Advanced Methods for Humidity Calibration & Uncertainty

International Training Course

DTI, Taastrup, Denmark, 11th April 2018

Martti Heinonen, VTT MIKES, Finland

Organisation

- Organiser: VTT, National Metrology Institute VTT MIKES, Finland
- Host: DTI, Denmark
- Trainers:
    - Martti Heinonen, VTT
    - Richard Högström, VTT
    - Jan Nielsen, DTI
- This course is provided by European research project HIT

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Objectives

In this course you will get

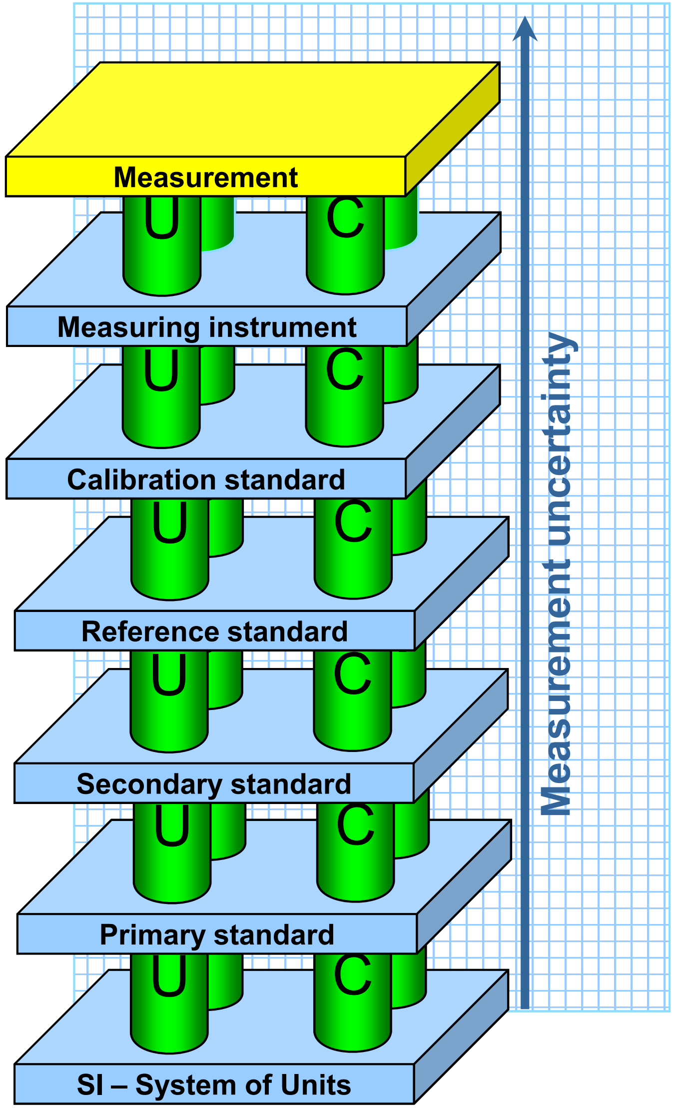
- an overview of current practices in humidity calibrations
- an insight into recent developments in humidity calibrations
    - High temperatures
    - Non-static conditions
- advice for estimating calibration uncertainty and validating calibration systems

Programme

09:00 - 09:30	Registration
09:30 - 09:45	Welcome and introduction
09:45 - 10:45	Metrological traceability in humidity measurements
	Current practices in humidity calibration: features and limitations
10:45 - 11:00	Break
11:00 - 12:15	Humidity calibration at high temperature
	Time dependent effects
	Uncertainty in humidity calibrations
12:15 - 13:15	Lunch
13:15 - 14:15	Exercises in 4 groups (non-static conditions, analysis of results)
14:15 - 14:30	Break
14:30 - 15:30	Exercises continue
15:30 - 15:50	Validation and summary of exercises
15:50 - 16:00	Summary and close

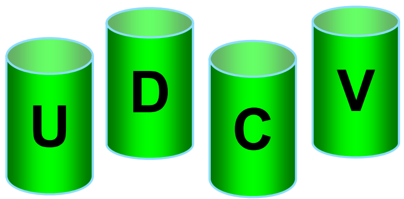
Metrological traceability in humidity measurements

Metrological traceability



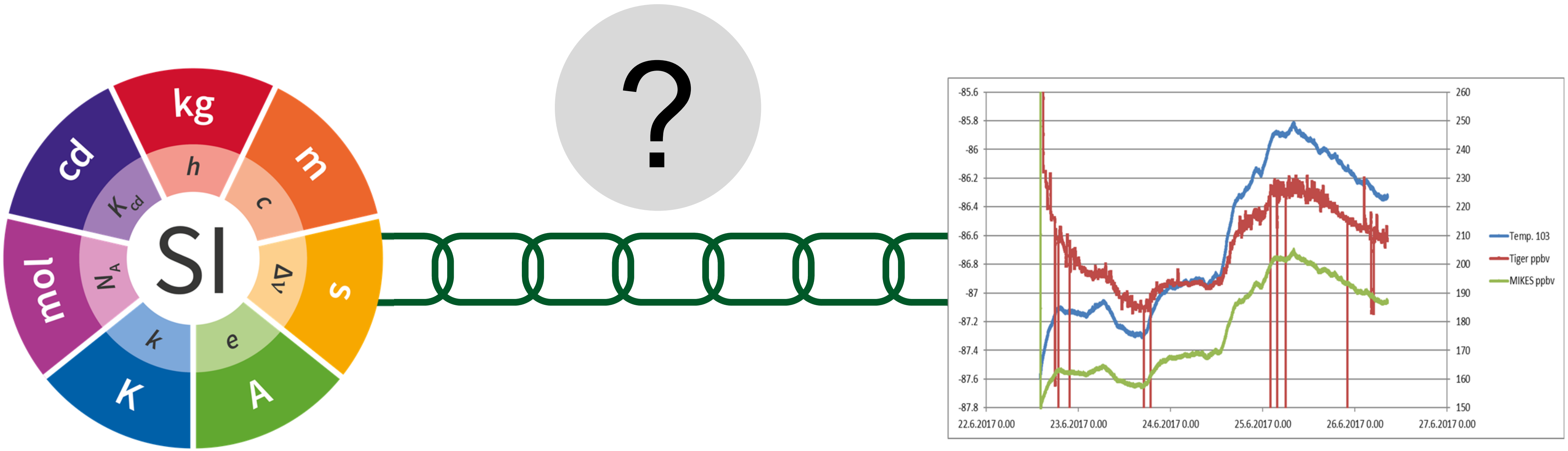
For each calibration of the chain:

- **U**ncertainty estimation
- **D**ocumented and generally acknowledged procedures, documented results
- **C**ompetence
- Calibration is **V**alid for the application. (interval of calibrations, conditions etc.)

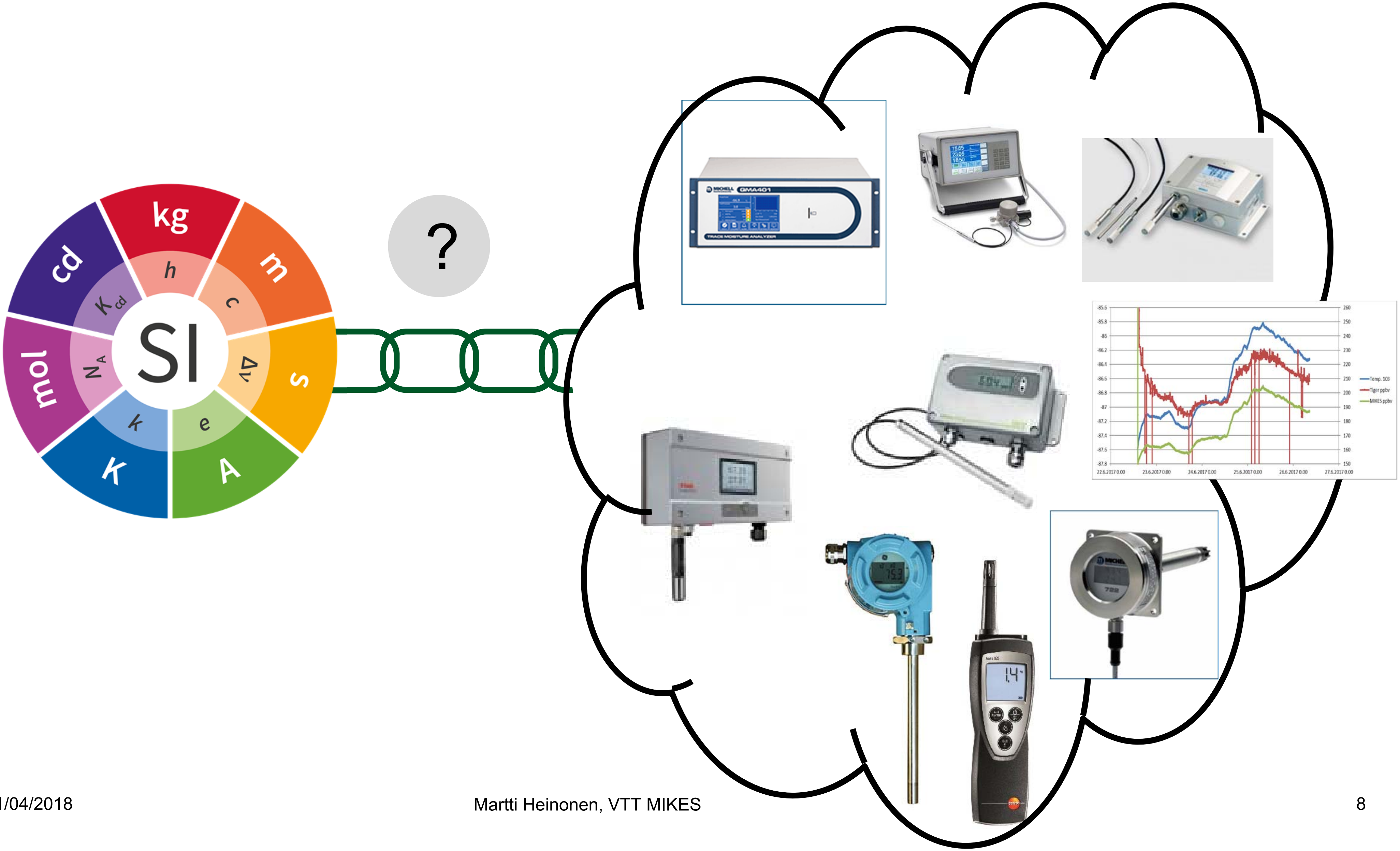


Uncertainty increases at each step upwards

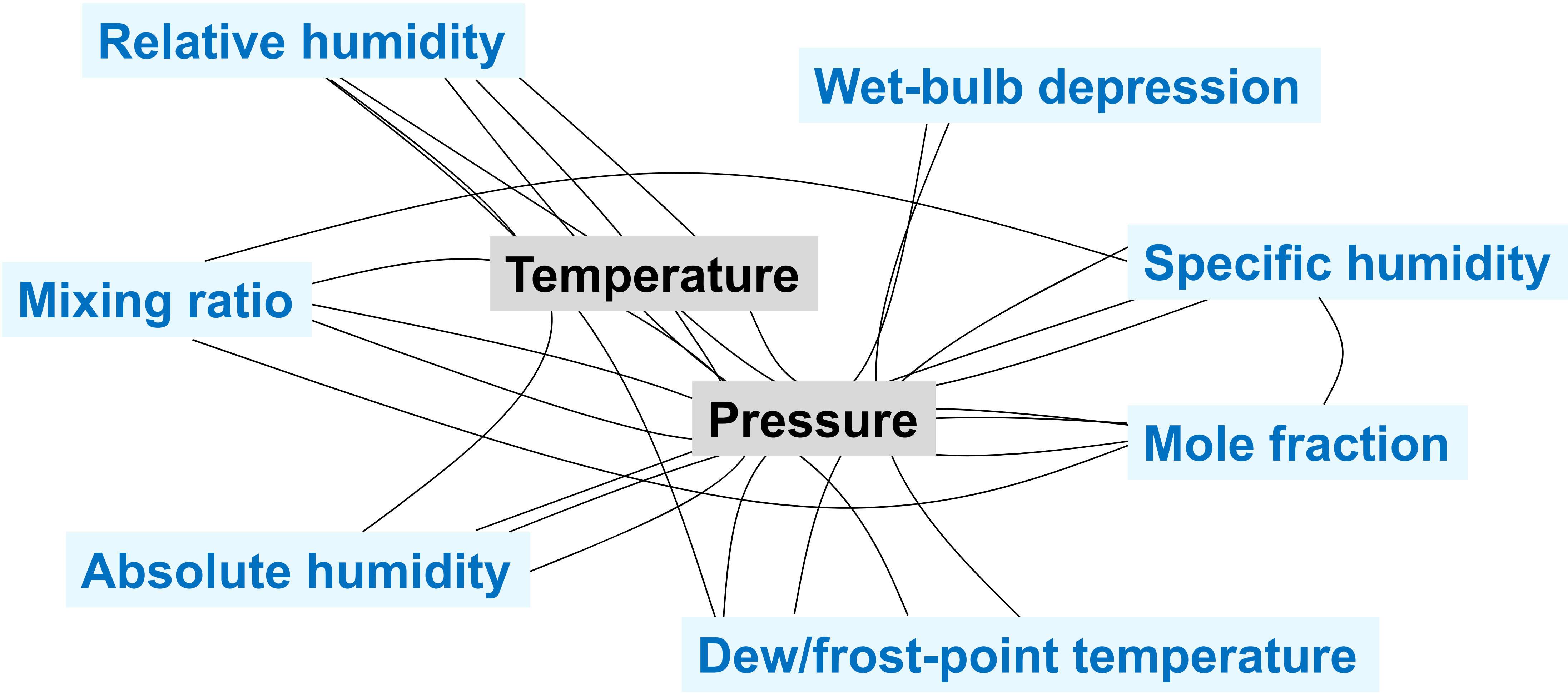
Traceability in humidity measurements?



Traceability in Humidity Measurements?



Measurands – humidity quantities



Example: Relative humidity vs. a few other humidity quantities

$$RH = \frac{f(p,t_d)e(t_d)}{f(p,t_a)e(t_a)} \times 100\ \%\text{rh} = \frac{x_w}{f(p,t_a)e(t_a)} \times 100\ \%\text{rh}$$

$$= \frac{p}{f(p,t_a)e(t_a)\left(1 - \frac{M_w}{M_g\, r}\right)} \times 100\ \%\text{rh} = \frac{\rho_w R T_d}{f(p,t_a)e(t_a)} \times 100\ \%\text{rh}$$

t_d = dew-point temperature
T_d = dew-point temperature in kelvin
x_w = mole fraction of water vapour
r = mixing ratio
ρ_w = absolute humidity

e = saturation pressure of pure water
f = water vapour enhancement factor
p = total gas pressure
t_a = gas temperature
M_w = molar mass of water
M_g = molar mass of dry gas
R = molar gas constant (8.314510 J mol^{-1} K^{-1})

Measurands – humidity quantities

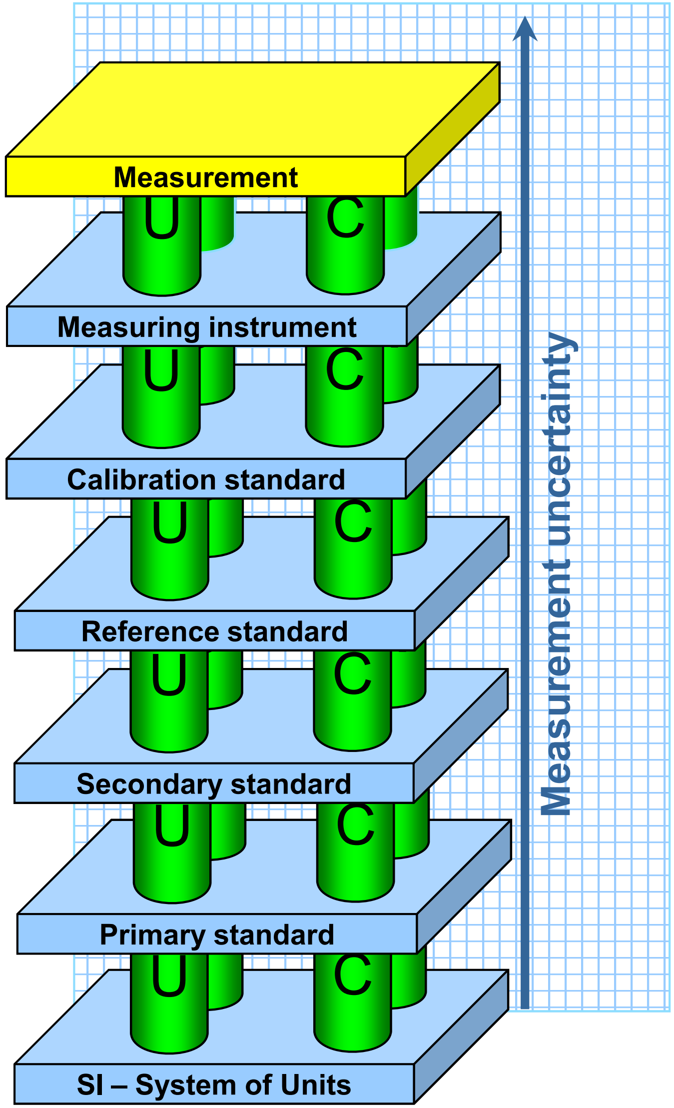
- If know the values of one humidity quantity, gas pressure and gas temperature, you can calculate the values of all other humidity quantities
  - Note: all three contribute to the final measurement uncertainty
- For the calculations you need
  - equation/data for saturation pressure of pure water vapour
  - equation/data for water vapour enhancement factor (in many practical applications it is sufficient to consider this only as an uncertainty component)

Note 1: equations themselves have uncertainties

Note 2: uncertainties of enhancement factor equations increase towards higher pressures

Note 3: enhancement factor data/equations are only available for most common gas mixtures

