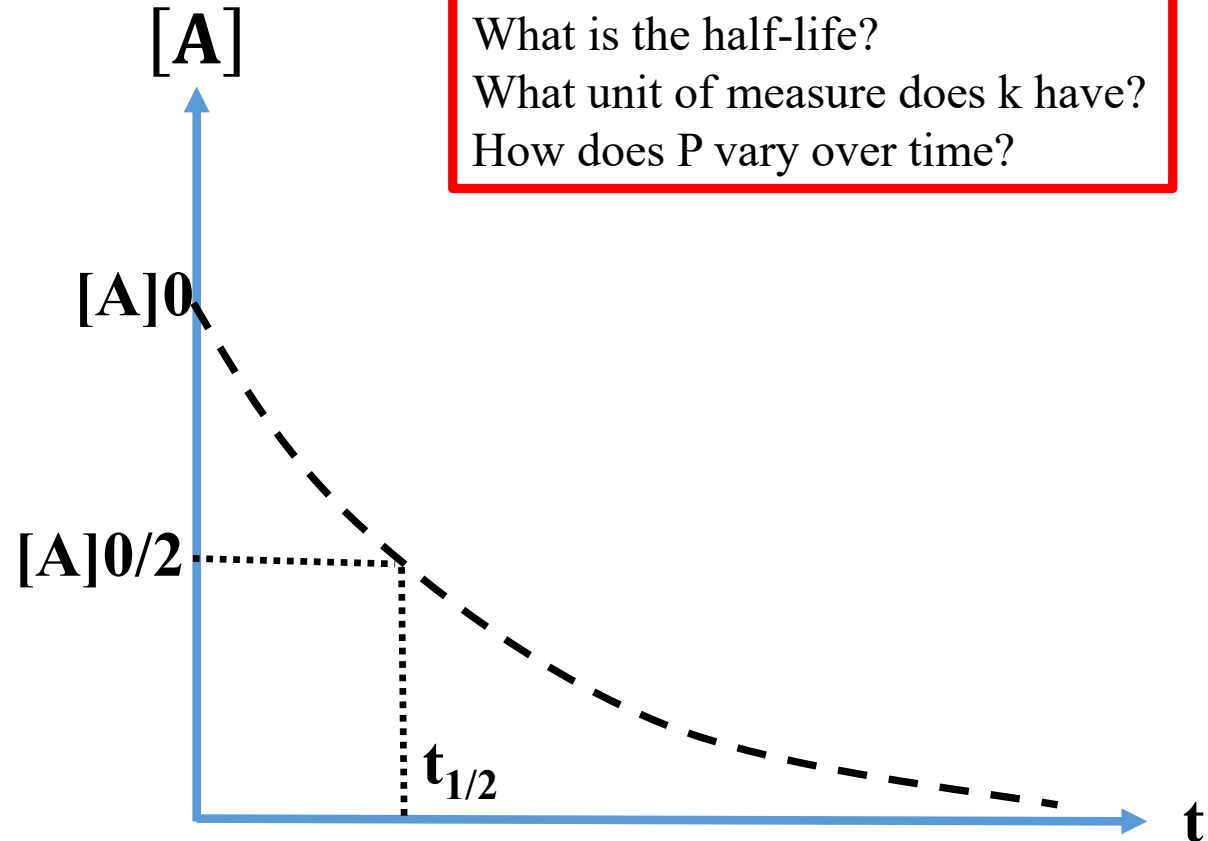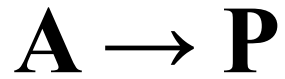
$$\frac{d[A]}{[A]} = -kdt$$

$$\ln[A] = -kt + cost$$

At t=0, $[A]=[A]_0$

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \quad \text{that is} \quad [A] = [A]_0 \cdot e^{-kt}$$

What is the half-life?
What unit of measure does k have?
How does P vary over time?

