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Reference techniques implemented at LNE-CETIAT

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SCOPE

Humidity measurement – introduction

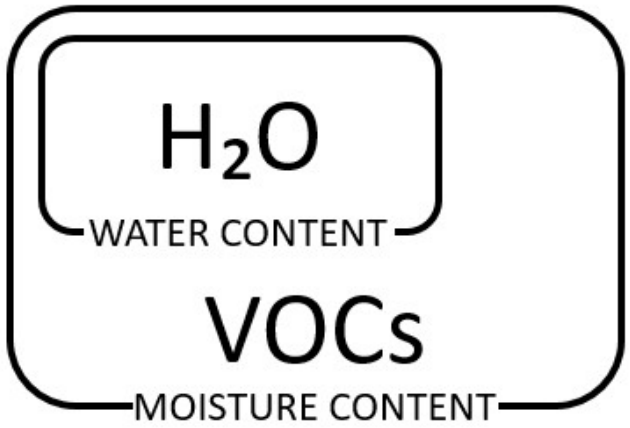
Humidity measurement at CETIAT

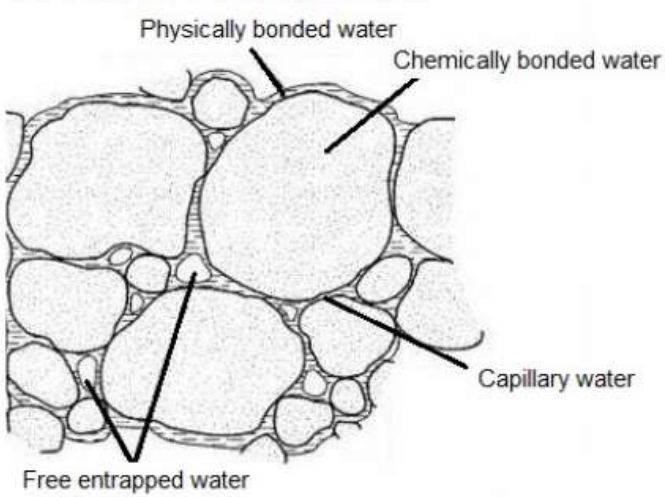
Conclusion

Humidity measurement - introduction (1/13)

Challenges with solids

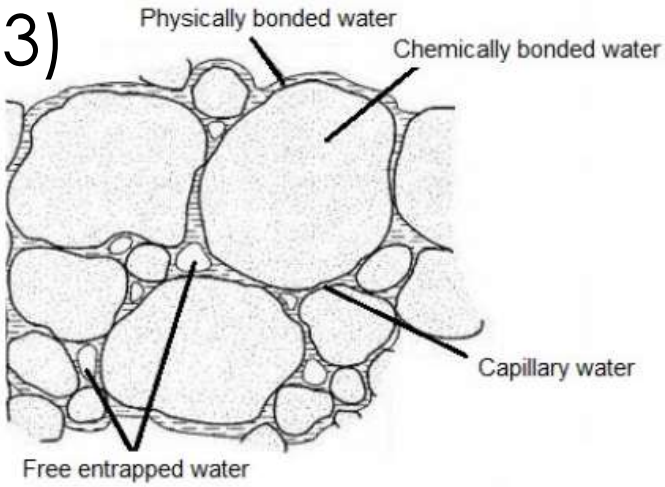
- Moisture content is not uniformly distributed in a material
  - How to access it?
- Moisture content is not water content
  - Volatile organic compounds
  - How to differentiate?
- Water is bound with varying strength
  - Free vs bound water





Humidity measurement - introduction (2/13)

Water bonding form



Increasing difficulty

- Free liquid water / Unbound (surface) moisture
  - Easily removed
  - Water may flow under the effect of gravity
- Physically bound water / Bound (internal) moisture
  - Water in a state of interaction with surface of solid matrix
  - Capillary water in small pores under the effect of surface tension
  - Different layers of water adsorbed on particle surface
- Chemically bound water/ Chemisorbed Moisture
  - Water is a part of solid matrix
  - Water of crystallization (Hydrates/Solvates)

Humidity measurement - introduction (3/13)

How to measure ?

