**Flomeko2019**
International Flow Measurement Conference

# Uncertainty of $SO_2$ measurements in dryers due to water droplet and water film condensation

**Stanislav Knotek[1]**
**Jan Geršl[1]**
**Aleš Paták[2]**

[1]Czech Metrology Institute
[2]Institute of Scientific Instruments of the Czech Academy of Sciences
Czech Republic

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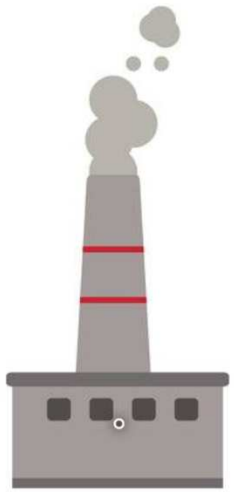
# SulfNorm – EMPIR project

## Motivation

- $SO_2$ pollution has significant impact on health of population
- Most of $SO_2$ is produced by industrial processes
- Accurate measurement is needed



## Intention of the project

- Prenormative work for **new Standard Reference Method (SRM)**
- SRM today – unconditioned sampling - based on analysis of $SO_2$ dissolved in water
- New SRM – conditioned sampling – using **P-AMS** (Portable Automated Measuring System) – cold and dry gas is needed for $SO_2$ measurement

## Main issue

- $SO_2$ bias due to physical and chemical processes during cooling and drying ?

# Tasks of CMI in the project

**A.2.2.7**
"… create a mathematical model of $SO_2$ losses in dryers based on cooling and condensation of water."

**A.2.2.11**
"… to obtain estimations of the $SO_2$ losses in the selected dryer."

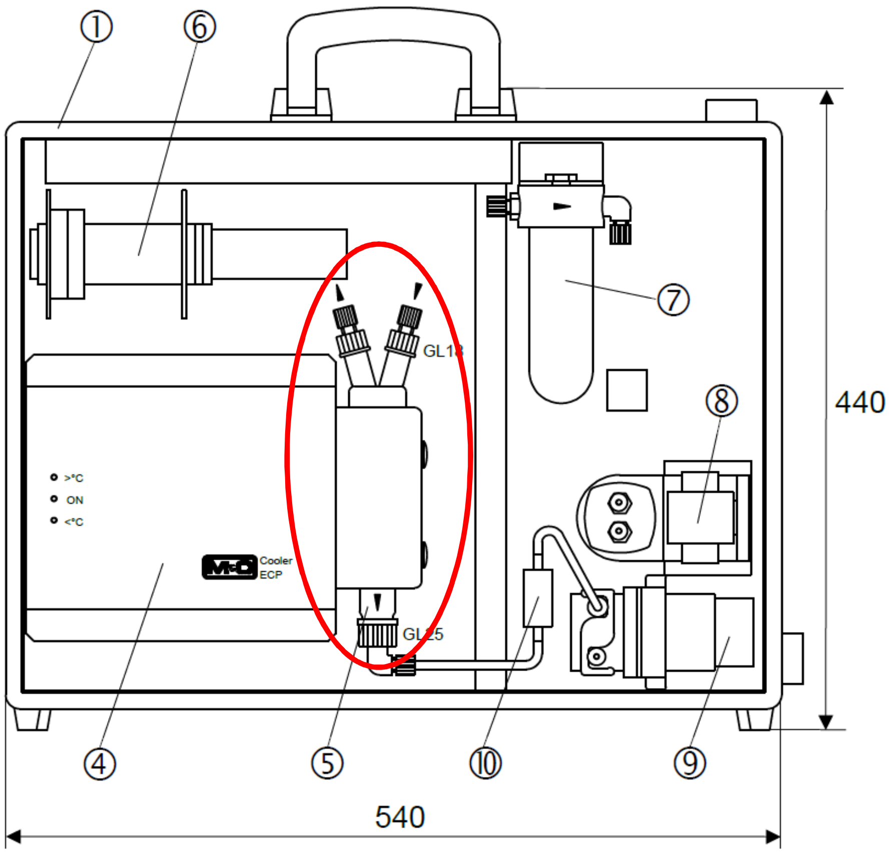
## Type of the measuring system

- Portable Automated Measuring System
  (P-AMS, M&C® PSS-5)