Humidity: Traceability in Europe



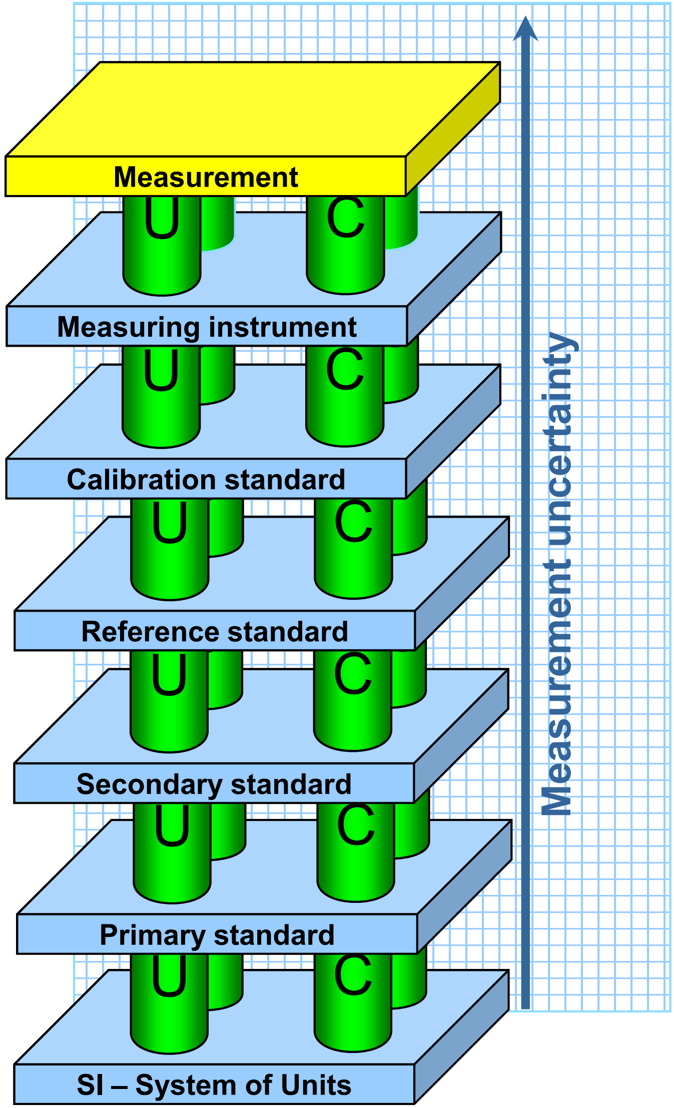
NMI/DIs, accred. labs, industrial labs

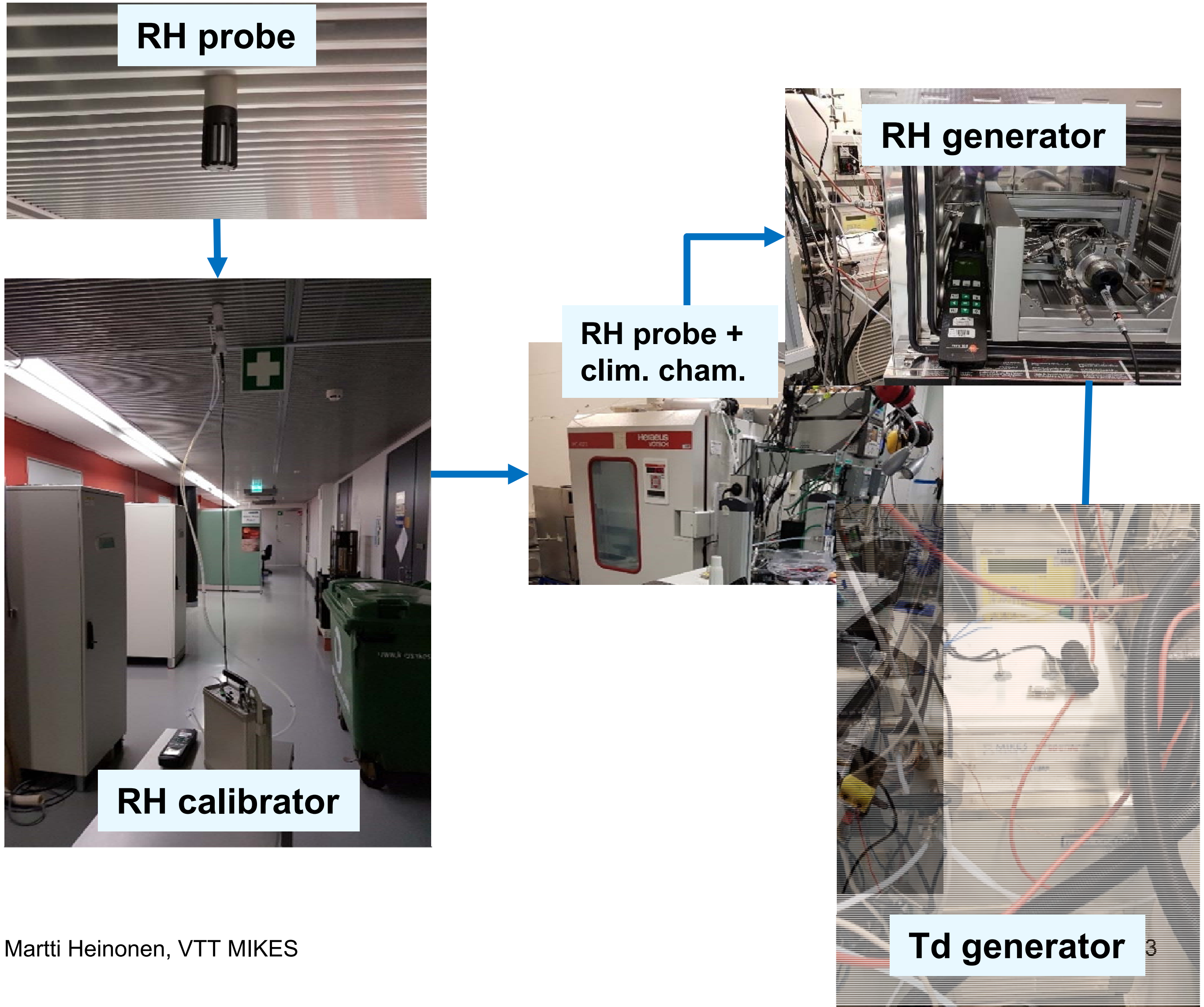
- Reference hygrometer + thermometers + humidity generator/calibrator/climatic chamber
- Reference hygrometer:
  - Chilled mirror hygrometer
  - RH hygrometers
  - Other types of hygrometers

National Metrology Institutes (NMI/DI)

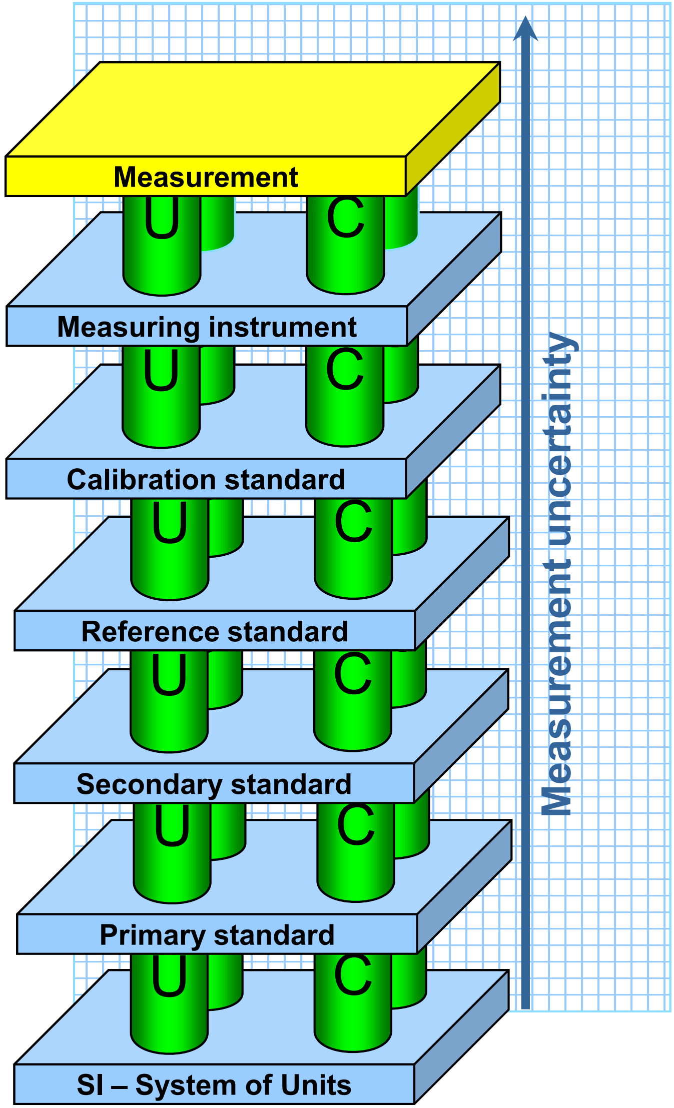
- Primary realisation: Dew-point temperature
  - Mixing ratio in some specific areas
- Secondary realisations: Relative humidity
  - Other calculated quantities in some specific cases
- Techniques: Saturation-based humidity generators

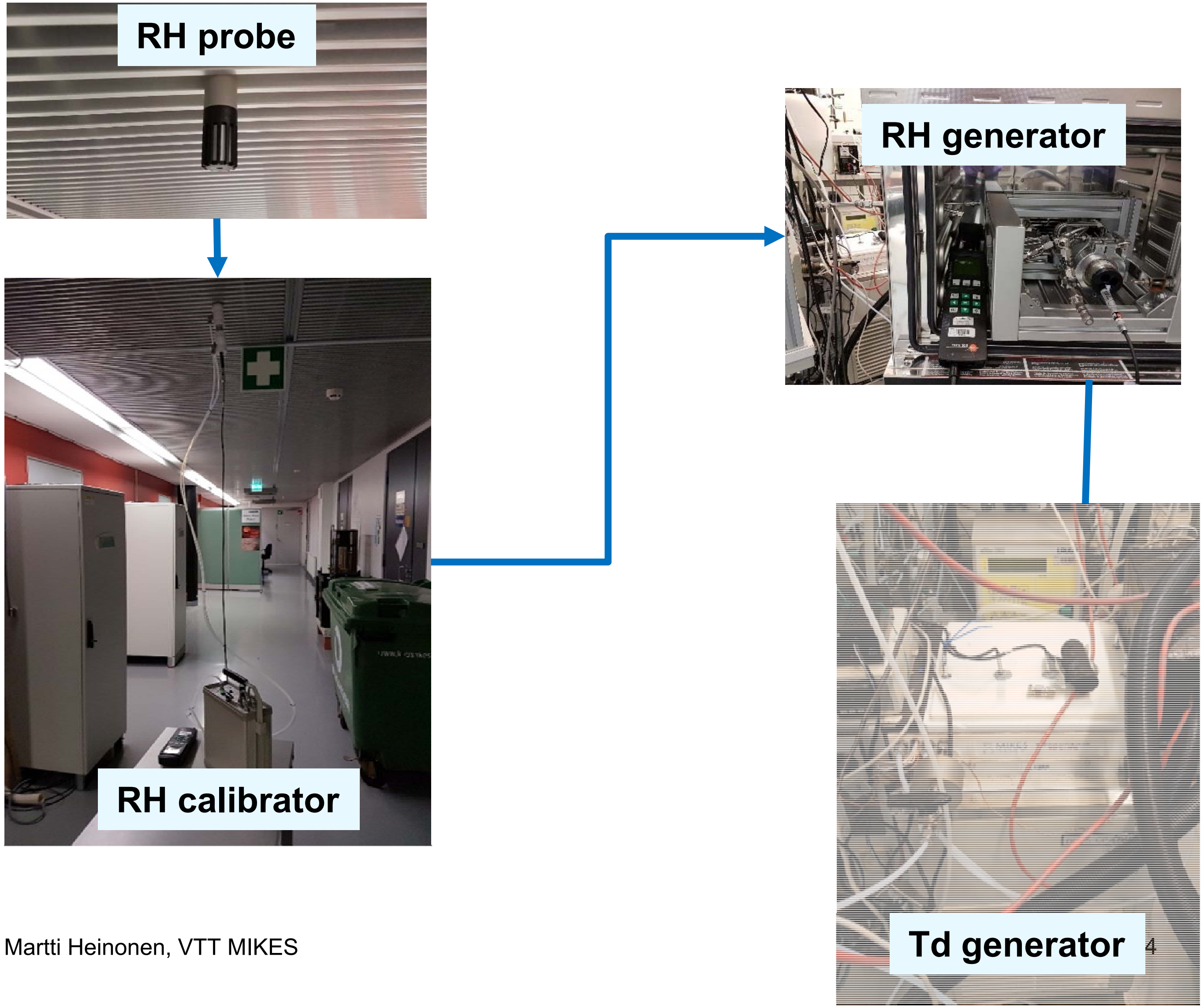
An example of different alternative traceability routes (1/5)



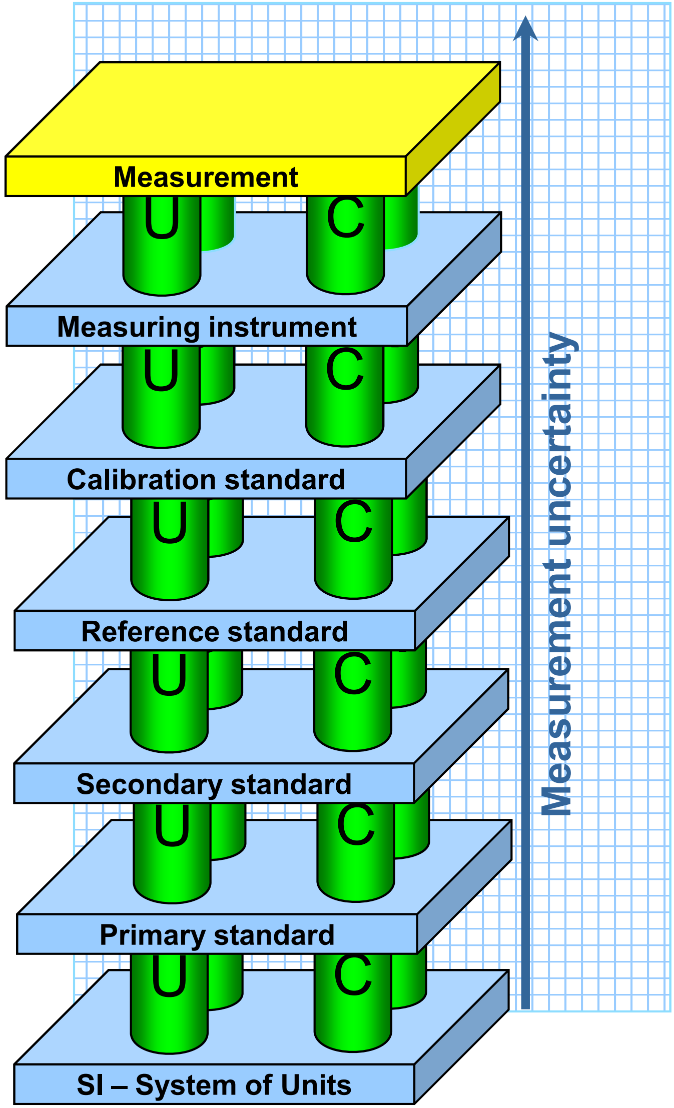


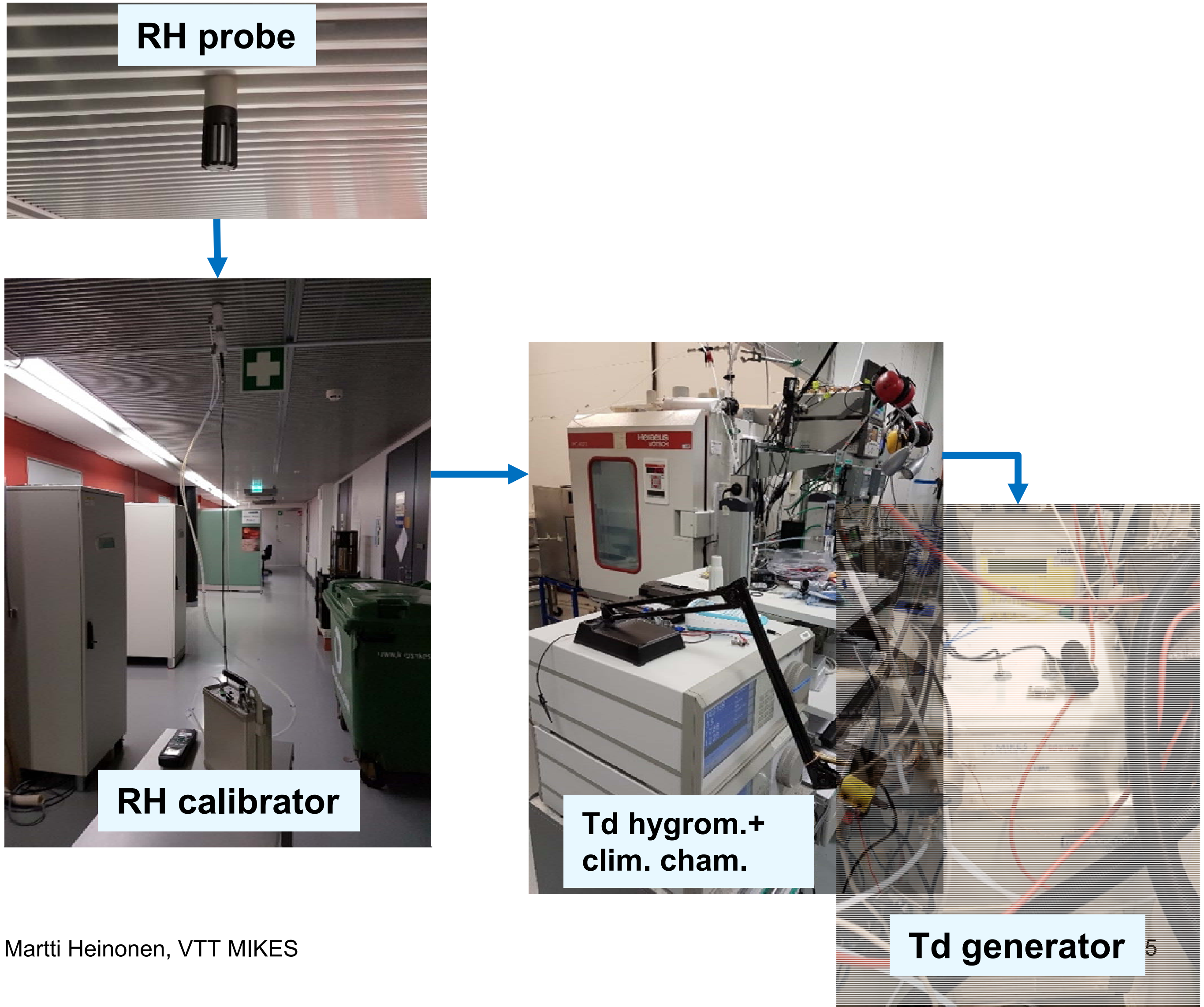
An example of different alternative traceability routes (2/5)



