Traceability of real-time reference gas generation for reactive gaseous compounds

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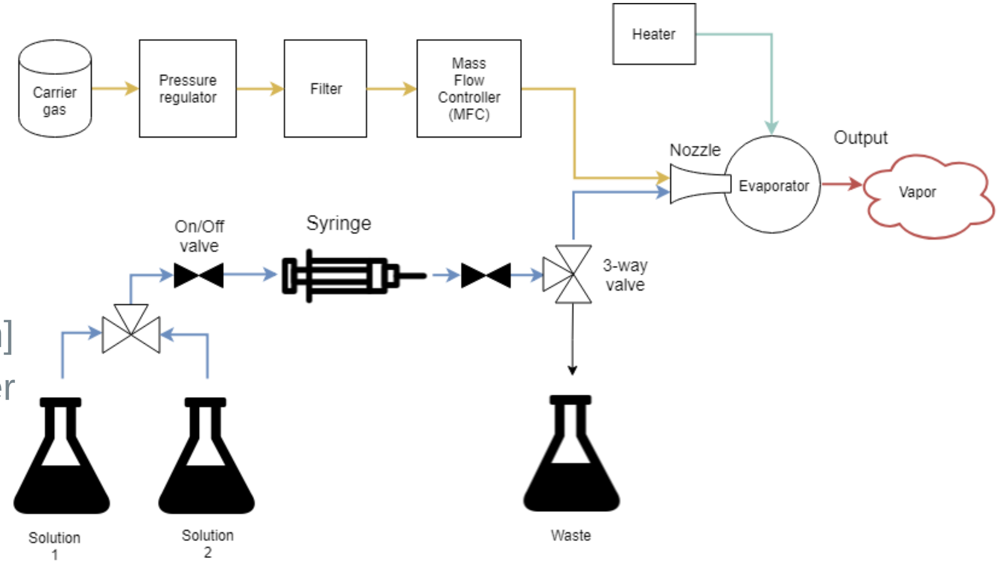
Dynamic calibration method for reactive gases: Liquid evaporative generator

Concentration of the target chemical in generated gas [µg/m^3]

$$c_{gen} = \frac{c_{sol}}{(q_{v,g} + q_{v,w})} \cdot q_{v,sol}$$

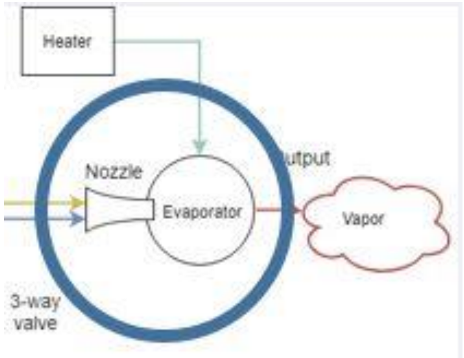
- c_{sol} concentration of the target chemical in solution [µg/l]
- $q_{v,g}$ flow rate of the carrier gas [l/min]
- $q_{v,w}$ flow rate of the evaporated water in gas phase [l/min]
- $q_{v,sol}$ flow rate of the liquid solution [ml/min]



Liquid evaporative generator
Details of the evaporation process

In order to reduce adsorption and to minimize response time, memory effect and uncertainty in gas concentration, critical part is gas formation, **evaporation**

- **Heated** evaporation chamber; t > 100 °C
- **Nozzle** to mix and spray the liquid solution with carrier gas, adjusted with evaporator geometry
- **Inert materials** for the inner parts of the nozzle, the evaporator chamber and all parts following them which are in contact with the humid gas: PTFE, PFA, glass
- **High flow rate** of the generated gas into and through the evaporator to ensure short exchange time of gas inside the evaporator chamber