## Key part of the dryer in P-AMS

- Gas cooler (ECP .000)
- Borosilicate glass heat exchanger

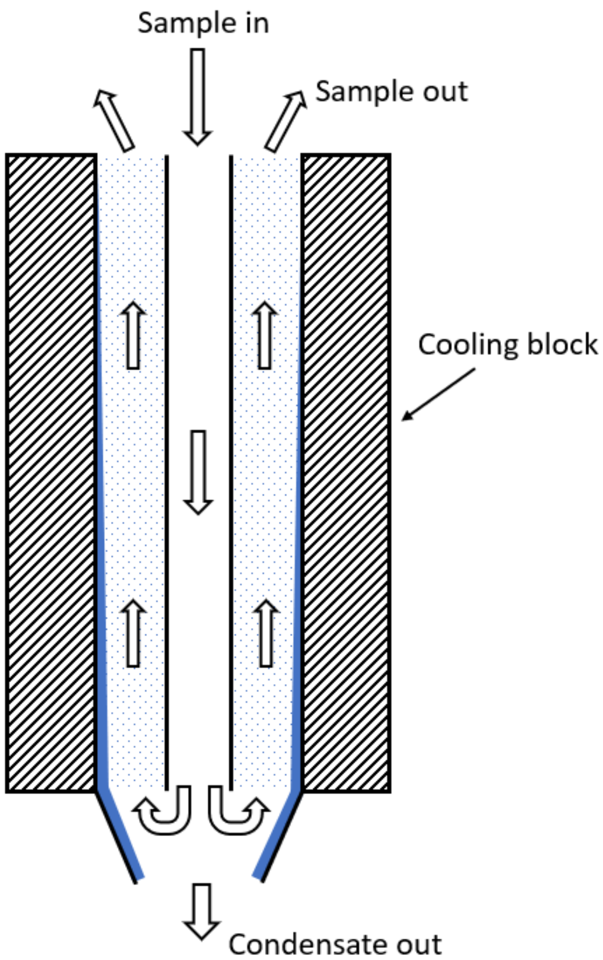
## Scheme of P-AMS



# Scheme of heat exchanger

## Gas cooler with jet-stream heat exchanger

## Scheme of glass heat exchanger

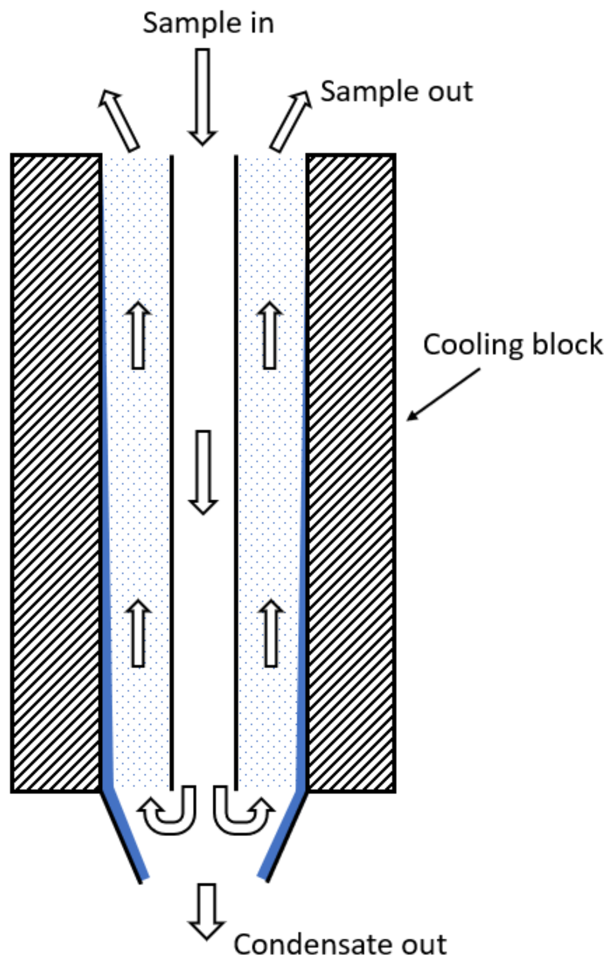


# Scheme of the processes in the dryer

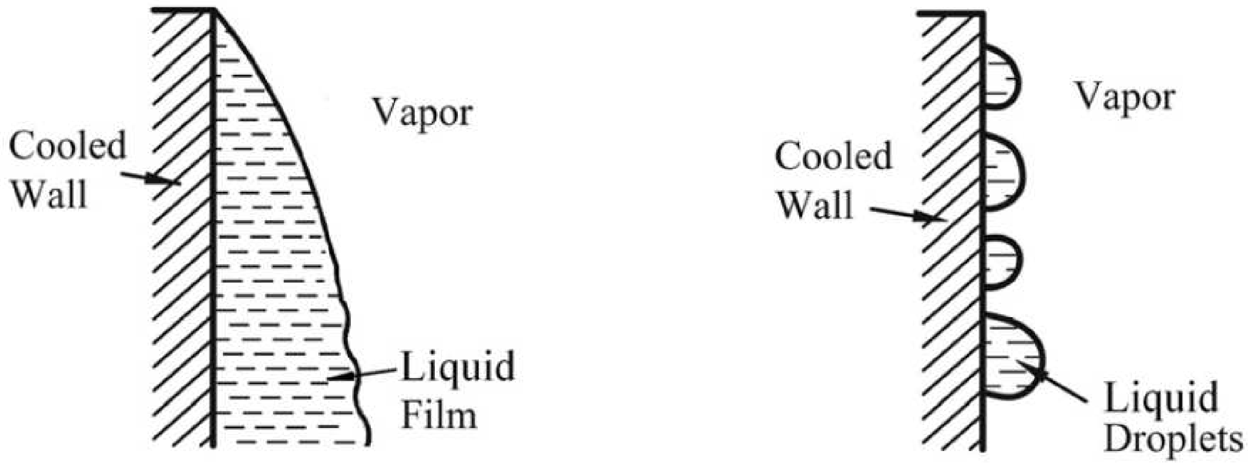
## Key processes

- Condensation (droplets, water film)
- Mass transfer through gas-liquid interface
- Chemical processes in liquid
- Diffusion

### Scheme of glass heat exchanger



# Condensation




(a) Filmwise condensation (b) Dropwise condensation

a) **Filmwise condensation** – on hydrophilic surface (borosilicate glass)

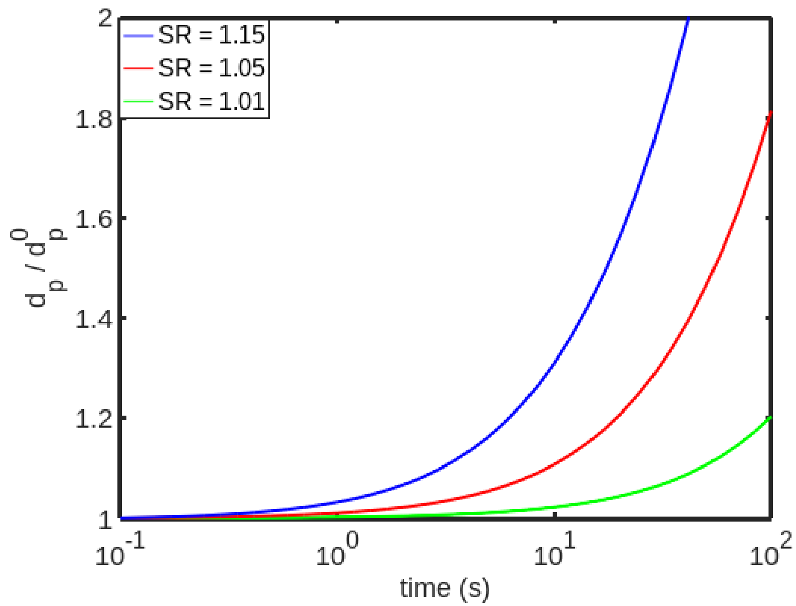
b) Dropwise condensation on wall – on hydrophobic surface