- Water changes:
  - length of organic materials
  - conductivity and weight of hygroscopic material and chemical absorbents
  - impedance of almost any material
  - color of chemicals
  - refractive index of air and liquids
  - velocity of sound in air
  - electromagnetic radiation in solids
  - thermal conductivity of gases, liquids, and solids

- Water absorbs:
  - infrared radiation
  - ultraviolet radiation
  - microwave radiation

Humidity measurement - introduction (4/13)

How to measure ?

- **Direct** moisture content measurement techniques
  - Directly measure the property of interest according to SI primary unit
  - Reference / absolute moisture content measurement techniques

Humidity measurement - introduction (5/13)

How to measure ?

- **Direct** / Reference / absolute moisture content measurement techniques
  - (Thermo)gravimetric methods
    - Loss on Drying method
    - Gain on wetting
    - Thermogravimetric analysis
  - Karl Fischer titration
    - Volumetric
      - Coulometric
    - … sometimes combined with oven







Humidity measurement - introduction (6/13)

How to measure ?

- **Indirect** moisture content measurement techniques
  - Measure another property and relate it to the property of interest through a calibration
  - Secondary / inferential moisture content measurement techniques

Humidity measurement - introduction (7/13)

How to measure ?

- **Indirect** / secondary / inferential moisture content measurement techniques
  - Electromagnetic techniques:
  - Electrical resistance / conductance
  - Electrical capacitance
  - Dielectric permittivity/spectroscopy
  - Micro waves and Radio frequencies absoprtion
  - Time Domain Reflectometry (TDR)

Humidity measurement - introduction (8/13)

How to measure ?

- **Indirect** / secondary / inferential moisture content measurement techniques
  - Thermal techniques
    - Infrared (IR) retrodiffusion / Near Infrared (NIR) spectroscopy
    - Hot ball
    - Dual needle heat pulse
  - Nuclear techniques
    - Nuclear Magnetic Resonance (NMR)
    - Neutron moderation + Gamma radiation
    - Gamma attenuation
  - ….

Humidity measurement - introduction (9/13)

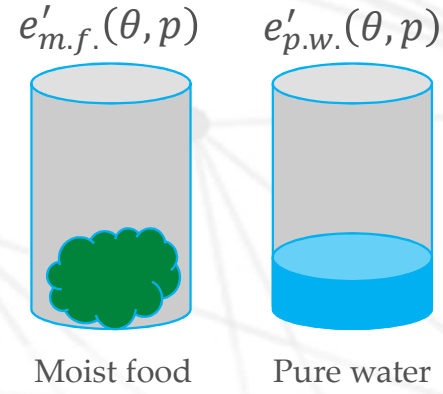
Industrial process measurement

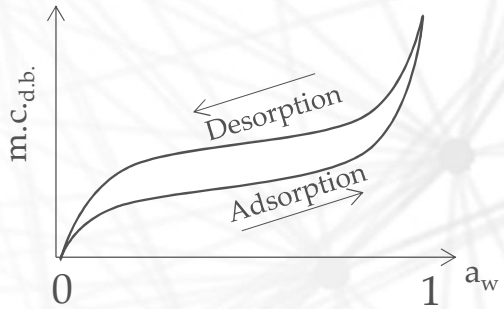
- Which measurand ?
  - Moisture content… from the point of view of Loss on Drying (LoD)
    - Moisture content « dry basis »: $m.c._{d.b.}$
      - Moisture content is calculated as a % of mass of dry solid
      - $m.c._{d.b.} = \frac{m_{w+VOC}}{m_d} \cdot 100\% = \frac{m_m - m_d}{m_d} \cdot 100\%$
    - Moisture content « wet basis »: $m.c._{w.b.}$
      - Moisture content is calculated as a % of mass of moist/wet solid
      - $m.c._{w.b.} = \frac{m_{w+VOC}}{m_m} \cdot 100\% = \frac{m_m - m_d}{m_{w+VOC} + m_d} \cdot 100\%$
    - Thus $m.c._{d.b.}$ and $m.c._{w.b.}$ are linked through the relation:
      - $m.c._{d.b.} = \frac{m.c._{w.b.}}{1 - m.c._{w.b.}}$ and $m.c._{w.b.} = \frac{m.c._{d.b.}}{1 + m.c._{d.b.}}$