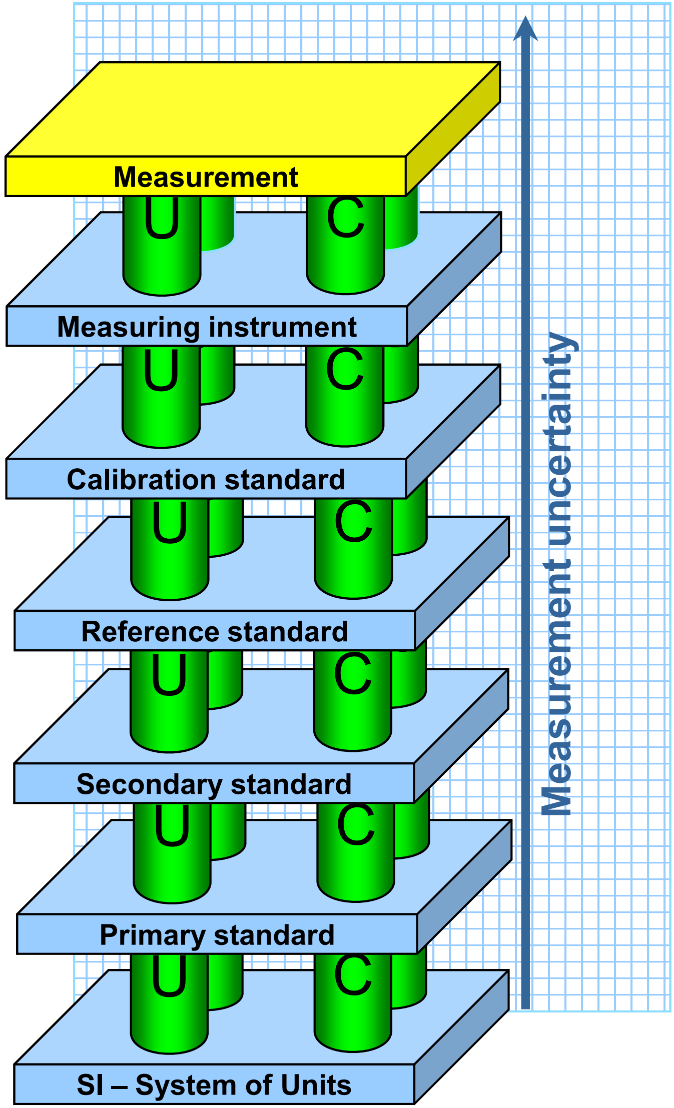


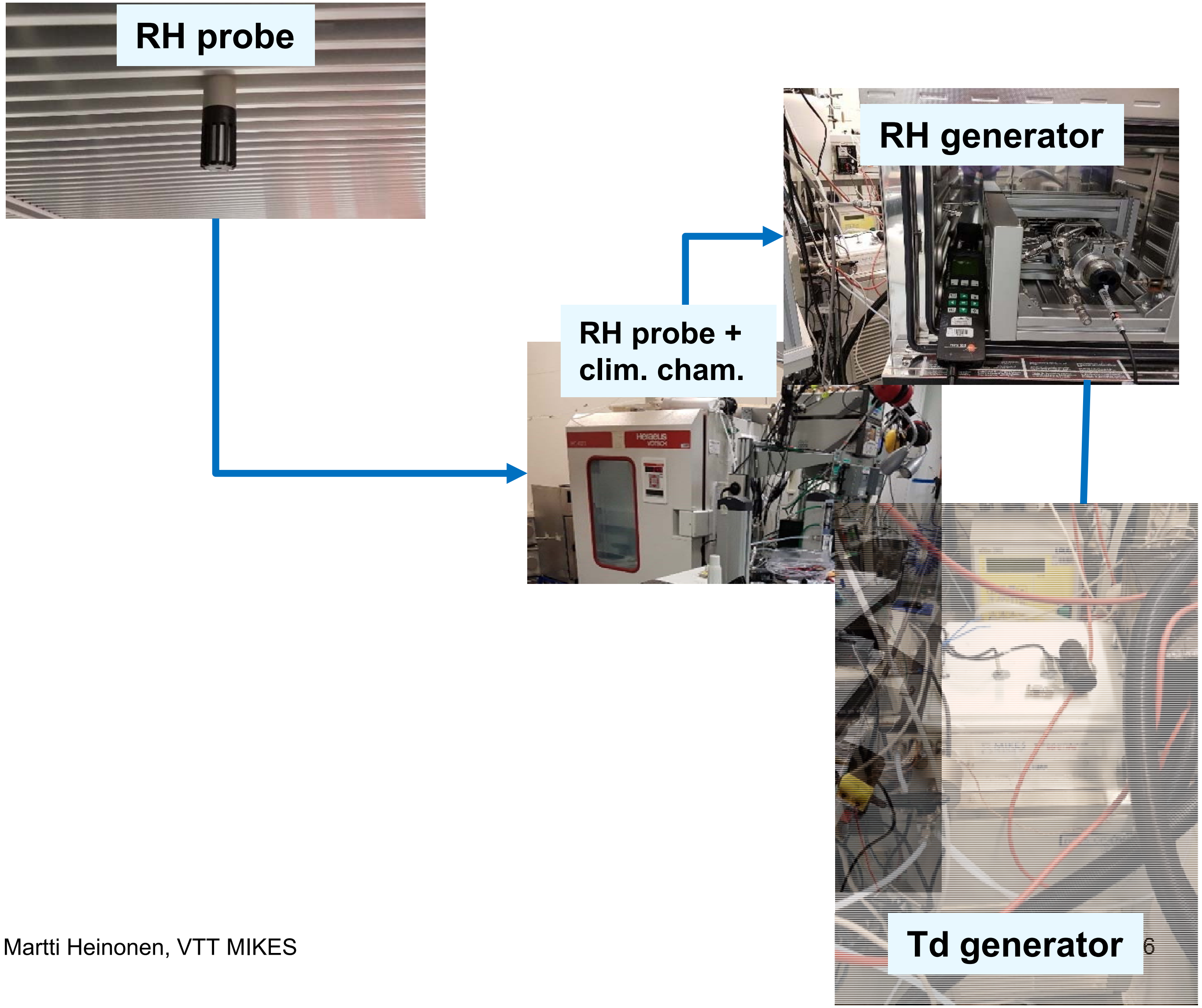
An example of different alternative traceability routes (3/5)



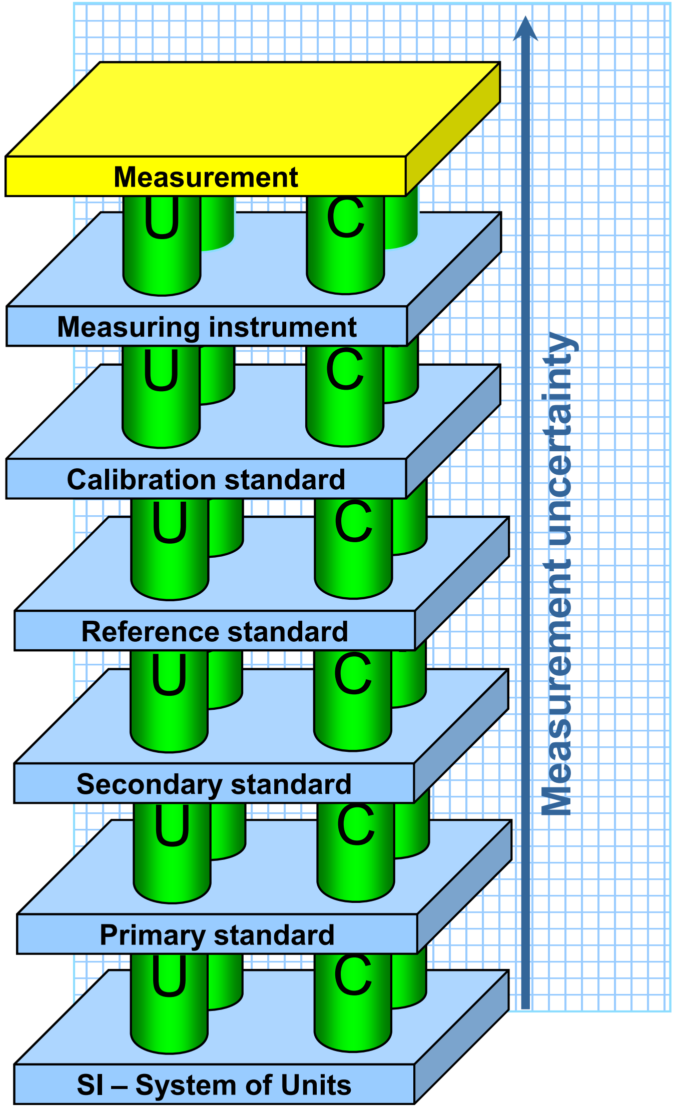


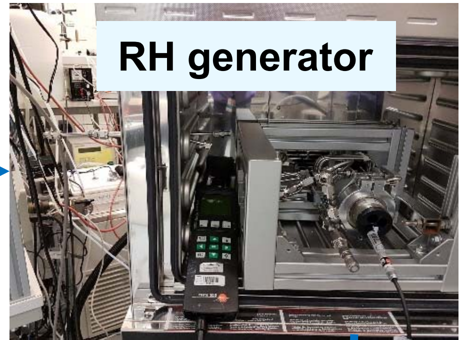
An example of different alternative traceability routes (4/5)

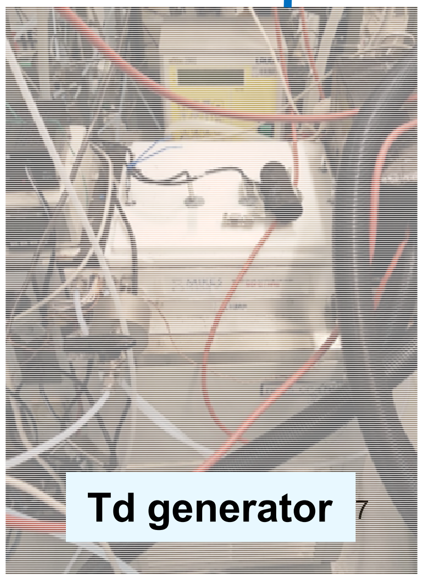




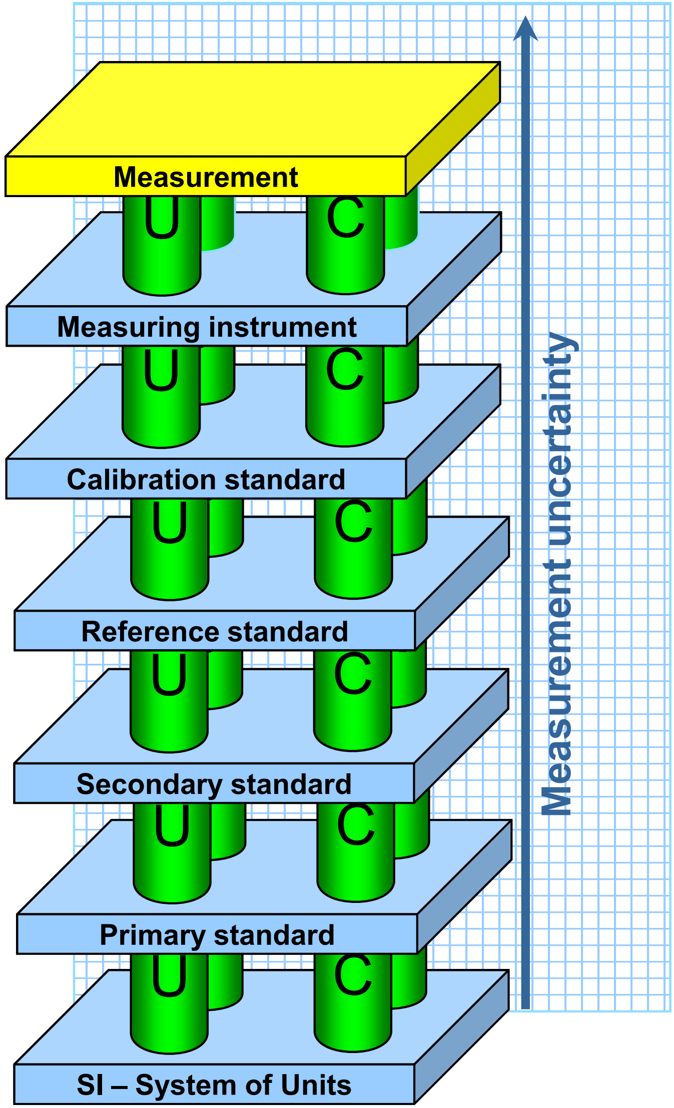
An example of different alternative traceability routes (5/5)

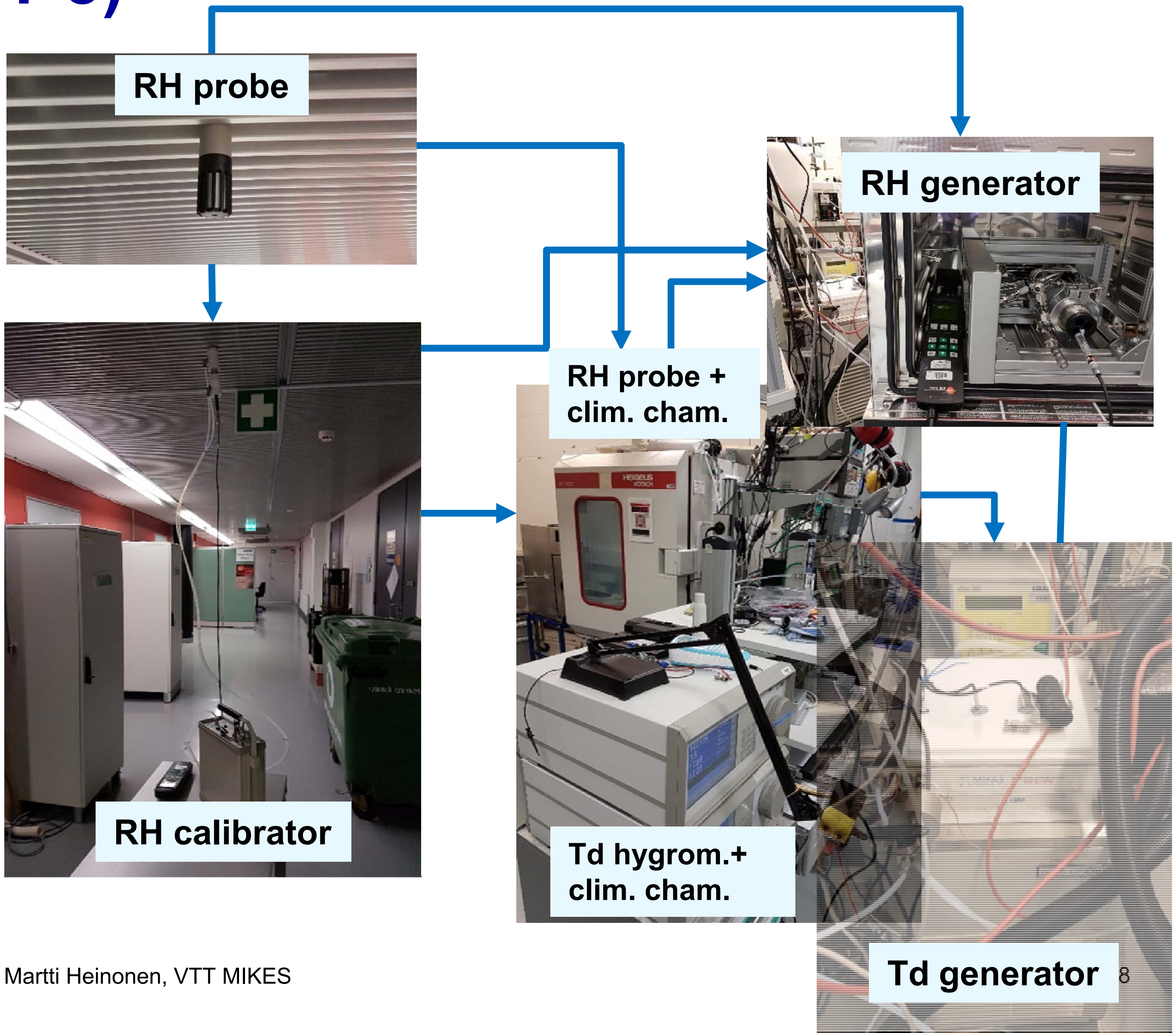






An example of different alternative traceability routes: summary (1-5)