Liquid evaporative generator
Overall uncertainty of the generated gas

Estimation of total uncertainty = $\sum_i$ standard uncertainty for component i

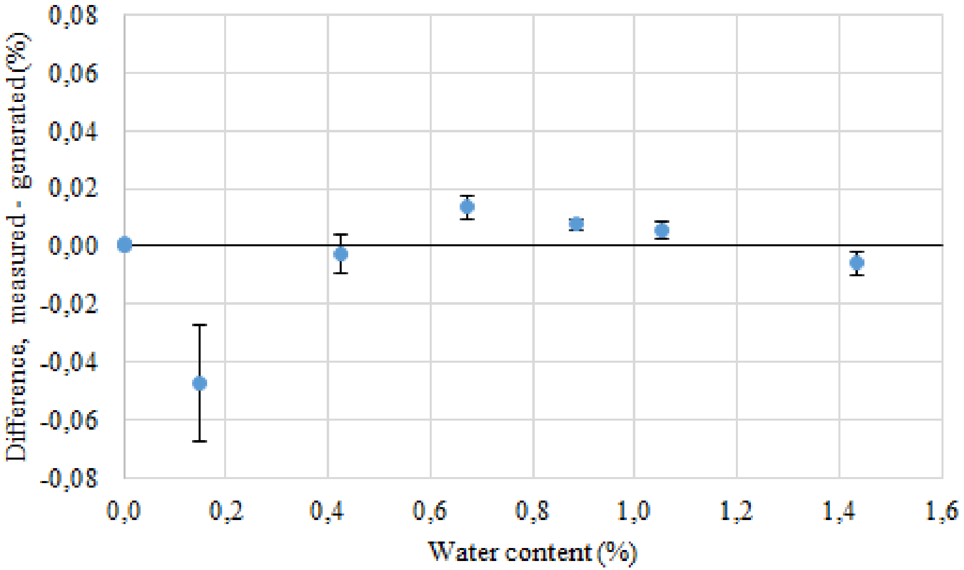
$$c_{\text{gen}} = \frac{c_{\text{sol}}}{(q_{\text{v,g}} + q_{\text{v,w}})} \cdot q_{\text{v,sol}} + \delta c_{\text{eva}} + \delta c_{\text{rep}}$$

- c_{eva} correction/effect of evaporator, due to adsorption losses [µg/m3]
- c_{rep} overall repeatability of the gas generator [µg/m3]

Term	Average value	Standard uncertainty	Distribution	Sensitivity coefficient	Contribution	Relative contribution
c_{sol}	1000 ug/L	0,55 ug/L	norm.	0,01	0,01 ug/m3	0,05 %
$q_{v,g}$	7 L/min	0,04 L/min	norm.	-1,4	-0,05 ug/m3	-0,49 %
$q_{v,w}$	0,09 L/min	0,00 L/min	rect.	-1,4	0,00 ug/m3	0,00 %
$q_{v,sol}$	0,07 mL/min	0,00 mL/min	norm.	141	0,03 ug/m3	0,30 %
δc_{eva}	0 ug/m3	0,06 ug/m3	rect.	1	0,06 ug/m3	0,58 %
δc_{rep}	0 ug/m3	0,06 ug/m3	rect.	1	0,06 ug/m3	0,58 %
c_{gen}	10 ug/m3			u (k = 1):	0,10 ug/m3	1,01 %
				U (k = 2):	0,20 ug/m3	**2,02 %**

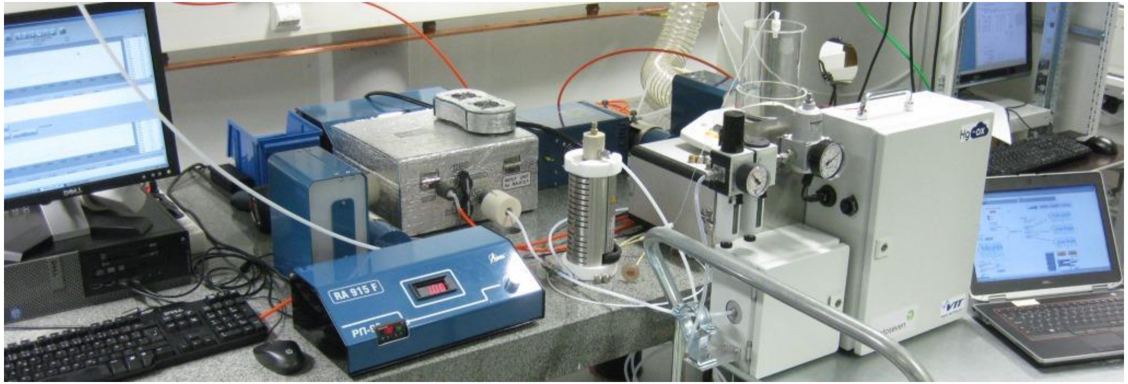
Liquid evaporative generator
Water vapor generation

Water measurement with MBW Dew Point Mirror → metrological traceability



Comparison of the Hg concentration in generated standard gas for $HgCl_2$

- Typical values in comparison measurements
  - Hg^{2+} reference gas concentration 0.1 … 10 µg/m3
  - Carrier gas flow rate 5 … 10 L/min
  - Water concentration max 1 … 2 Vol%
    - Mercury standard solution volume flow rate 0.01 … 0.1 mL/min
    - Mercury solution concentration 100 … 1000 µg/L
- Detailed study of response time, sensitivity, linearity and cross sensitivities



Comparison of the Hg concentration in generated standard gas for $HgCl_2$

Preliminary results: generators output is ~8 % below the expected Hg concentration