Humidity measurement - introduction (10/13)

Industrial process measurement

- Which measurand ?
  - Water activity a_w and ERH … from the point of view of food industry
    - a_w: The water activity (a_w) represents the ratio of the water vapor pressure of the material to the water vapor pressure of pure water under the same conditions
    - ERH: The (value of) relative humidity of the air at which there is no net exchange of moisture with any nearby substance
    - In some case, a_w is in practice usually measured as ERH
    - a_w and $m.c._{d.b.}$: sorption isotherm

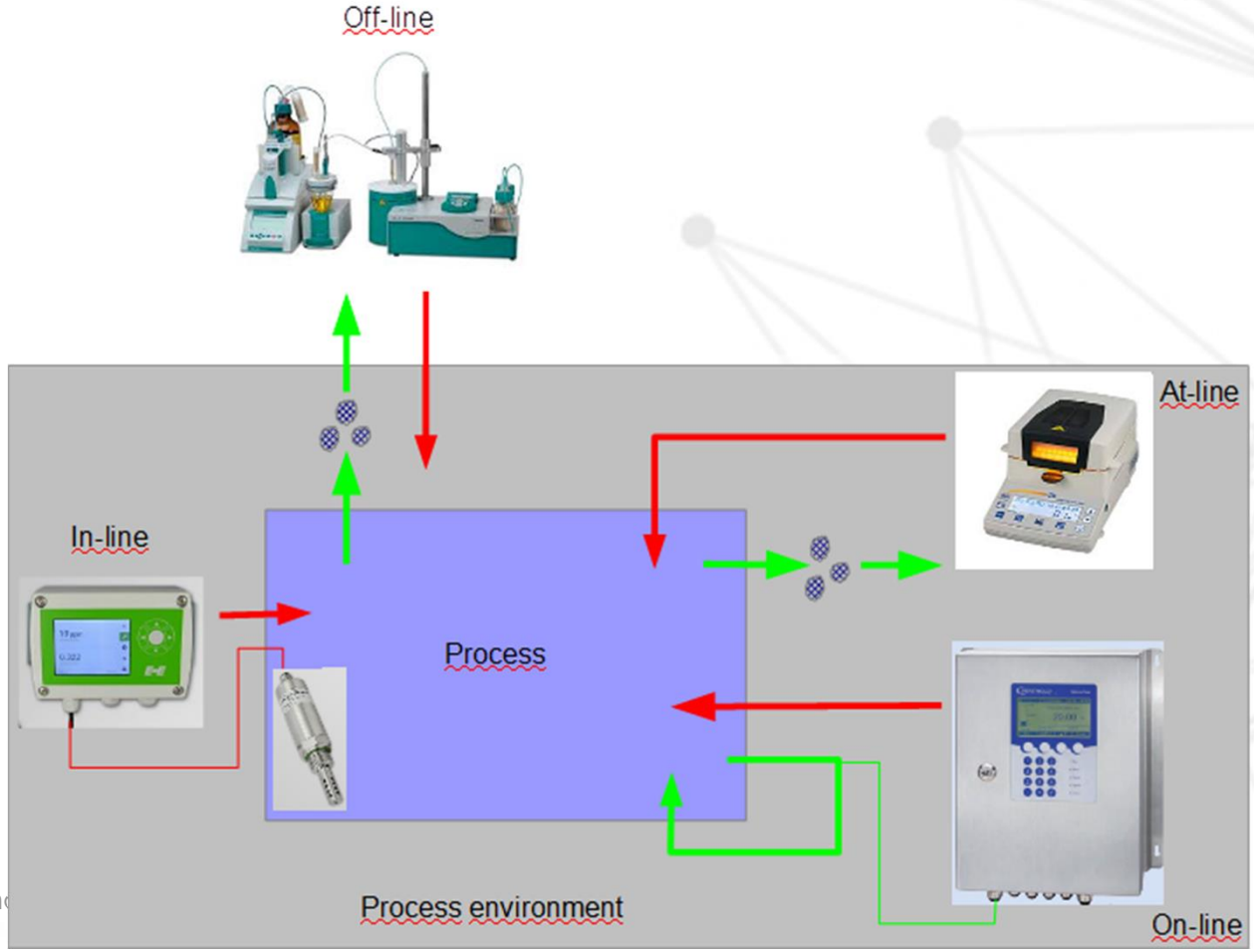




Humidity measurement - introduction (11/13)