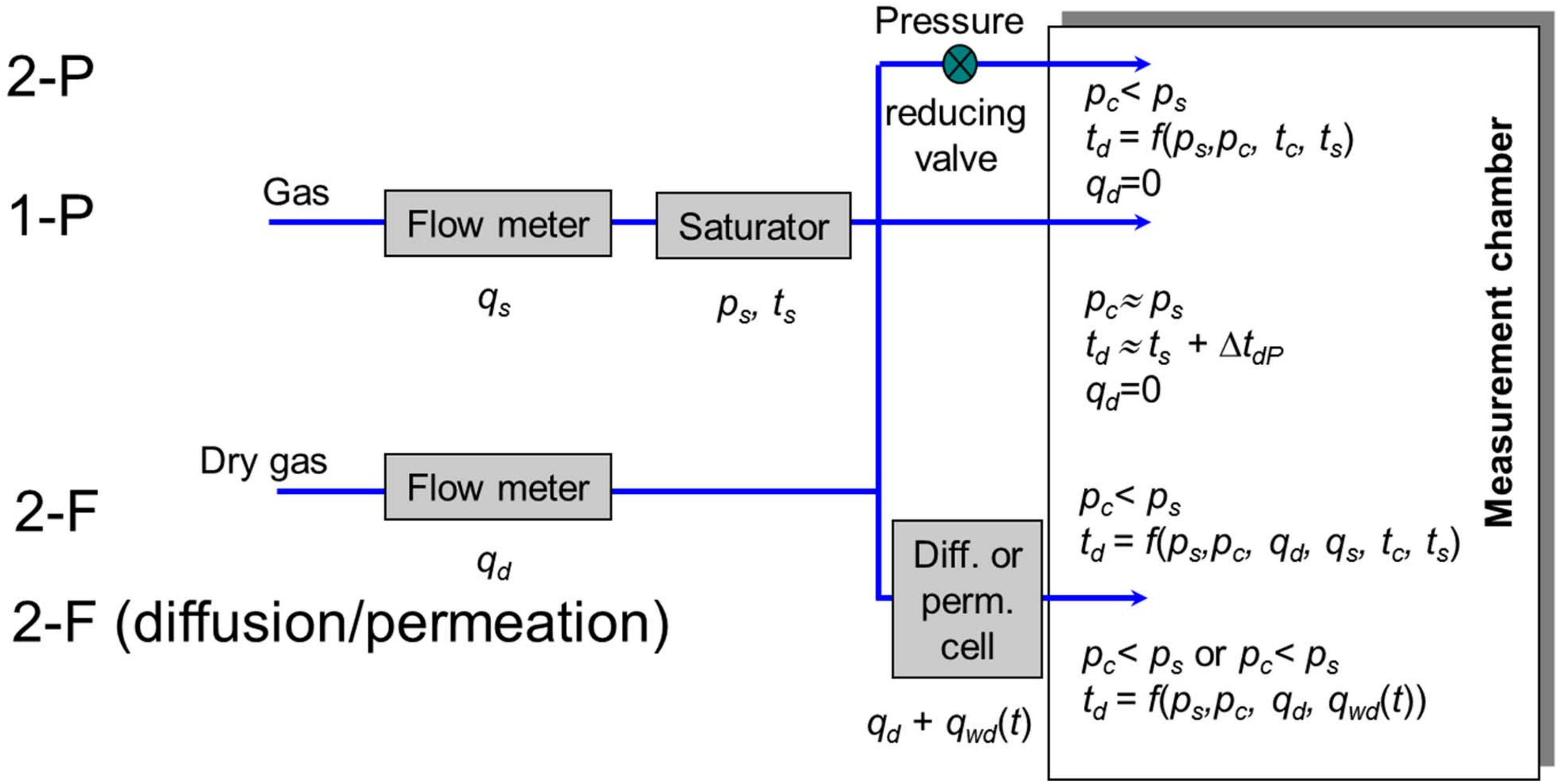


Current practices in humidity calibration: features and limitations

Calibration techniques: Overview

- Primary humidity generators (1-P, 2-P, 2-F, Coulometric)
- Salt solutions
- Climatic chambers
- Humidity calibrators
- Uncontrolled environment

Calibration techniques: 1. Primary humidity generators (1/2)



In all methods a saturator is the core of the system

Calibration techniques:
1. Primary humidity generators (2/2)

Method	1-P	2-P	2-F	2-F(diff./perm.)	Coulometric
Typical applications	Primary dew-point temp. calibrations Primary RH calibrations	Primary dew-point temp. calibrations Primary RH calibrations	Secondary calibrations Primary calibrations in the very low range	Primary calibrations in the very low mixing ratio range Secondary calibrations in the very low mixing range	Primary calibrations in the low/very low humidity range
Advantages	Best uncertainties can be achieved Simplest construction	Faster than 1-P Can be operated in the range below 0 °C without freezing the saturator	Faster than 1-P Easy to adapt in RH applications	Simple construction (especially in secondary calibrations) A direct water vapour mass determination	Solid chemical basis for the operation
Disadvantages	Relatively slow in use If recirculation is used, the pump is a potential source of problems	More complicate than 1-P More significant unc. components than in 1-P Enhancement factor has to be known Unc. of ew and f limit the achievable uncertainty	Poorer uncertainty than with 1-P or 2-P Inaccuracy of flow meters limits the achievable accuracy More complicate than 1-P Number of significant unc. components is larger than in 1-P Enhancement factor has to be known Unc. of ew and f limit the achievable uncertainty	Unc. limited by carrier gas flow measurements Time & temperature dependence of the permeation(/diffusion) characteristics	Unc. limited by carrier gas flow measurements
Notes	A large range can be covered with a single system but usually different saturators are preferred for low and high ranges	Usually not used in the range below -60 °C			In use only at PTB

Calibration techniques:
2. Salt solutions

TABLE 2. *Equilibrium Relative Humidity of Selected Saturated Salt Solutions from 0 to 100 °C*

T °C	Relative Humidity, %									
	Cesium Fluoride	Lithium Bromide	Zinc Bromide	Potassium Hydroxide	Sodium Hydroxide	Lithium Chloride	Calcium Bromide	Lithium Iodide	Potassium Acetate	Potassium Fluoride
0		7.75 ± 0.83				11.23 ± 0.54				
5	5.52 ± 1.9	7.43 ± 0.76	8.86 ± 0.89	14.34 ± 1.7		11.26 ± 0.47		21.68 ± 0.30		
10	4.89 ± 1.6	7.14 ± 0.69	8.49 ± 0.74	12.34 ± 1.4		11.29 ± 0.41	21.62 ± 0.50	20.61 ± 0.25	23.38 ± 0.53	
15	4.33 ± 1.4	6.86 ± 0.63	8.19 ± 0.61	10.68 ± 1.1	9.57 ± 2.8	11.30 ± 0.35	20.20 ± 0.50	19.57 ± 0.20	23.40 ± 0.32	
20	3.83 ± 1.1	6.61 ± 0.58	7.94 ± 0.49	9.32 ± 0.90	8.91 ± 2.4	11.31 ± 0.31	18.50 ± 0.50	18.56 ± 0.16	23.11 ± 0.25	
25	3.39 ± 0.94	6.37 ± 0.52	7.75 ± 0.39	8.23 ± 0.72	8.24 ± 2.1	11.30 ± 0.27	16.50 ± 0.20	17.56 ± 0.13	22.51 ± 0.32	30.85 ± 1.3
30	3.01 ± 0.77	6.16 ± 0.47	7.62 ± 0.31	7.38 ± 0.56	7.58 ± 1.7	11.28 ± 0.24		16.57 ± 0.10	21.61 ± 0.53	27.27 ± 1.1
35	2.69 ± 0.63	5.97 ± 0.43	7.55 ± 0.25	6.73 ± 0.44	6.92 ± 1.5	11.25 ± 0.22		15.57 ± 0.08		24.59 ± 0.94
40	2.44 ± 0.52	5.80 ± 0.39	7.54 ± 0.20	6.26 ± 0.35	6.26 ± 1.2	11.21 ± 0.21		14.55 ± 0.06		22.68 ± 0.81
45	2.24 ± 0.44	5.65 ± 0.35	7.59 ± 0.17	5.94 ± 0.29	5.60 ± 1.0	11.16 ± 0.21		13.49 ± 0.05		21.46 ± 0.70
50	2.11 ± 0.40	5.53 ± 0.31	7.70 ± 0.16	5.72 ± 0.27	4.94 ± 0.85	11.10 ± 0.22		12.38 ± 0.05		20.80 ± 0.62
55	2.04 ± 0.38	5.42 ± 0.28	7.87 ± 0.17	5.58 ± 0.28	4.27 ± 0.73	11.03 ± 0.23		11.22 ± 0.05		20.60 ± 0.56
60	2.03 ± 0.40	5.33 ± 0.25	8.09 ± 0.19	5.49 ± 0.32	3.61 ± 0.65	10.95 ± 0.26		9.98 ± 0.06		20.77 ± 0.53
65	2.08 ± 0.44	5.27 ± 0.23	8.38 ± 0.24	5.41 ± 0.39	2.95 ± 0.60	10.86 ± 0.29		8.65 ± 0.07		21.18 ± 0.53
70	2.20 ± 0.52	5.23 ± 0.21	8.72 ± 0.30	5.32 ± 0.50	2.29 ± 0.60	10.75 ± 0.33		7.23 ± 0.09		21.74 ± 0.56
75	2.37 ± 0.62	5.20 ± 0.19			1.63 ± 0.64	10.64 ± 0.38				22.33 ± 0.61
80	2.61 ± 0.76	5.20 ± 0.18				10.51 ± 0.44				22.85 ± 0.69
85		5.22 ± 0.17				10.38 ± 0.51				23.20 ± 0.80
90		5.26 ± 0.17				10.23 ± 0.59				23.27 ± 0.93
95		5.32 ± 0.16				10.07 ± 0.67				
100		5.41 ± 0.17				9.90 ± 0.77				

TABLE 2. *Equilibrium Relative Humidity of Selected Saturated Salt Solutions from 0 to 100 °C—Continued*

T °C	Relative Humidity, %									
	Magnesium Chloride	Sodium Iodide	Potassium Carbonate	Magnesium Nitrate	Sodium Bromide	Cobalt Chloride	Potassium Iodide	Strontium Chloride	Sodium Nitrate	Sodium Chloride
0	33.66 ± 0.33		43.13 ± 0.66	60.35 ± 0.55						75.51 ± 0.34
5	33.60 ± 0.28	42.42 ± 0.99	43.13 ± 0.50	58.86 ± 0.43	63.51 ± 0.72		73.30 ± 0.34	77.13 ± 0.12	78.57 ± 0.52	75.65 ± 0.27
10	33.47 ± 0.24	41.83 ± 0.83	43.14 ± 0.39	57.36 ± 0.33	62.15 ± 0.60		72.11 ± 0.31	75.66 ± 0.09	77.53 ± 0.45	75.67 ± 0.22
15	33.30 ± 0.21	40.88 ± 0.70	43.15 ± 0.33	55.87 ± 0.27	60.68 ± 0.51		70.98 ± 0.28	74.13 ± 0.06	76.46 ± 0.39	75.61 ± 0.18
20	33.07 ± 0.18	39.65 ± 0.59	43.16 ± 0.33	54.38 ± 0.23	59.14 ± 0.44		69.90 ± 0.26	72.52 ± 0.05	75.36 ± 0.35	75.47 ± 0.14
25	32.78 ± 0.16	38.17 ± 0.50	43.16 ± 0.39	52.89 ± 0.22	57.57 ± 0.40	64.92 ± 3.5	68.86 ± 0.24	70.85 ± 0.04	74.25 ± 0.32	75.29 ± 0.12
30	32.44 ± 0.14	36.15 ± 0.43	43.17 ± 0.50	51.40 ± 0.24	56.03 ± 0.38	61.83 ± 2.8	67.89 ± 0.23	69.12 ± 0.03	73.14 ± 0.31	75.09 ± 0.11
35	32.05 ± 0.13	34.73 ± 0.39		49.91 ± 0.29	54.55 ± 0.38	58.63 ± 2.2	66.96 ± 0.23		72.06 ± 0.32	74.87 ± 0.12
40	31.60 ± 0.13	32.88 ± 0.37		48.42 ± 0.37	53.17 ± 0.41	55.48 ± 1.8	66.09 ± 0.23		71.00 ± 0.34	74.68 ± 0.13
45	31.10 ± 0.13	31.02 ± 0.37		46.93 ± 0.47	51.95 ± 0.47	52.56 ± 1.5	65.26 ± 0.24		69.99 ± 0.37	74.52 ± 0.16
50	30.54 ± 0.14	29.21 ± 0.40		45.44 ± 0.60	50.93 ± 0.55	50.01 ± 1.4	64.49 ± 0.26		69.04 ± 0.42	74.43 ± 0.19
55	29.93 ± 0.16	27.50 ± 0.45			50.15 ± 0.65	48.02 ± 1.4	63.78 ± 0.28		68.15 ± 0.49	74.41 ± 0.24
60	29.26 ± 0.18	25.95 ± 0.52			49.66 ± 0.78	46.74 ± 1.5	63.11 ± 0.31		67.35 ± 0.57	74.50 ± 0.30
65	28.54 ± 0.21	24.62 ± 0.62			49.49 ± 0.94	46.33 ± 1.9	62.50 ± 0.34		66.64 ± 0.67	74.71 ± 0.37
70	27.77 ± 0.25	23.57 ± 0.74			49.70 ± 1.1	46.97 ± 2.3	61.93 ± 0.38		66.04 ± 0.78	75.06 ± 0.45
75	26.94 ± 0.29	22.85 ± 0.88			50.33 ± 1.3	48.80 ± 2.9	61.43 ± 0.43		65.56 ± 0.91	75.58 ± 0.55
80	26.05 ± 0.34	22.52 ± 1.0			51.43 ± 1.5	52.01 ± 3.7	60.97 ± 0.48		65.22 ± 1.1	76.29 ± 0.65
85	25.11 ± 0.39	22.63 ± 1.2					60.56 ± 0.54		65.03 ± 1.2	
90	24.12 ± 0.46	23.25 ± 1.4					60.21 ± 0.61		65.00 ± 1.4	
95	23.07 ± 0.52									
100	21.97 ± 0.60									

TABLE 2. *Equilibrium Relative Humidity of Selected Saturated Salt Solutions from 0 to 100 °C—Continued*

T °C	Relative Humidity, %							
	Ammonium Chloride	Potassium Bromide	Ammonium Sulfate	Potassium Chloride	Strontium Nitrate	Potassium Nitrate	Potassium Sulfate	Potassium Chromate
0			82.27 ± 0.90	88.61 ± 0.53		96.33 ± 2.9	98.77 ± 1.1	
5		85.09 ± 0.26	82.42 ± 0.68	87.67 ± 0.45	92.38 ± 0.56	96.27 ± 2.1	98.48 ± 0.91	
10	80.55 ± 0.96	83.75 ± 0.24	82.06 ± 0.51	86.77 ± 0.39	90.55 ± 0.38	95.96 ± 1.4	98.18 ± 0.76	
15	79.89 ± 0.59	82.62 ± 0.22	81.70 ± 0.38	85.92 ± 0.33	88.72 ± 0.28	95.41 ± 0.96	97.89 ± 0.63	
20	79.23 ± 0.44	81.67 ± 0.21	81.34 ± 0.31	85.11 ± 0.29	86.89 ± 0.29	94.62 ± 0.66	97.59 ± 0.53	
25	78.57 ± 0.40	80.89 ± 0.21	80.99 ± 0.28	84.34 ± 0.26	85.06 ± 0.38	93.58 ± 0.55	97.30 ± 0.45	97.88 ± 0.49
30	77.90 ± 0.57	80.27 ± 0.21	80.63 ± 0.30	83.62 ± 0.25		92.31 ± 0.60	97.00 ± 0.40	97.08 ± 0.41
35		79.78 ± 0.22	80.27 ± 0.37	82.95 ± 0.25		90.79 ± 0.83	96.71 ± 0.38	96.42 ± 0.37
40		79.43 ± 0.24	79.91 ± 0.49	82.32 ± 0.25		89.03 ± 1.2	96.41 ± 0.38	95.89 ± 0.37
45		79.18 ± 0.26	79.56 ± 0.65	81.74 ± 0.28		87.03 ± 1.8	96.12 ± 0.40	95.50 ± 0.40
50		79.02 ± 0.28	79.20 ± 0.87	81.20 ± 0.31		84.78 ± 2.5	95.82 ± 0.45	95.25 ± 0.48
55		78.95 ± 0.32		80.70 ± 0.35				
60		78.94 ± 0.35		80.25 ± 0.41				
65		78.99 ± 0.40		79.85 ± 0.48				
70		79.07 ± 0.45		79.49 ± 0.57				
75		79.16 ± 0.50		79.17 ± 0.66				
80		79.27 ± 0.57		78.90 ± 0.77				
85				78.68 ± 0.89				
90				78.50 ± 1.0				
95								
100								

[L. Greenspan, J. Res. NBS, Vol 81A, No. 1, p. 89 - 96]

Calibration techniques:
2. Salt solutions

TABLE 2. *Equilibrium Relative Humidity of Selected Saturated Salt Solutions from 0 to 100 °C*