Second order kinetics

$$A \rightarrow P$$

$$\frac{d[A]}{dt} = -k \cdot [A]^2$$

$$\frac{d[A]}{[A]^2} = -kdt$$

$$-\frac{1}{[A]} = -kt + cost$$

At t=0, $[A]=[A]_0$
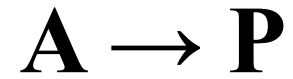
$$-\frac{1}{[A]} = -kt - \frac{1}{[A]_0}$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$
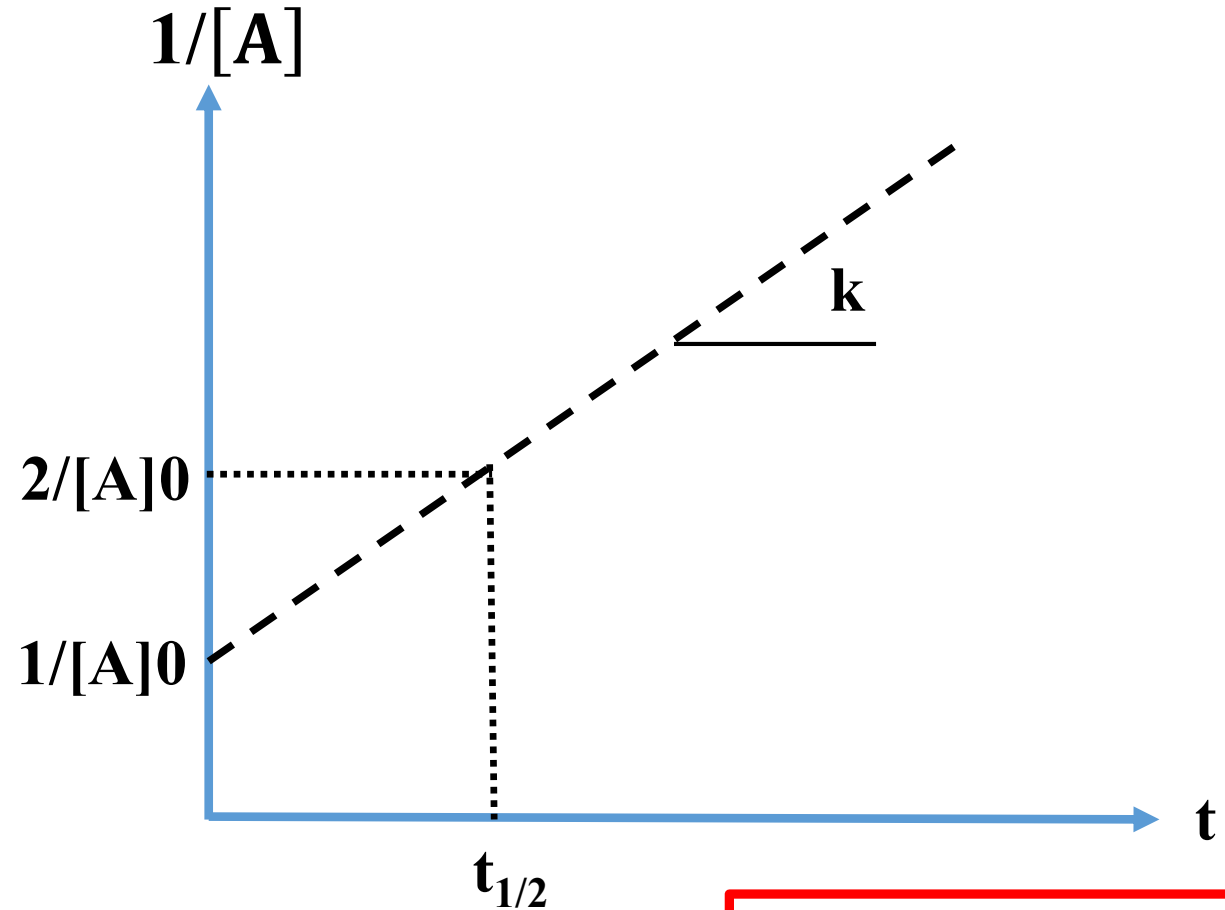
What is the half-life?
What unit of measure does k have?
How does P vary over time?

n-order kinetics

$$A \rightarrow P$$
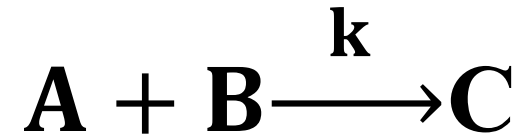
$$\frac{d[A]}{dt} = -k \cdot [A]^n$$

$$\frac{d[A]}{[A]^n} = -kdt$$

$$\frac{[A]^{1-n}}{1-n} = -kt + cost$$

How do you understand the order of a reaction?? We do many experimental tests and we see which pair of k and n give the theoretical trends that best intercept the experimental points.
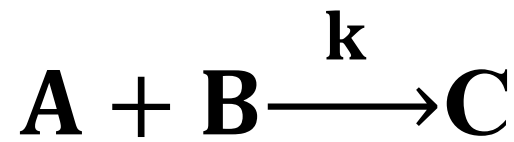
n-order kinetics

$$A + B \xrightarrow{k} C$$

$$\frac{d[A]}{dt} = -k \cdot [A]^{\alpha} \cdot [B]^{\beta} \qquad \frac{d[B]}{dt} = -k \cdot [A]^{\alpha} \cdot [B]^{\beta}$$

$$\frac{d[C]}{dt} = +k \cdot [A]^{\alpha} \cdot [B]^{\beta}$$

The exponents (**α and β**), which can be fractional, are called partial orders of reaction and their sum is the overall order of reaction.

In a dilute solution, an elementary reaction (one having a single step with a single transition state) is empirically found to obey the law of mass action. This predicts that the rate depends only on the concentrations of the reactants, raised to the powers of their stoichiometric coefficients

$$A + B \xrightarrow{k} C$$

$\alpha = 1$
$\beta = 1$
$\alpha + \beta = 2$

$$\frac{d[C]}{dt} = +k \cdot [A] \cdot [B]$$

We have a second order kinetics