Industrial process measurement

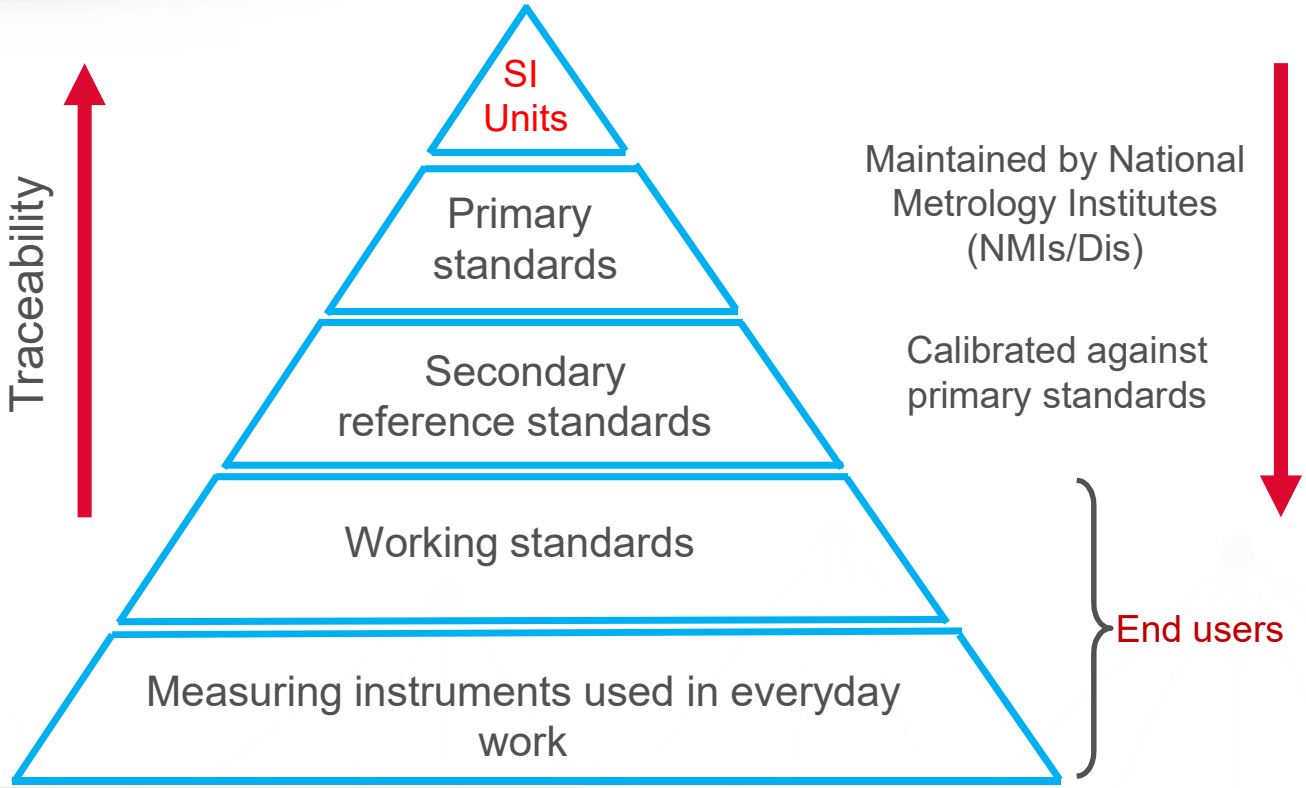
- Which context ?