c) **Droplets condensation** in air – for temperature under dew point

## Droplet growth by condensation

$$d_p(t) = \sqrt{\frac{8DM}{R\rho}\left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d}\right)(t - t^0) + \left(d_p^0\right)^2}$$

Fluids properties — Ambient conditions — Droplet properties — Initial droplet diameter




### Vapor partial pressure (Kelvin eq.)

$$\frac{p_d}{p_s} = \exp\left(\frac{4\gamma M}{\rho R T d}\right)$$

$p_s$ … saturation vapor pressure

### Droplet temperature

$$T_d = T_\infty + \frac{(6.65 + 0.345T_\infty + 0.0031T_\infty^2)(S_R - 1)}{1 + (0.082 + 0.00782T_\infty)S_R}$$

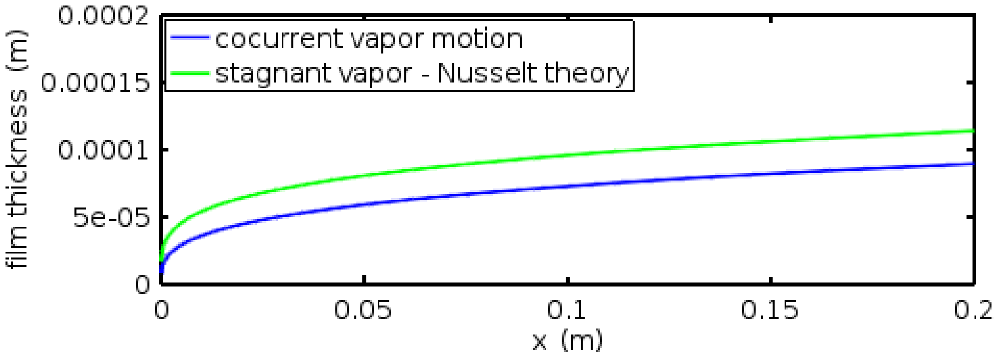
$S_R$ … relative humidity

# Condensation of liquid film

## Liquid film thickness by Nusselt theory

$$\delta(x) = \left(\frac{4k_l\mu_l x\Delta T}{\rho_l(\rho_l - \rho_v)gh_{lv}}\right)^{1/4}$$