T °C	Relative Humidity, %									
	Cesium Fluoride	Lithium Bromide	Zinc Bromide	Potassium Hydroxide	Sodium Hydroxide	Lithium Chloride	Calcium Bromide	Lithium Iodide	Potassium Acetate	Potassium Fluoride
0		7.75 ± 0.83				11.23 ± 0.54				
5	5.52 ± 1.9	7.43 ± 0.76	8.86 ± 0.89	14.34 ± 1.7		11.26 ± 0.47		21.68 ± 0.30		
10	4.89 ± 1.6	7.14 ± 0.69	8.49 ± 0.74	12.34 ± 1.4		11.29 ± 0.41	21.62 ± 0.50	20.61 ± 0.25	23.38 ± 0.53	
15	4.33 ± 1.4	6.86 ± 0.63	8.19 ± 0.61	10.68 ± 1.1	9.57 ± 2.8	11.30 ± 0.35	20.20 ± 0.50	19.57 ± 0.20	23.40 ± 0.32	
20	3.83 ± 1.1	6.61 ± 0.58	7.94 ± 0.49	9.32 ± 0.90	8.91 ± 2.4	11.31 ± 0.31	18.50 ± 0.50	18.56 ± 0.16	23.11 ± 0.25	
25	3.39 ± 0.94	6.37 ± 0.52	7.75 ± 0.39	8.23 ± 0.72	8.24 ± 2.1	11.30 ± 0.27	16.50 ± 0.20	17.56 ± 0.13	22.51 ± 0.32	30.85 ± 1.3
30	3.01 ± 0.77	6.16 ± 0.47	7.62 ± 0.31	7.38 ± 0.56	7.58 ± 1.7	11.28 ± 0.24		16.57 ± 0.10	21.61 ± 0.53	27.27 ± 1.1
35	2.69 ± 0.63	5.97 ± 0.43	7.55 ± 0.25	6.73 ± 0.44	6.92 ± 1.5	11.25 ± 0.22		15.57 ± 0.08		24.59 ± 0.94
40	2.44 ± 0.52	5.80 ± 0.39	7.54 ± 0.20	6.26 ± 0.35	6.26 ± 1.2	11.21 ± 0.21		14.55 ± 0.06		22.68 ± 0.81
45	2.24 ± 0.44	5.65 ± 0.35	7.59 ± 0.17	5.94 ± 0.29	5.60 ± 1.0	11.16 ± 0.21		13.49 ± 0.05		21.46 ± 0.70
50	2.11 ± 0.40	5.53 ± 0.31	7.70 ± 0.16	5.72 ± 0.27	4.94 ± 0.85	11.10 ± 0.22		12.38 ± 0.05		20.80 ± 0.62
55	2.04 ± 0.38	5.42 ± 0.28	7.87 ± 0.17	5.58 ± 0.28	4.27 ± 0.73	11.03 ± 0.23		11.22 ± 0.05		20.60 ± 0.56
60	2.03 ± 0.40	5.33 ± 0.25	8.09 ± 0.19	5.49 ± 0.32	3.61 ± 0.65	10.95 ± 0.26		9.98 ± 0.06		20.77 ± 0.53
65	2.08 ± 0.44	5.27 ± 0.23	8.38 ± 0.24	5.41 ± 0.39	2.95 ± 0.60	10.86 ± 0.29		8.65 ± 0.07		21.18 ± 0.53
70	2.20 ± 0.52	5.23 ± 0.21	8.72 ± 0.30	5.32 ± 0.50	2.29 ± 0.60	10.75 ± 0.33		7.23 ± 0.09		21.74 ± 0.56
75	2.37 ± 0.62	5.20 ± 0.19			1.63 ± 0.64	10.64 ± 0.38				22.33 ± 0.61
80	2.61 ± 0.76	5.20 ± 0.18				10.51 ± 0.44				22.85 ± 0.69
85		5.22 ± 0.17				10.38 ± 0.51				23.20 ± 0.80
90		5.26 ± 0.17				10.23 ± 0.59				23.27 ± 0.93
95		[illegible]				10.07 ± 0.67				
100		[illegible]				9.90 ± 0.77				

Limitations:

- Sensitivity to contamination, leaks and temperature gradients
- Poor applicability to measurements at different temperatures
- Static ⇒ slow, heat dissipation from RH probe causes an error and mismatch with measurements in a gas stream
- Filter of a probe needs to be removed for the calibration
- Skilled operator is needed
- Monitoring of operators and method is needed
- Measurements in air at amb. pressure

Features:

- Saturated and unsaturated salt solutions
- Traceability routes:
  1. Certified reference materials available (+ validation of complete method is crucial)
  2. Calibrated reference RH instrument
- Simple and low cost

[L. Greenspan, J. Res. NBS, Vol 81A, No. 1, p. 89 - 96]

Calibration techniques:
3. Climatic chambers

Climatic chamber

Controlling humidity and temperature

+

Humidity reference

Chilled mirror or RH hygrometer

Thermometer

PRT or thermistor + digital bridge

Calibration techniques:
3. Climatic chambers

Features:

- Separate reference hygrometer and thermometer (or thermo-hygrometer)
- Traceability route: Calibrated reference instruments
- Applicable for a larger amount of devices
- Achievable uncertainty depends on the instruments types and the approach for calibrating and monitoring the references and chamber
- Cost depends on the target uncertainty and range
- Regular check of temperature and humidity inhomogenities (input to uncertainty)

Limitations:

- Usually applicable only for measurements in air at ambient pressure
- Typically limited range at dry end
- For some types: leaks in lead-through may significantly affect
- Thermal radiation needs to be considered

Calibration techniques:
4. Humidity calibrators

Calibration techniques:
4. Humidity calibrators

Features:

- Two traceability routes:
  1. Calibrated reference instrument(s)
  2. Direct calibration of the calibrator (rarely followed route)
- Commercial systems from expensive primary-type generators to low cost simple calibrators
  - With best instruments better uncertainty than in climatic chamber
- Several operation principles
- Achievable uncertainty depends on the types of calibrator and reference
- Regular check of temperature and humidity inhomogenities (input to uncertainty)

Limitations:

- Practicality is typically limited by probe fittings
- Typically more limited in temperature range and practicality in large scale calibration work than climatic chamber
- Usually applicable only for measurements in air at ambient pressure
- Low cost calibrators usually only for ambient air temperature range
- In many systems, heat flow through probes needs to be considered when operating temperatures different from ambient temperature

Calibration techniques:
4. Uncontrolled environment

Features:

- Calibration of a fixed mounted instrument by locating a reference instrument close to it
- Typically only one point calibration
  $\Rightarrow$ traceability is only achieved by combining the calibration result with less frequent (or – in some cases – initial) characterisation of the instrument
- Traceability through reference instrument

Limitations:

- Typically only one measurement point (ambient humidity & temp.)
- Due to uncontrolled environment and limited scope of the calibration, overall uncertainty is larger
- Challenge to determine the effect of temperature and humidity differences close to the devices
- Operator affects the results
- It may be challenging to find an appropriate recording method.

Calibration techniques: Humidity reference

- Chilled mirror hygrometers
  - Most accurate and stable in long term
  - Wide range
  - Very expensive
  - Needs skilled operator and maintenance

- Capacitive RH hygrometers
  - Easy to maintain to implement in automatic systems
  - Less expensive
  - Hysteresis, temperature dependency
  - Drift may be difficult to predict (especially if operated in extreme ranges)

- Psychrometers
  - Rarely used anymore
  - Maintenance (wick, water) and humidifying effect

- Spectroscopic
  - Trace humidity range
  - Expensive and sophisticated instruments

Calibration methods: Overview

- Laboratory and on-site calibrations
- Measurement procedures

Calibration methods: Laboratory vs. on site

- Calibrations in laboratory
  - Coverage of multipoint calibration matches with actual operation range
  - Better uncertainty
  - Probe calibration: Effect of data recording and analysis system?
  - Installing & uninstalling
  - Effect of transportation?
- On-site calibrations
  - No effects from transportation, installing, different recording system
  - Typically more limited in range and uncertainty

Calibration methods: Measurement procedures

- Relative humidity:
  - Coverage in terms of humidity and temperature
    - Cost vs. needed uncertainty in full range
    - Currently no calibration services for temperatures above 100 °C
  - Hysteresis needs to be considered in calibration
    - Calibration certificate should indicate if this is covered or not in calibration result and uncertainty
  - Acclimatisation before actual calibration measurements
  - Time of stabilisation
    - Calibrations are only carried out at ”stable” conditions
  - At temperatures below 0 °C, relative humidity may be expressed with respect to ice (e.g. many NMIs) or supercooled water (e.g. WMO)
    - Calibration certificate should specify which one is reported

Calibration methods: Measurement procedures

- Dew-point temperature:
  - Coverage in pressure if relevant
  - In the range 0 °C, dew or frost may be detected
    - Calibration certificate should specify which one is reported
  - Measurement points usually from dry to wet
    - Repeatability of measurement points should be studied and included in the results
  - Measurements at stable conditions
  - Effect of measurement head temperature should be considered
  - In case of capacitive dew-point temperature sensor, the effect of purging/autocalibration procedure should be studied and included in the results

Humidity calibration at high temperature

Humidity at high temperatures

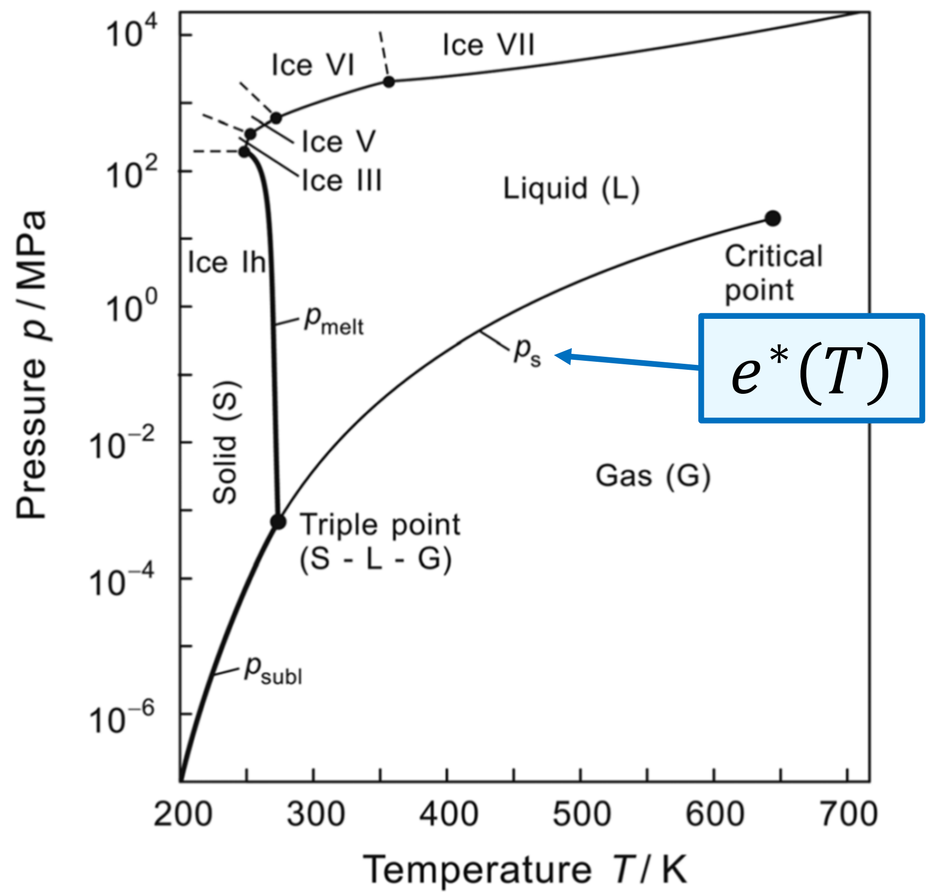
- At a temperature above boiling point of water saturation can only be achieved by increasing pressure
- Standard definitions of RH do not apply to temperatures above boiling point of water

$$RH = \frac{f(p, t_d)e(t_d)}{f(p, t_a)e(t_a)} \times 100\ \%\text{rh}$$

- Pragmatic solution:

$$RH = \frac{f(p^*, t_d)e^*(t_d{}^*)}{f(p^*, t_a)e^*(t_a)} \times 100\ \%\text{rh}$$

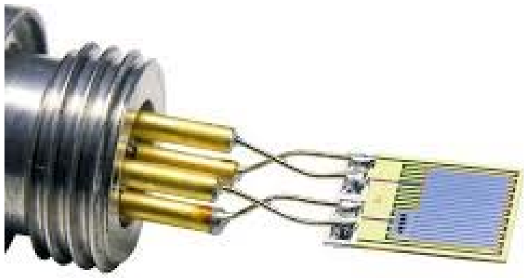
Phase diagram of water



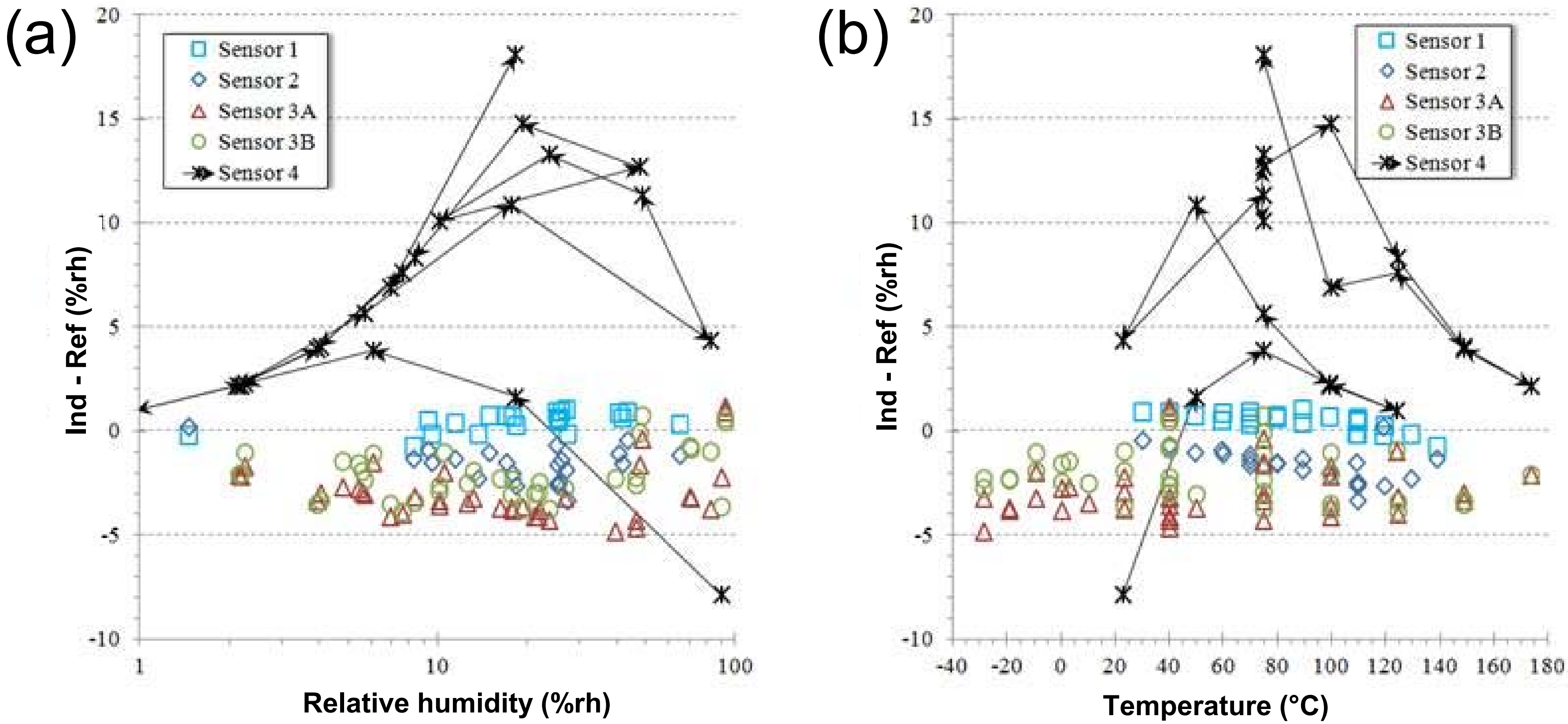
[R. Feistel, J. Lovell-Smith, Metrologia **54** (2017) 566–576]

Effect of high temperature on a capacitive humidity sensor

- Temperature compensation
- Thermal stress (expansion)
    - Polymer and sensor layers
    - Wires and bondings
    - Temperature sensor
- Heat transport:
    - Thermal radiation
    - Conductive thermal flow along the probe
- Chemical effects
- Potential leak current



Example



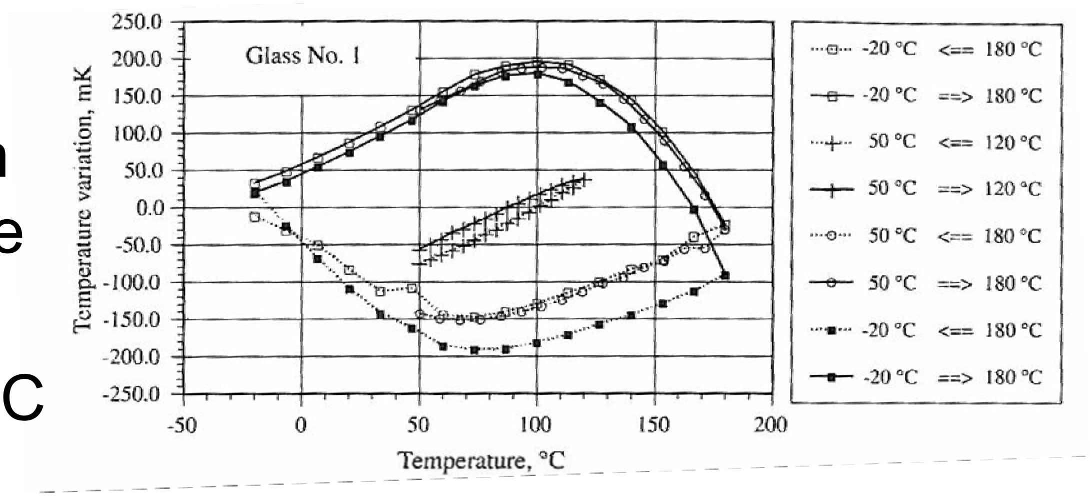
Difference of the sensor humidity reading and the reference relative humidity as a function of the (a) relative humidity and (b) the chamber temperature. Sensor type 4 shows an increased deviation after exposure at high temperatures, which is not visible with the other sensor types.