Humidity measurement - introduction (12/13)

Industrial process measurement

- Traceability



International vocabulary of metrology – Basic and general concepts and associated terms (VIM) – JCGM 200/2012

2.41 (6.10)
metrological traceability
property of a **measurement result** whereby the result can be related to a reference through a documented unbroken chain of **calibrations**, each contributing to the **measurement uncertainty**

2.42 (6.10 Note 2)
metrological traceability chain
traceability chain
sequence of **measurement standards** and **calibrations** that is used to relate a **measurement result** to a reference

2.43
metrological traceability to a measurement unit
metrological traceability to a unit
metrological traceability where the reference is the definition of a **measurement unit** through its practical realization

Humidity measurement - introduction (13/13)

Means for establishing traceability routes (examples)

- Primary measurement standard
  - measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention
  - provide traceability to SI and related uncertainty
- Secondary measurement standard
  - measurement standard established through calibration with respect to a primary measurement standard for a quantity of the same kind
  - provide traceability to SI and related uncertainty
- Certified Reference Materials (CRMs)
  - ready made sample for calibrating measuring device
  - provide traceability to SI and related uncertainty

Humidity measurement - introduction (13/13)

Means for establishing traceability routes (example)

- Primary measurement standard

Why traceability is so important ?

- Secondary measurement standard

Reliability & comparability of your mesurements

- Certified Reference Materials (CRMs)
  - ready made sample for calibrating measuring device
  - provide traceability to SI and related uncertainty

Humidity measurement at CETIAT (1/10)

Reference methods: Loss on Drying - LoD


Empty mass


Mass with sample

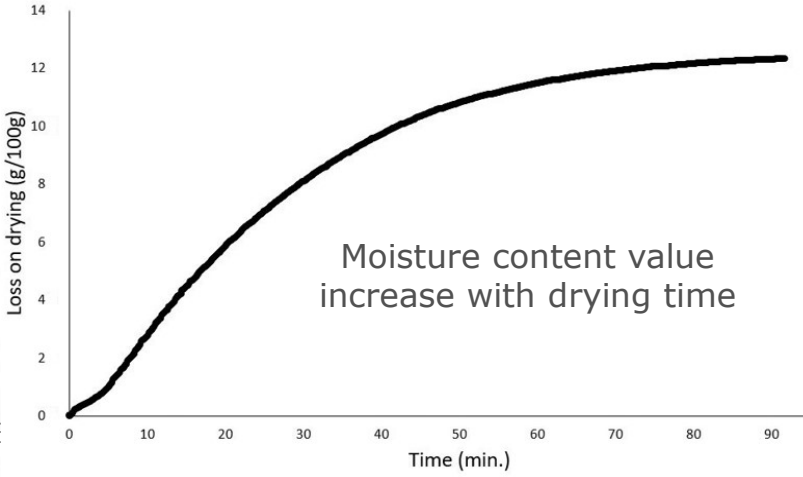
Drying


Cooling


Mass after drying

- Standard method for moisture determination
- Drying temperature and time are critical
- $Moisture\ content = \frac{Mass\ with\ sample - Mas\ \ after\ drying}{Mass\ with\ sample - Empty\ mass}$

Calcium oxalate monohydrate analysis with moisture balance



Humidity measurement at CETIAT (2/10)

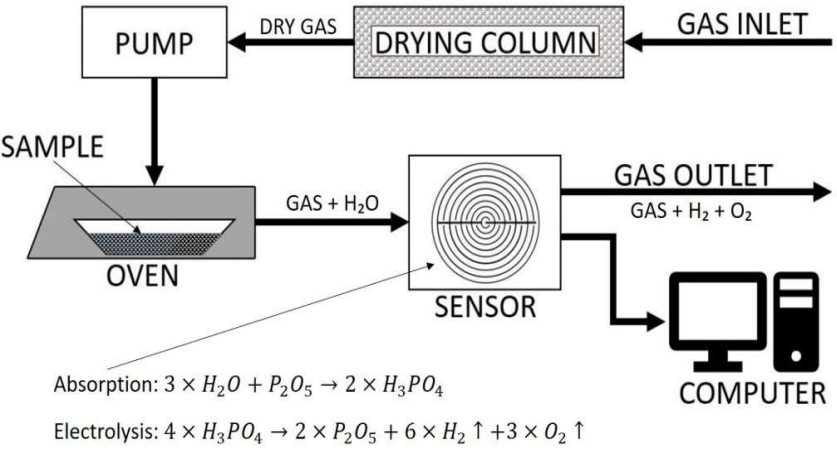
Reference method: Oven coulometric Karl Fischer titration - O-cKF