- Vertical wall
- Stagnant vapor
- Laminar flow regime
- Smooth film surface

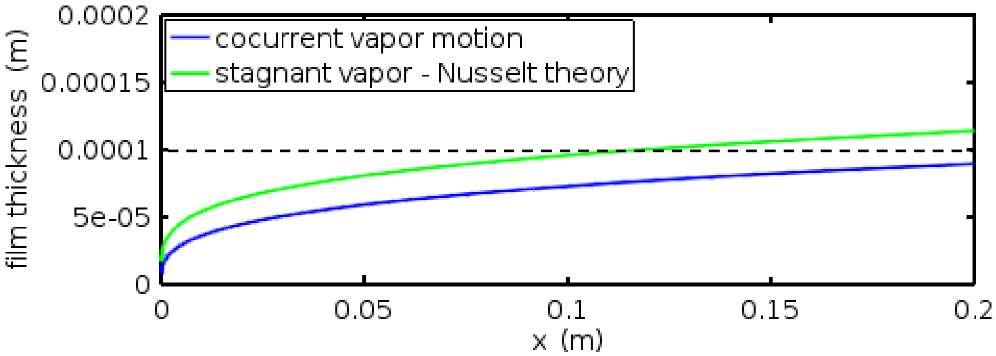


# Condensation of liquid film

## Liquid film thickness by Nusselt theory

$$\delta(x) = \left(\frac{4k_l\mu_l x\Delta T}{\rho_l(\rho_l - \rho_v)gh_{lv}}\right)^{1/4}$$

- Vertical wall ✔
- Stagnant vapor ✖
- Laminar flow regime ✔
- Smooth film surface ?




- ❑ Our case - countercurrent vapor motion
  – relatively complex models

- ❑ Our assumption – Nusselt theory gives acceptable estimate of the film thickness

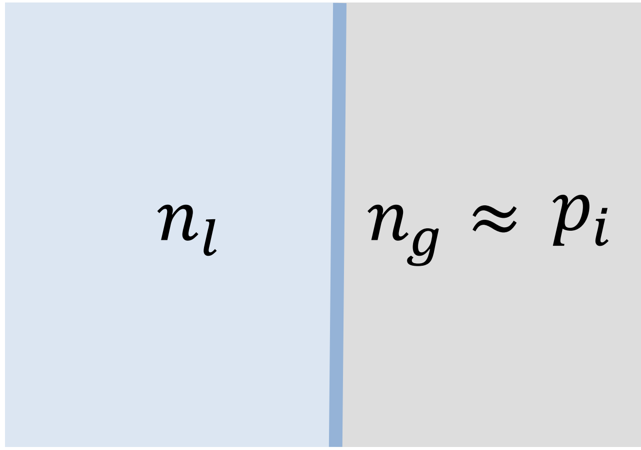
# Mass transfer through gas-liquid interface

## Henry's Law

$$n_l = H^{cp}(T)p_i$$

$$n_l = H^{cc}(T)n_g$$

$$H(T) = H^0 \exp\left[-\frac{\Delta h}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right]$$




## Mass accommodation coefficient, α

The ratio of molecules absorbed through the gas-liquid interface
to the number of molecules which hit the liquid surface.

$\alpha = (5.4 \pm 0.6)\ \%$ at 295 K

# Chemical processes of $SO_2$ in water

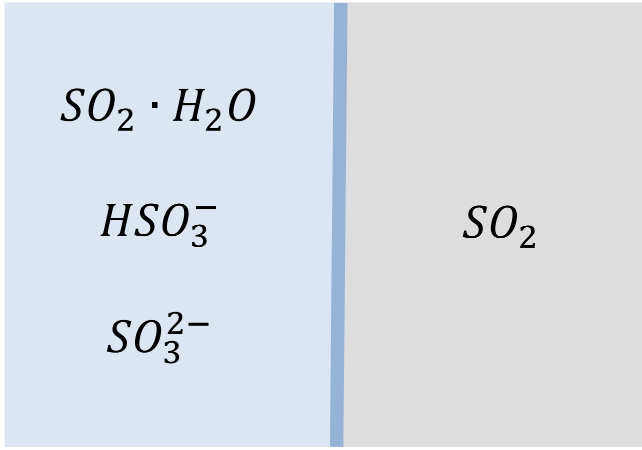
## Chemical reactions

$$SO_2(g) + H_2O \xrightarrow{K_H} SO_2 \cdot H_2O\ , \quad \text{where} \quad K_H = \frac{[SO_2{\cdot}H_2O]}{p_{SO_2}}$$

$$SO_2 \cdot H_2O \xrightarrow{K_1} H^+ + HSO_3^-\ , \quad \text{where} \quad K_1 = \frac{[H^+][HSO_3^-]}{[SO_2{\cdot}H_2O]}$$

$$HSO_3^- \xrightarrow{K_2} H^+ + SO_3^{2-}\ , \quad \text{where} \quad K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$$