[R. Bosma, A. Peruzzi, Int J Thermophys (2014) 35:738–747]

Hysteresis

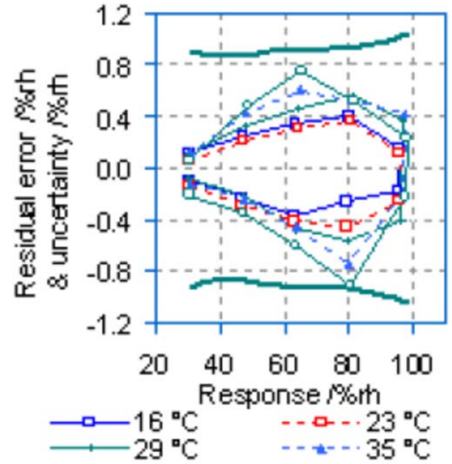
- Hysteresis typically increases with wider operation temperature range
- For industrial platinum resistance thermometers, hysteresis of ±0.2°C has been reported
- For RH probes, hysteresis is typically between ±0.1 %rh and ±0.8 %rh
  - No clear correlation with temperature
  - Note: temperature affects time constant
  - Note: temperature may affect repeatability

Industrial platinum resistance thermometers



[D. R. White et al, Int J Thermophys (2010) 31:1676-1684]

RH probes

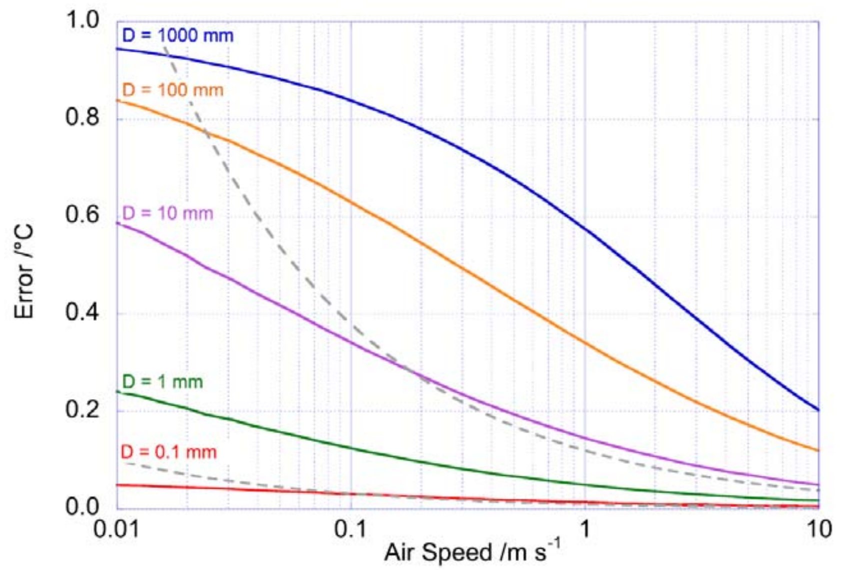


[https://www.measurement.govt.nz/research/temperature-and-humidity/humidity-sensor-calibration]

Thermal radiation effect

- At high temperatures, chamber wall temperature may significantly differ from air temperature
  $\Rightarrow$ radiative heat transfer between
  a sensor and the wall
- The heat transfer is dependent on the surface emissivity: less transferred heat with lower emissivity
- Emissivity (scale 0 to 1) varies depending on surface structure, e.g.[1)] :
  - Steel: 0.07 to 0.80
  - Copper: 0.03 to 0.87

Radiative error



t_{Air} = 20 °C; t_{Wall} = 21 °C); L = 15 mm
sensor surface black (ε_s = 1)

[Michael de Podesta et al 2018 Metrologia 55 229]

- Visually shining surface does not necessarily mean low emissivity
- EURAMET Guide cg-20: ”*Depending on the model of the climatic chamber, differences of several kelvin are possible above 150 °C*” [2)]

1) https://www.omega.com/literature/transactions/volume1/emissivitya.html

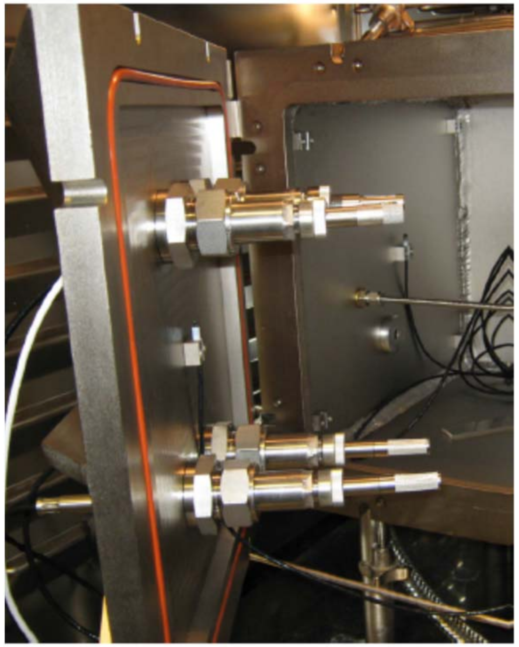
2) https://www.euramet.org/publications-media-centre/calibration-guidelines/

Radiative error on humidity probes

- Emissivity of the filter and probe body
  - Lower emissivity ⇒ smaller error
- Radiation shield may used for studying and/or reducing the radiative error
  - Suffcient air speed inside the shield must be ensured
- Radiative error in calibration:
  - ”isothermal” measurement chamber ⇒ negligible error

Heat conduction

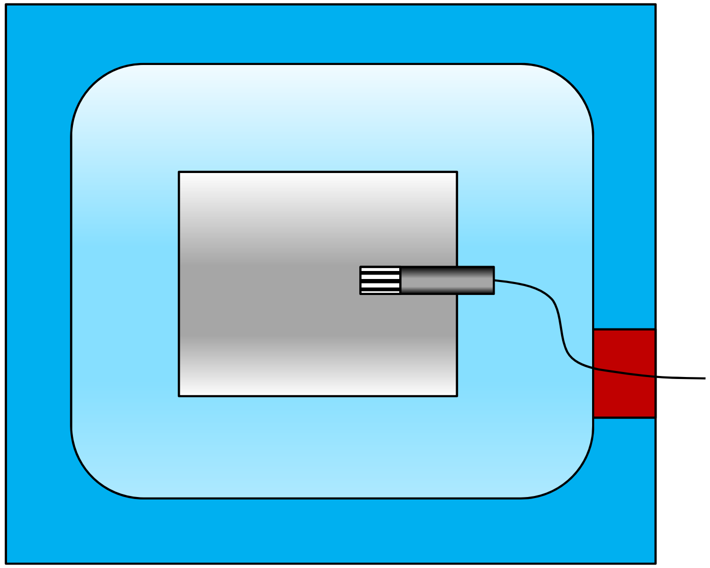
- High temperature probes are often designed for partly immersion:
  - Large temperature difference between measurement volume and ambient causes significant conductive thermal flow along the probe
  - The effect is high dependent on the installation and ambient conditions
  - If calibrated immersed fully, how the result is applied in normal operation?
- Sensor wires may significantly conduct heat



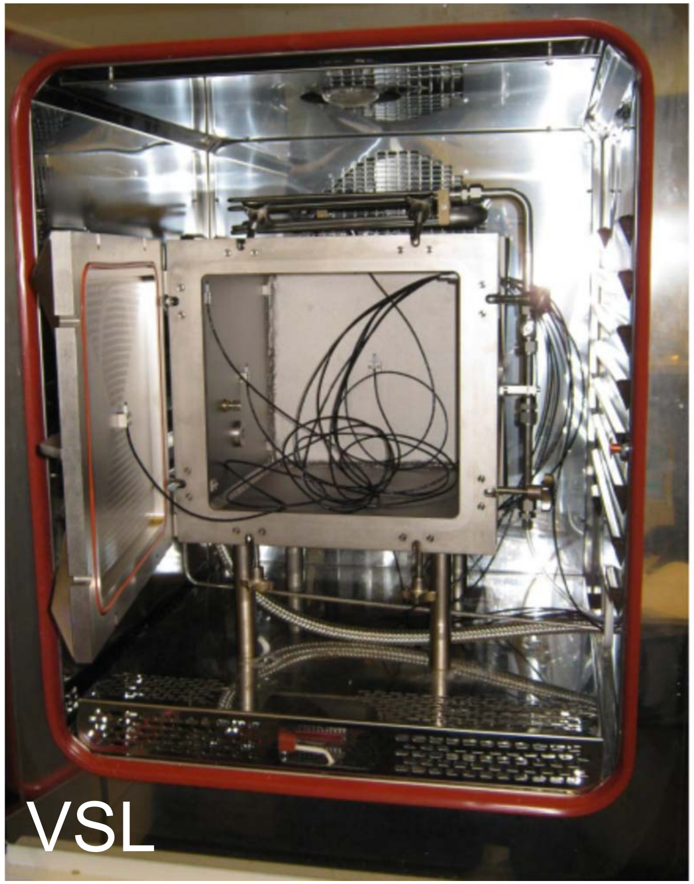
[R. Bosma, A. Peruzzi, Int J Thermophys (2014) 35:738–747]

Use of an inner chamber

- Minimizes
  - heat conduction along the probe
  - thermal radiation error
    (isothermal walls of the inner chamber)
- Challenges
  - Sufficient gas circulation in the inner chamber
  - Thermalising input gas when using a separate humidity control system
  - More complicated to set up
- Note: heat flow along probe cable

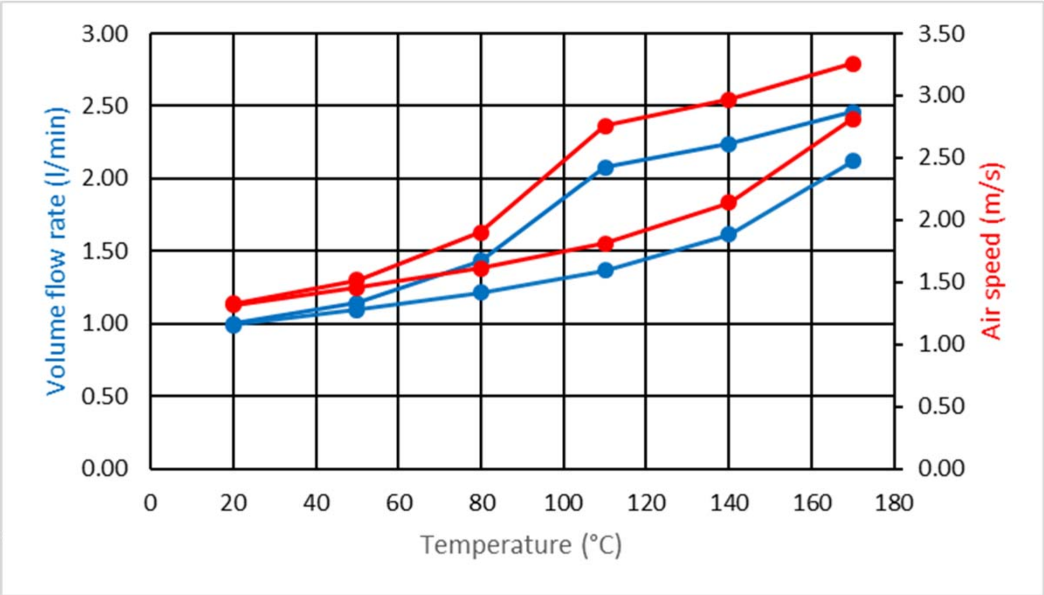


Use of an inner chamber



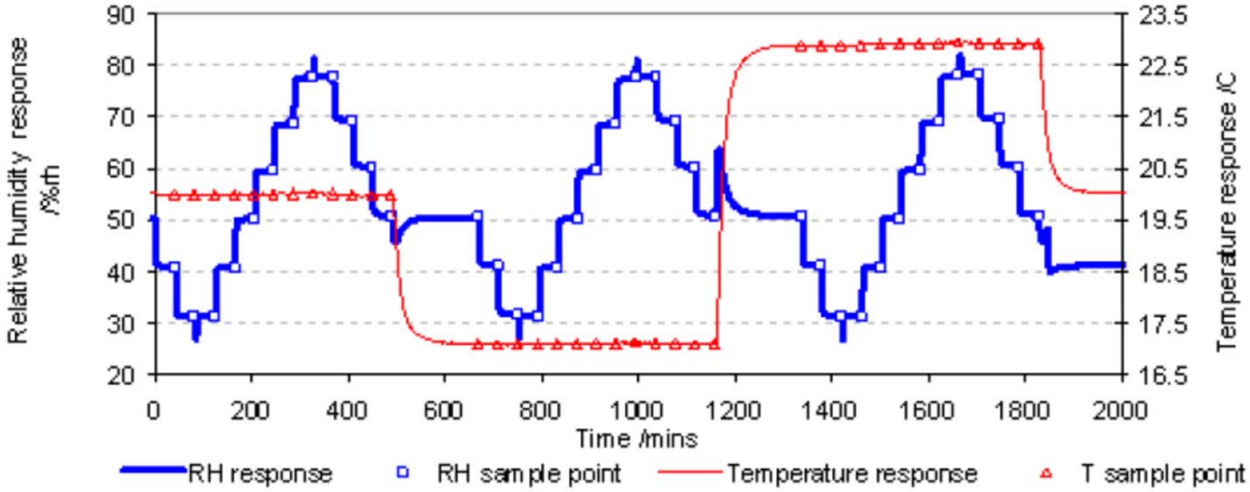
Calibration set up for high temperature: further notes

- Larger temperature difference between measurement volume and ambient ⇒ probability of heat leak errors and their significance increase
- High humidity gas contain a lot of water:
  - Sufficient heating of all tubing outside are crucial
  - Large amount water is consumed in humidification
- With fixed mass flow rate, volume flow rate measured inside and outside are very different



Calibration procedure to cover a temperature range

- MSL approach:
  (for very limited temperature range)



- Current MIKES approach:
  - At least 3 humidity points at one temperature
    - whole RH range of interest
    - each point measured twice; measurements in ascending and descending order
    - typically close to ambient temperature
  - Single humidity point measured at temperature in > 10 °C intervals
    - RH value same as one in the complete set
    - RH point measured twice; measurements in ascending and descending order

Calibration procedure to cover a temperature range

- Trade-off between completeness (uncertainty) and amount of work (cost)
  - MSL approach is too time consuming for a wide temperature range
  - MIKES approach does not reveal potential changes in characteristic curve at high (or low) temperature
- Within HIT, an alternative approach based on randomly selected points at RH-T plane was introduced by Shahin Tabandeh
- Within HIT, a recommendation is under preparation for selecting an appropriate calibration procedure

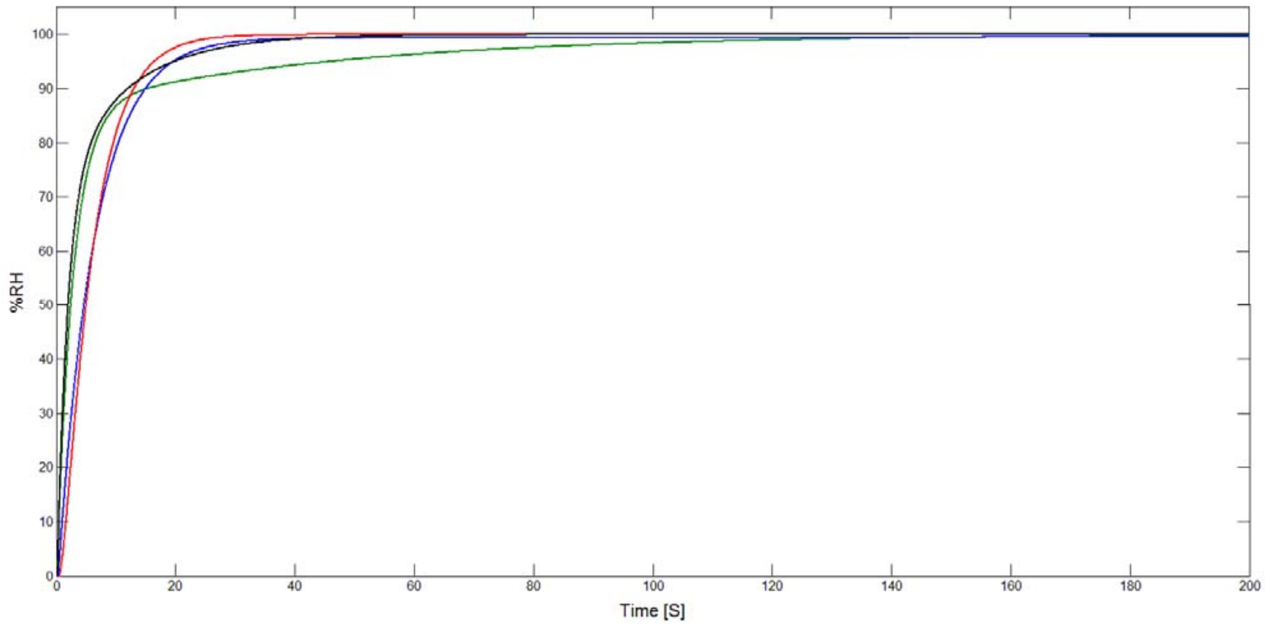
Time dependent effects

Origins of time dependent errors

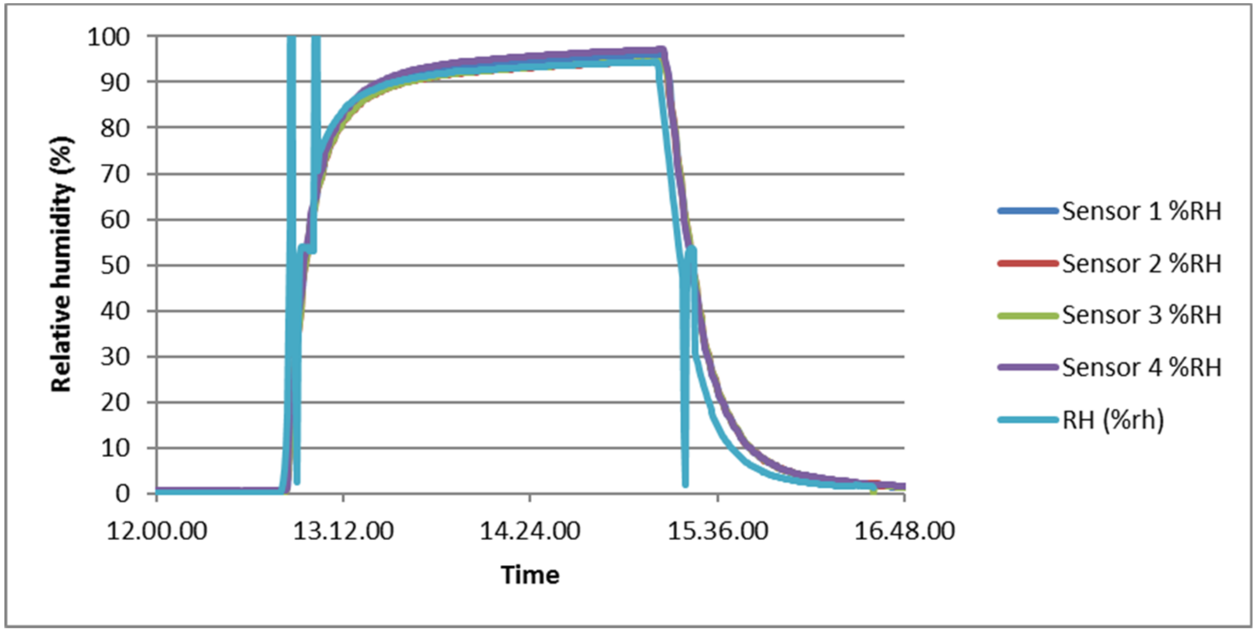
- Gas dynamics:
  - Diffusion: slow
  - Convection: fast
- Permeation, adsorption, desorption of water vapour
  - Surfaces
  - Sensor
- Thermal effects
  - Gas
  - Sensor
- Sensor design
  - Measurement circuit
  - Humidity sensitive material
  - Temperature compensation