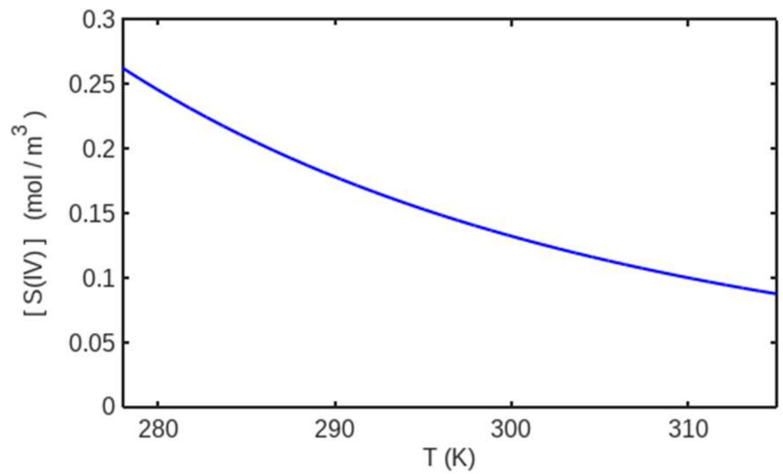
Dissociation const. $K_H$, $K_1$, $K_2$ = f(T)




## Resulting concentration

$$[S(IV)] = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{2-}]$$

(maximal concentration for given temperature and partial pressure of SO2)

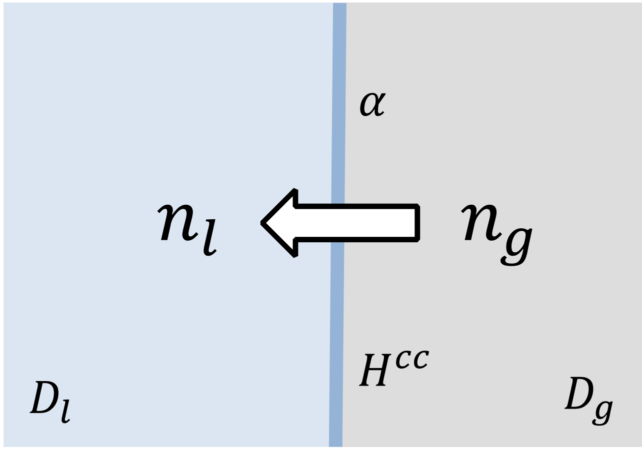


# Diffusion processes

## Governing equations

$$\frac{\partial n_g(x,t)}{\partial t} = D_g \frac{\partial^2 n_g(x,t)}{\partial x^2}$$

$$\frac{\partial n_l(x,t)}{\partial t} = D_l \frac{\partial^2 n_l(x,t)}{\partial x^2}$$




## Boundary conditions on gas-liquid interface

$$-D_g \frac{\partial}{\partial x} n_g(x_i,t) = \frac{\alpha\,\bar{v}}{4}\left(n_g(x_i,t) - \frac{n_l(x_i,t)}{H^{cc}}\right)$$

$$-D_l \frac{\partial}{\partial x} n_l(x_i,t) = \frac{\alpha\,\bar{v}}{4}\left(n_g(x_i,t) - \frac{n_l(x_i,t)}{H^{cc}}\right)$$

$H^{cc}$ … Henry's Law constant

$\alpha$ … mass accommodation coefficient

$D_g$, $D_l$ … diffusion coefficients

$\bar{v}$ … mean thermal velocity of $SO_2$

$x_i$ … location of the interface

# Simulations of diffusion into growing droplet

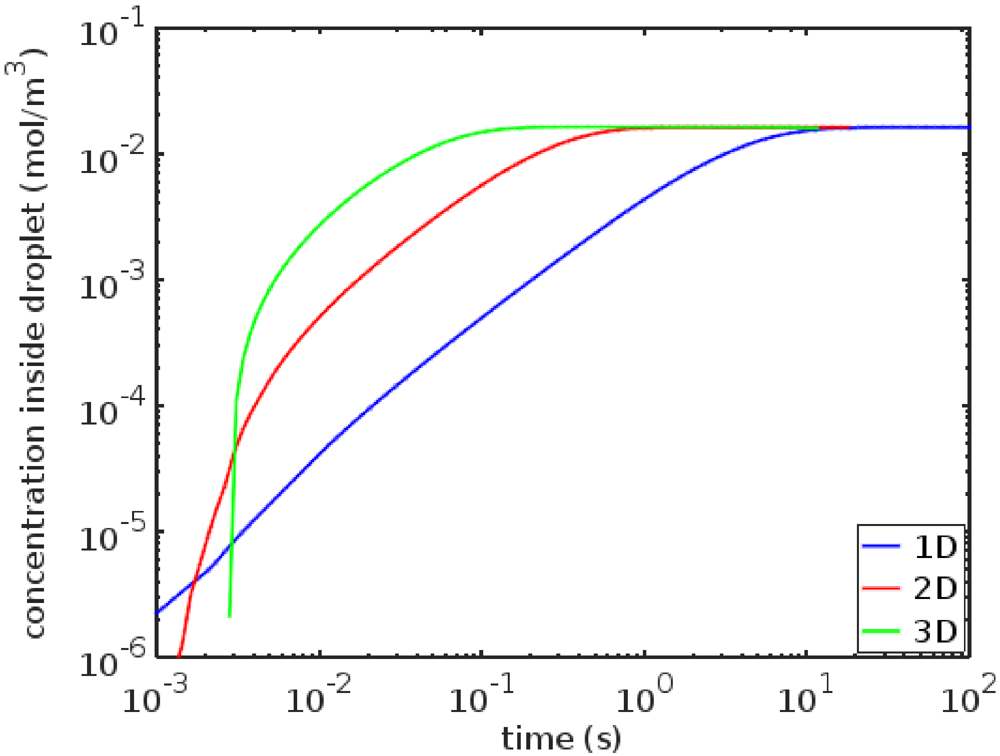
## Dependence on dimensionality

**Ambient conditions**

- 0.01 ppm $SO_2$ in air
- T=293 K
- Relative humidity 101%

**Conclusion**

- 3D simulation needed



# Simulations of diffusion into growing droplet

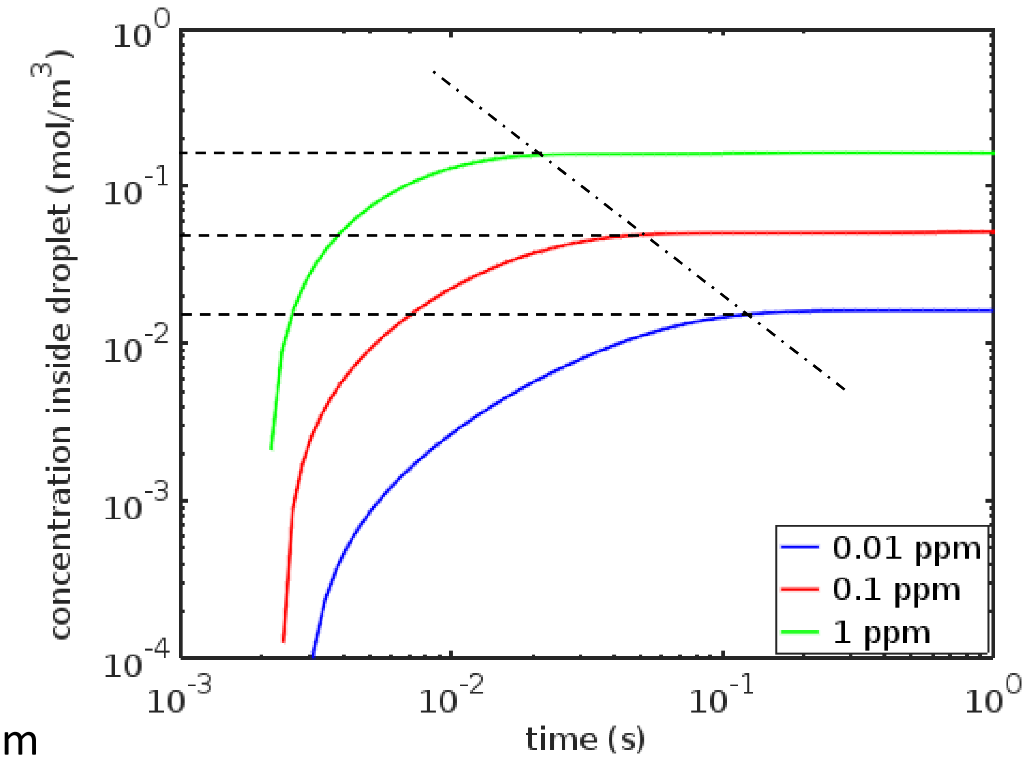
## Dependence on initial concentration of $SO_2$ in stack gas