Response time

- Sensor

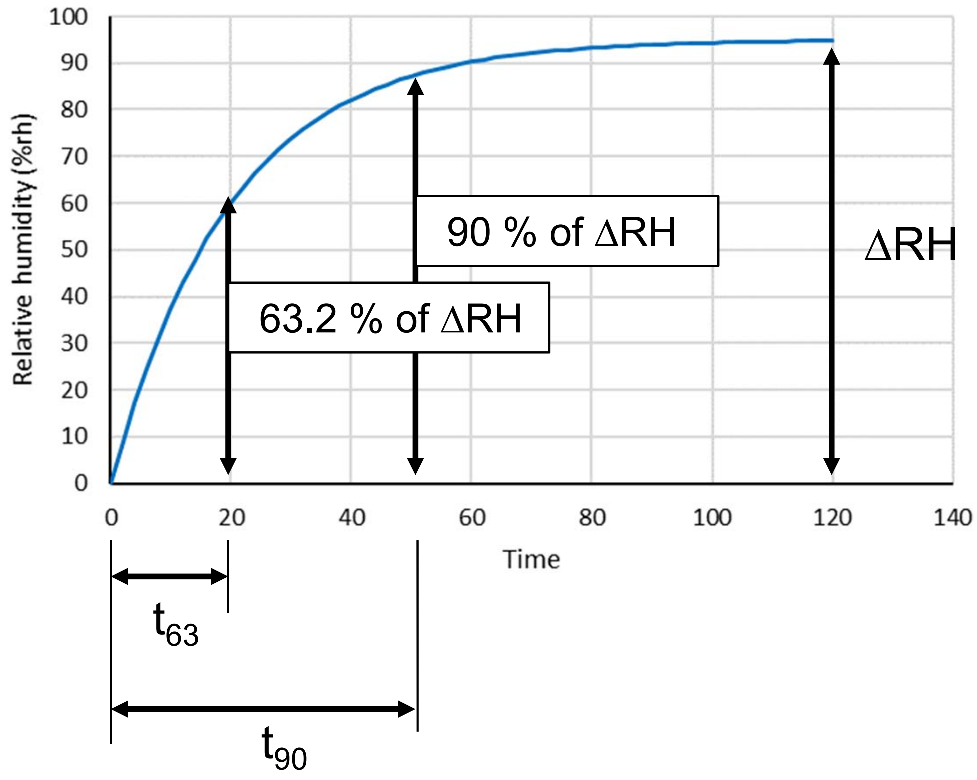


- System

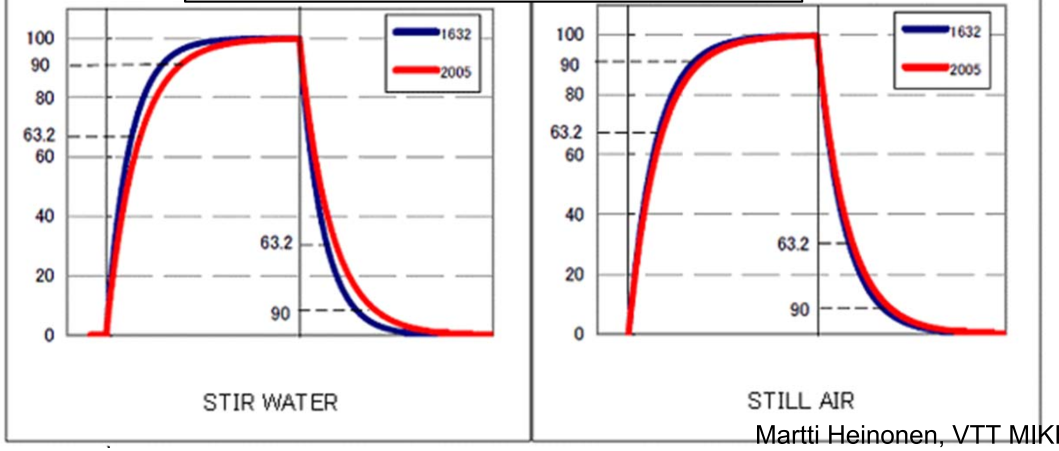


Response time of a sensor

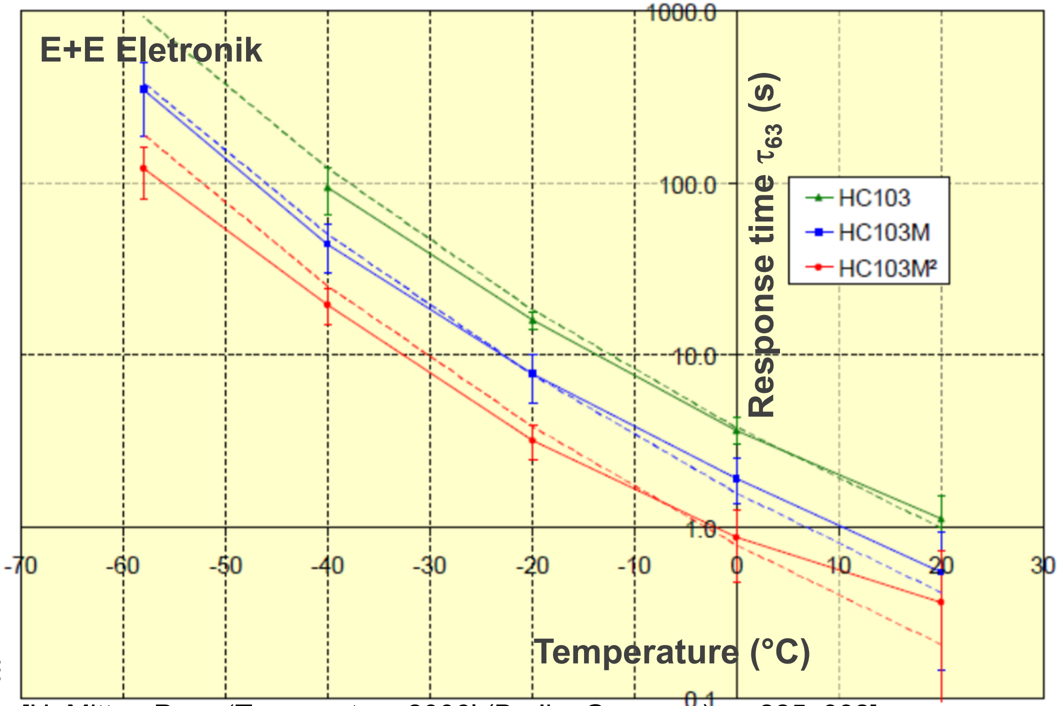
- Single constant response time is idealisation:
  - Several time dependent phenomena
  - Dependent of conditions
- Effect of
  - filter
  - gas speed



Response time of Pt thin film RTD



[http://www.hayashidenko.co.jp/en/info16.html]



[H. Mitter, Proc. 'Temperature 2006' (Berlin, Germany) pp 225–332]

Response time of a sensor: examples

- Vaisala HMT330:

Response time (90%) at +20 °C (+68 °F) in still air	8 s/17 s** with grid filter 20 s/50 s** with grid + steel netting filter 40 s/60 s** with sintered filter

- Rotronic HygroClip:

Filter	Only carrier	Wire mesh filter	PE filter	PTFE filter	Stainless steel
Filter				2	
Material	PC / 1.4301	1.4401	Polyethylene	PTFE	1.4404
Pore size	-	10 µm	40 µm	10 µm	25 µm
Temperature range	-	-100...+200 °C	-50...+100 °C	-80...+200 °C	-100...+200 °C
Response time %RH[2]	12 s	12 s	15 s	18 s	15 s
Response time °C[3]	80 s	180 s	180 s	170 s	-
Response time °C[4]	120 s	190 s	210 s	210 s	200 s

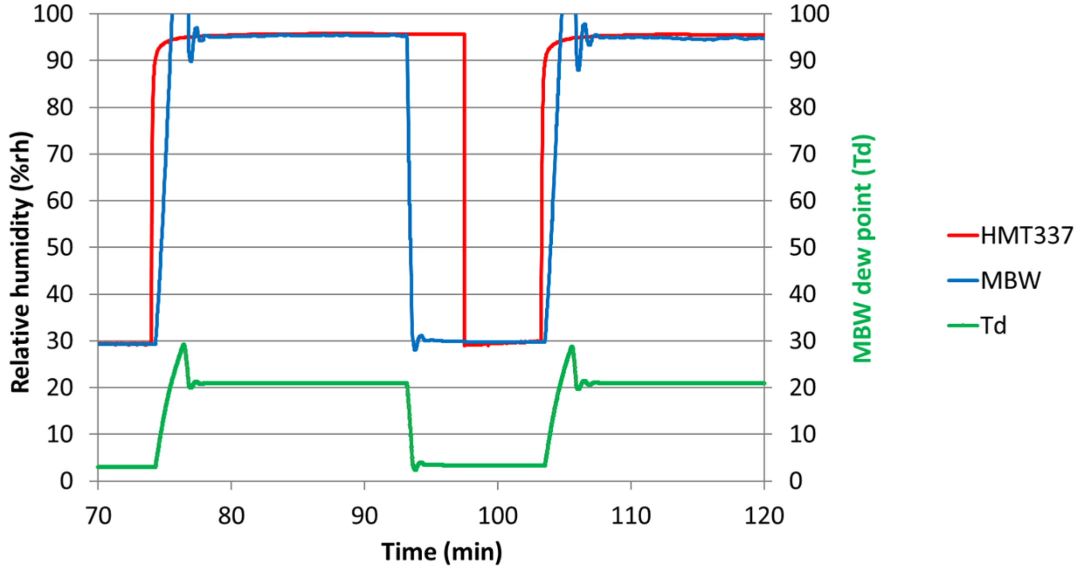
[2] T63: 100 %RH → 30 %RH

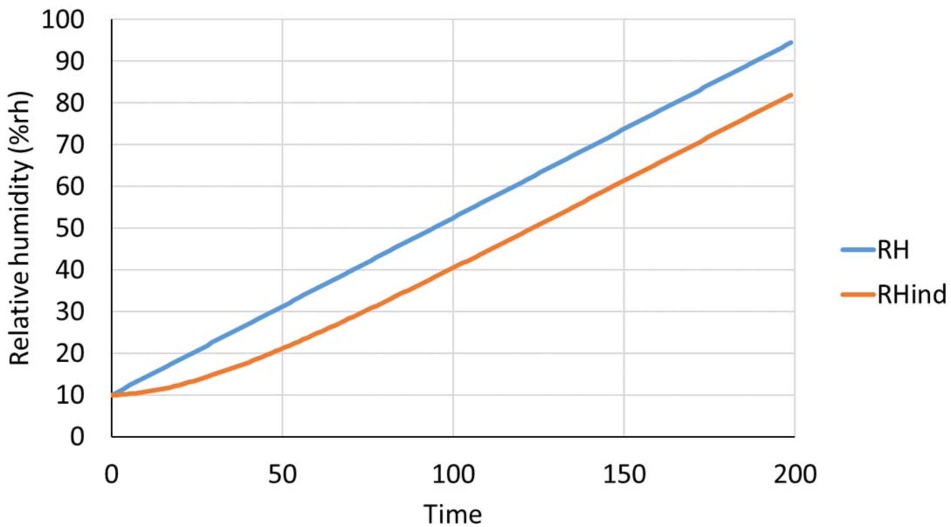
- Testo 6621:

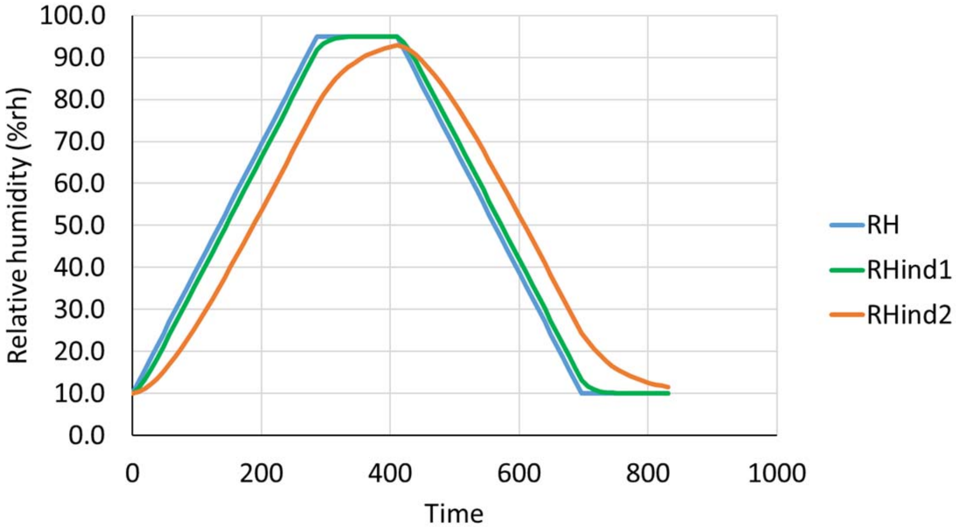
Reaction time	t90: ‹ 15 s at 2 m/s; When calibrating, make note of adjustment: The response time may be considerably higher in stagnant air

Effect of different response times/types

- Chilled mirror hygrometer behaves differently from RH sensors
- Linear change
  ⇒ linear response (with a delay)



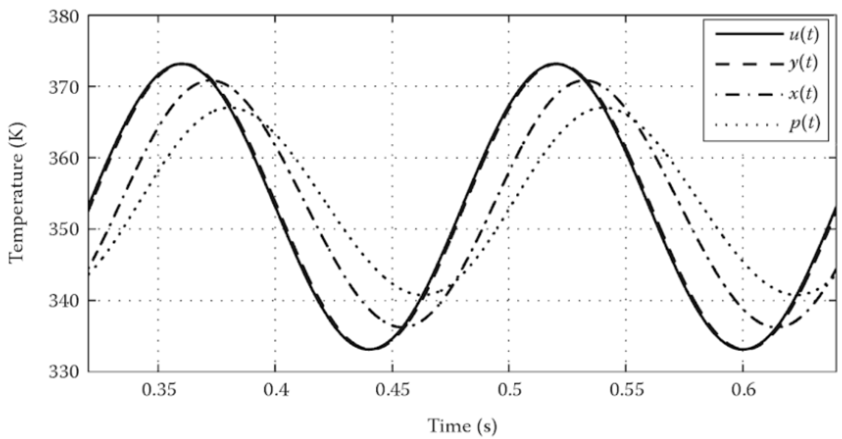




Comparing sensors with different response times

- Larger differences in sensor response times to be compared in non-static conditions
  ⇒ larger comparison uncertainty
- Slower sensor with respect to humidity change speed
  ⇒ larger measurement uncertainty

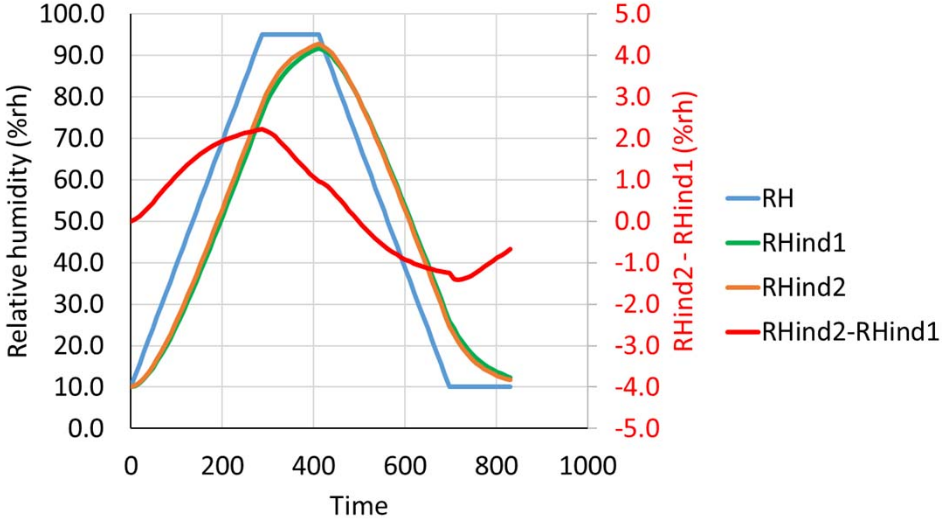
Sensors with different time constants with oscillating input

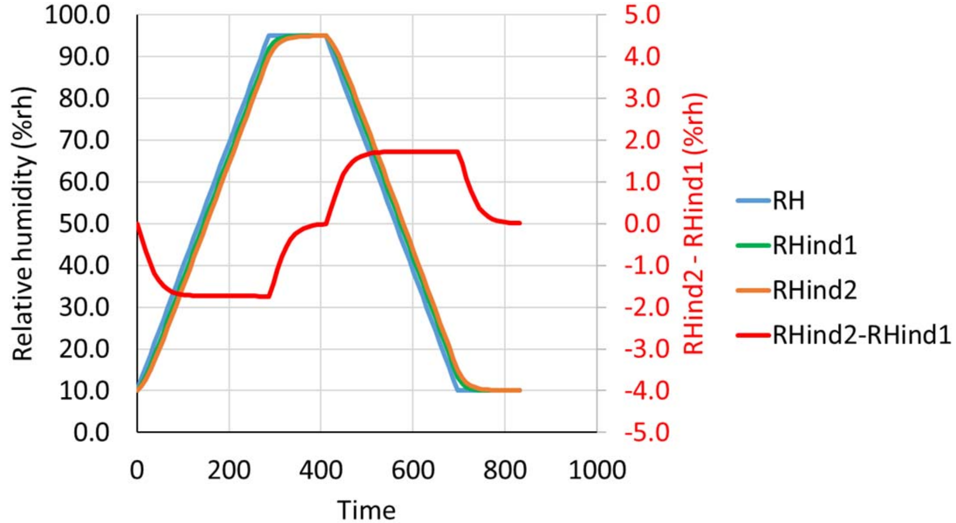


[Krzysztof Iniewski (ed.), Smart Sensors for Industrial Applications, CRC Press 2017, p. 238]