**Ambient conditions**

- 0.01 – 1 ppm $SO_2$ in air
- T=293 K
- Relative humidity 101%

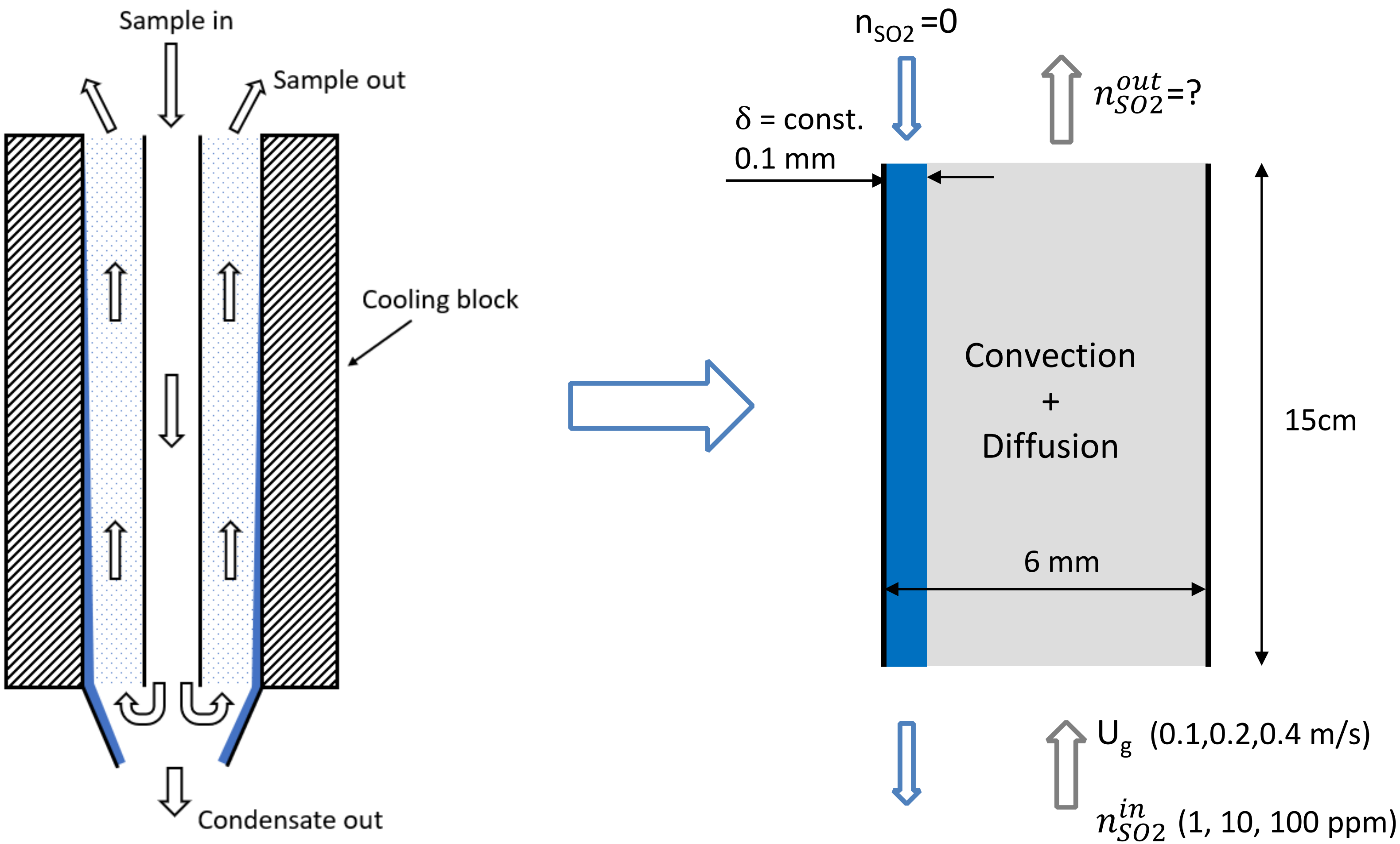
**Conclusions**

- Maximal concentration is in agreement with Henry's Law
- The time to equilibrium state decreases with increasing ppm