Two ideal sensors with different time constants

(Simplified theoretical calculation)

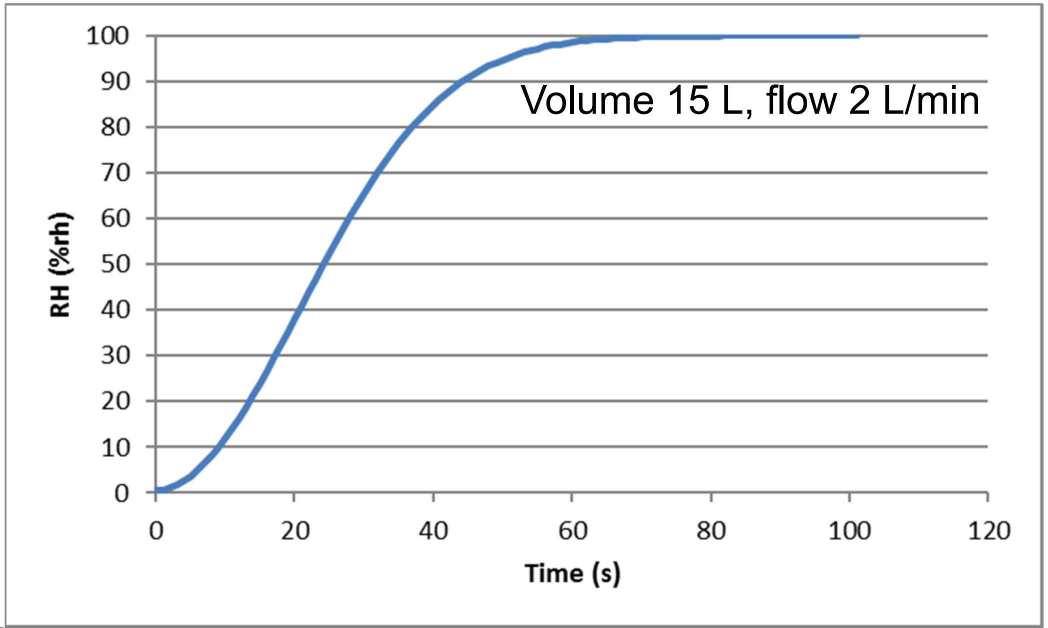


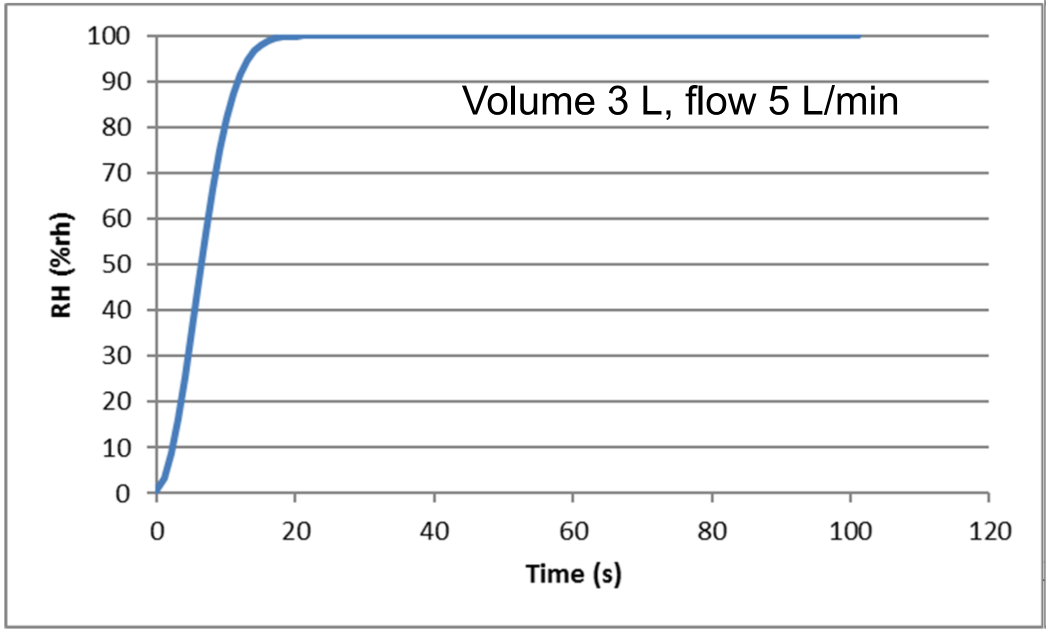


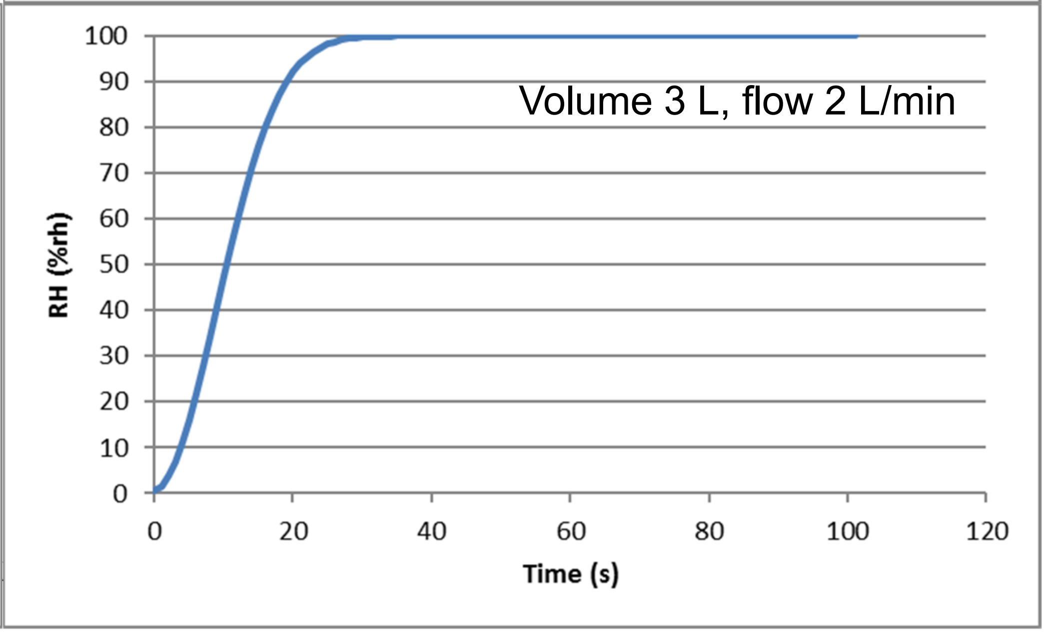
τ_1	τ_2	$\tau_1 - \tau_2$	std.unc (%rh)
15	21	-6	1.00
15	8.5	6.5	1.05
40	46.8	-6.8	1.04
40	33.5	6.5	1.03
70	78.5	-8.5	1.04
70	62	8	1.05

Response time: calibration system

- Volume and flow rate dominate
- Other:
  - Dead spaces
  - Flow profile
  - Materials







Response time: calibration system

- Volume and flow rate dominate in overall humidity change speed
  - Note: flow profile in the system significantly affect the water vapour mixing and thus the humidity homogeneity
- Typically humidity inhomogeneity increases with increasing instability of humidity
- In particular in the trace humidity range, the surface quality of inner walls and dead spaces in the system are major factors in response time of the system

Uncertainty in Humidity Calibrations

Sources of uncertainty

- Calibration standard: Reference hygrometer
- Measurement chamber / calibration setup
- Calibration procedure
- Device under calibration (DUC)

Sources of uncertainty

- Calibration standard: Reference hygrometer
  - Calibration correction
  - Non-linearity (fitting of calibration equation)
  - Drift since the last calibration
  - Repeatability / reproducibility
  - Resolution
  - Time of stabilisation / Response time
  - Hysteresis
  - (Stability)
  - Temperature and pressure dependency

  - Note: some of these may be included in the calibration uncertainty

Sources of uncertainty

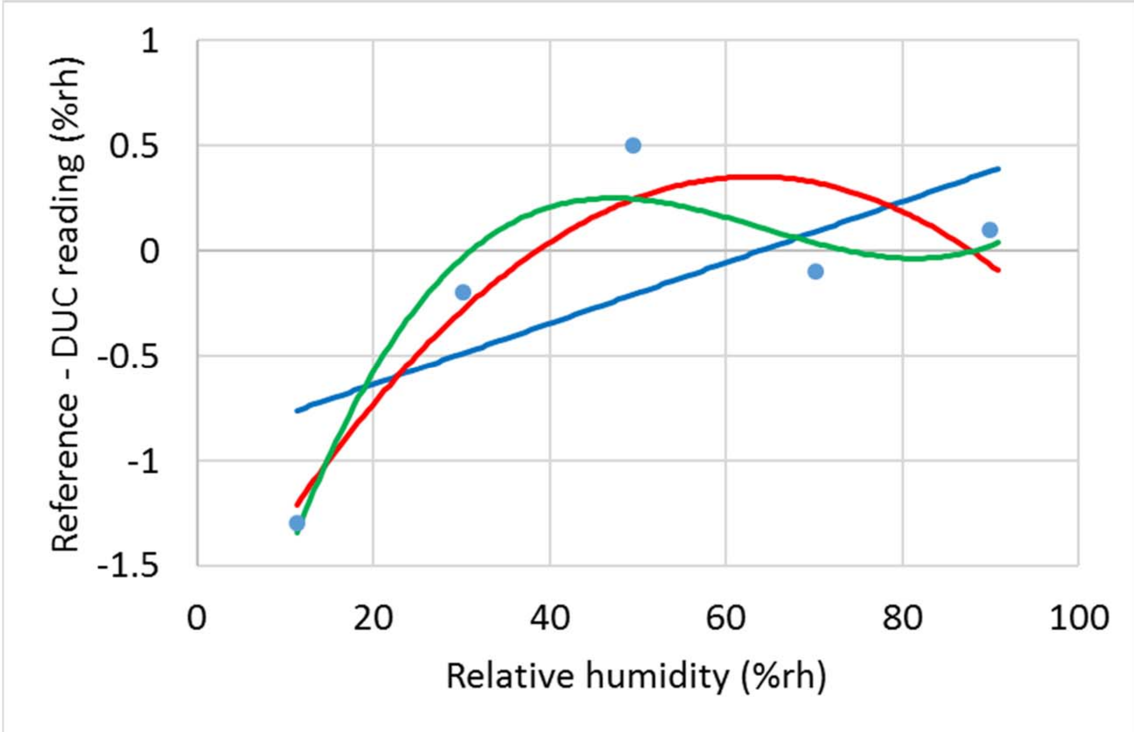
- Calibration setup
  - Measurement chamber
    - Instability of humidity or humidity change rate
    - Inhomogenous temperature and dew-point temperature / water vapour pressure
      - Note: Effects of DUCs (flow profile, heat dissipation, heat conduction)
      - Note: Correlation with instability / humidity change rate
    - Temperature measurement
      - Thermometer: calibration, stability, hysteresis, drift, resolution
      - Self heating, thermal radiation
  - Pressure difference between the reference and DUC

Sources of uncertainty

- Calibration procedure
  - Sufficiency of the time of stabilisation
    or match of response times between reference and DUC
  - Recording frequency vs. stability of conditions
  - Effect of ambient conditions
- Device under calibration (DUC)
  - Repeatability
  - Resolution
  - Hysteresis
  - Response time (if relevant)
  - Note: thermal effects (see ”Calibration setup”)

Uncertainty: Error of fitting

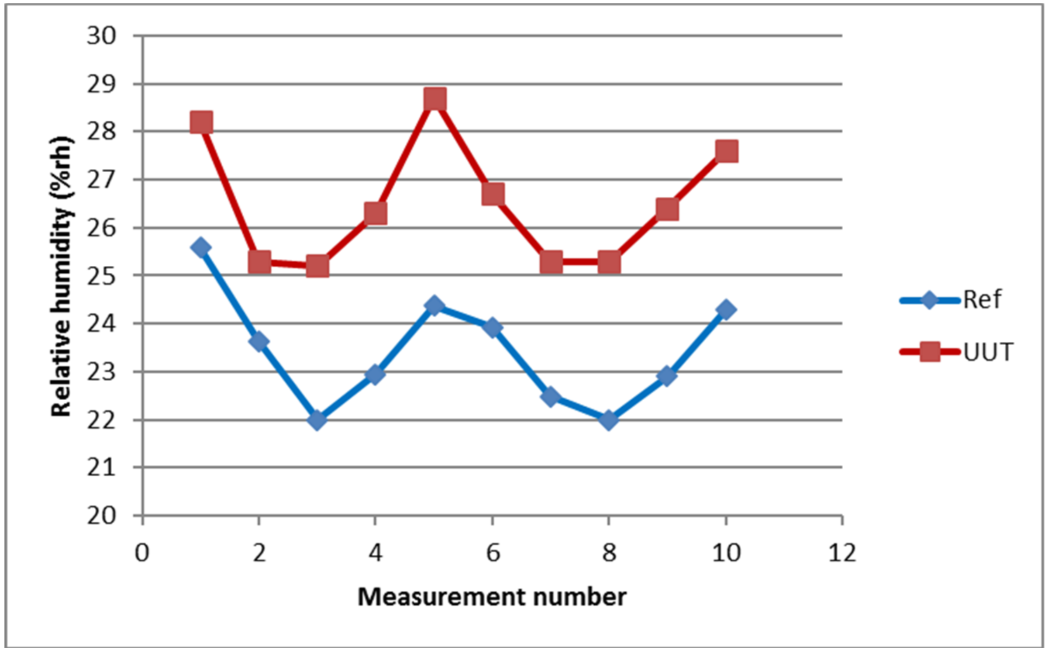
- The better fitting the lower uncertainty due to fit
- BUT:
  - No change to uncertainty of individual points
  - The better fitting the lower number of degrees of freedom ⇒ This may increase the coverage factor needed to obtain 95 % confidence level ! (*k* > 2)



std. unc:	0.36	0.20	0.12
Degrees of freedom (unc. of fit):	3	2	1

Uncertainty

- In particular when operating with a climatic chamber, humidity fluctuates more or less. This affects both the reference and DUC.
- The correlation between the reference and DUC readings should be considered when estimating uncertainty
- See: Example_correlation.xlsx



Calibration at Non-static Conditions

Exercises

Exercises

1. Calibration of an RH transmitter in non-static conditions
2. Errors in non-ideal non-static conditions
3. Time dependent factors in humidity measurements
4. Analysing results and estimating uncertainty

Four groups

- Memory stick for recording results

Time schedule

13:15 - 13:45 Timeslot 1

13:45 - 14:15 Timeslot 2

14:15 - 14:30 Break

14:30 - 15:00 Timeslot 3

15:00 - 15:30 Timeslot 4

Exercise 1:
Calibration of an RH transmitter in non-static conditions

- Calibration setup:
  - Mass flow controller based flow mixing
  - Capacitive reference sensor
  - Open measurement tube
  - Enable fast linear ramps at room temperature
  - Computer control & recording
- Measurements
  - Ascending and descending ramps
  - Study:
    - Difference between static vs. non-static
    - Effect of time response: ramp speed, filter
- Trainer: Richard Högström

Exercise 2:
Errors in non-ideal non-static conditions

- Experimental measurement setup:
  - Fan based flow mixing
  - Capacitive sensors
  - Non-ideal humidity control
  - Computer control & recording
- Measurements
  - Non-linear ramps, unstable humidity
  - Study:
    - Differences in sensor response at non-static conditions
- Independent work

Exercise 3:
Time dependent factors in humidity measurements

- Experimental measurement setup:
  - Flow switch to generate step changes
  - Tubing with different volumes
  - Old capacitive humidity sensors
- Measurements
  - Step changes at inlet
  - Visual monitoring of sensor readings
  - Study:
    - Effect of different tubings
    - Differences between sensors
- Independent work

Exercise 4:
Analysing results and estimating uncertainty

- Excel template to be completed
  - Incl. all needed input data
  - Incl. correlation
  - Incl. time dependent contributions
- To be done:
  - Identify uncertainty components
  - Estimate the uncertainty of the components
- The excel file is on the memory stick of your group
  - Please save your modified file on the memory stick
- Independent work

Validation & Summary of Exercises

Summary of Exercises

- ..
- ..
- ..
- ..

Validation

- Appropriate calibration of a reference hygrometer does not ensure traceability of your calibrations
- Appropriate uncertainty budget for your calibration does not ensure traceability of your calibrations
- These are mandatory but you also need to validate your uncertainty analysis
  - Note: Evidence is needed that the validation is up to date

Validation

- Typically includes several actions:
  - Inter-laboratory comparisons
  - In-house measurements:
    - Comparison of results obtained with different instruments/setups
    - Comparison of results obtained with different operators
    - Studying calibration history of own devices
    - Monitoring inhomogeneities in the measurement chamber
- If calibrations are performed at non-static conditions, you also need:
    - Dynamic characteristics of the calibration system need to be monitored
    - Comparison with static calibration

Validation: Coverage and documenting

- Coverage:
  - Relative humidity:
    - Max. temperature: min RH to max RH
    - Min. temperature: min RH to max RH
    - Also high pressure if needed
  - Dew-point temperature
    - Minimum to maximum
    - Also high (and vacuum) pressure if needed
  - Typically inter-laboratory comparisons don’t have a full coverage
    - In-house actions should complete the coverage
- Outcomes of all validation actions should support the estimated uncertainty in complete range
- If results are not documented, they do not exist and validation is not completed $\Rightarrow$ no metrological traceability

Summary

Thank You for Your Participation!

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