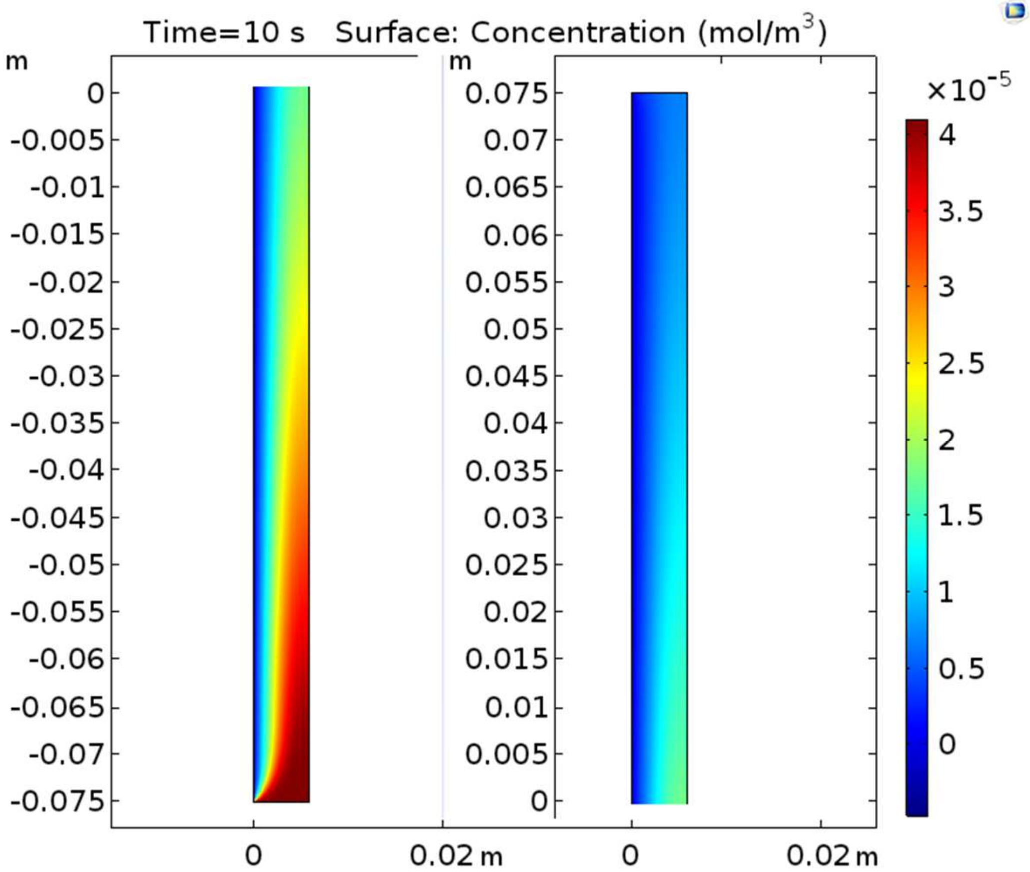
# Simulations of diffusion into water film

## Simulations on simplified geometry



# Simulations of diffusion into water film

## Resulting concentration of $SO_2$ in gas using COMSOL Multiphysics®



# Simulations of diffusion into water film

## Resulting concentration of $SO_2$ in gas after passing through the cooler

| | $n_g^{SO2}$ =1 ppm | $n_g^{SO2}$ =10ppm | $n_g^{SO2}$ =100ppm |
|---|---|---|---|
| $U_g$=0.4 m/s | 46.9 % | 48.4 % | 52.4 % |
| $U_g$=0.2 m/s | 28.6 % | 29.9 % | 33.8 % |
| $U_g$=0.1 m/s | 12.6 % | 13.4 % | 16.0 % |

**Initial conditions**

- 1 – 100 ppm $SO_2$ in gas
- $T_\infty$= 20 °C
- $T_w$=5 °C
- Gas relative humidity = 101%

**Conclusion**

- The $SO_2$ losses increase slightly with decreasing concentration
- The $SO_2$ losses increase strongly with decreasing gas flow rate

# Summary of simplifications and challenges

**Used simplifications**

- The 2D simplified geometry with given dimensions (D=6mm, L=15cm)
- Constant water film thickness along the whole tube (t=0.1 mm)
- Water film thickness estimated using Nusselt theory (stagnant vapor)
- Constant temperature of the gas and water film ($T_{\infty}$= 20 °C, $T_w$=5 °C)
- Relative humidity 101 %
- …

**Remaining challenges**

- Better modeling of the film thickness (countercurrent vapor flow)
- Initial gas properties (temperature, humidity) on inlet
- Validation

# Conclusions

- First attempt using several simplifications – qualitative results
- Although the maximal concentration of $SO_2$ in water droplet can be reached in time less than 0.1s, the droplet growth is slow
- Filmwise condensation is dominating in dryers
- The $SO_2$ losses increase slightly with decreasing concentration
- The $SO_2$ losses increase strongly with decreasing gas flow rate

**Thank you for your attention**

Czech Metrology Institute
Stanislav Knotek
Tel.: +420 702 166 992
Email: sknotek@cmi.cz