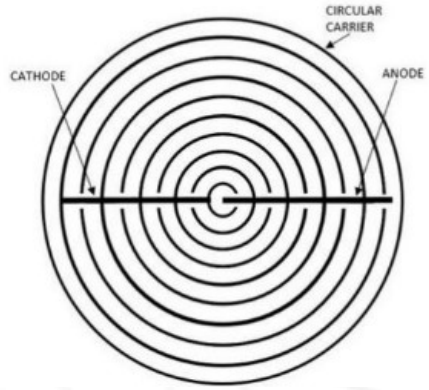
I stage $ROH + SO_2 + R'N \rightarrow [R'NH]SO_3R$

II stage $[R'NH]SO_3R + H_2O + I_2 + 2 \times R'N \rightarrow 2 \times [R'NH]I + [R'NH]SO_4R$

Humidity measurement at CETIAT (3/10)

Reference method: Evolved Water Vapour – EVW (TC)





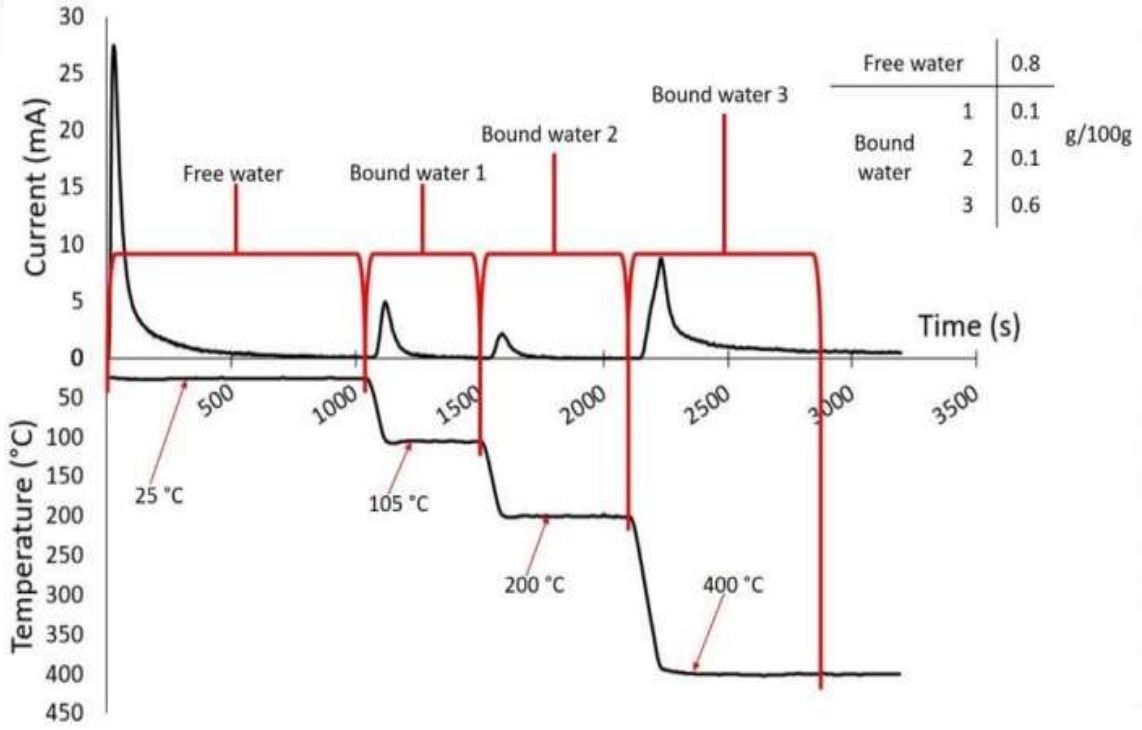
$$m = \frac{M \times \int i(t)dt}{Z \times F}$$

m – mass of water;
M – molar mass (water: 18.016 g/mol)
i(t)dt – electrical charge per time
Z – number of released electrons (2)
F – Faradays constant (96484.56 C/mol)

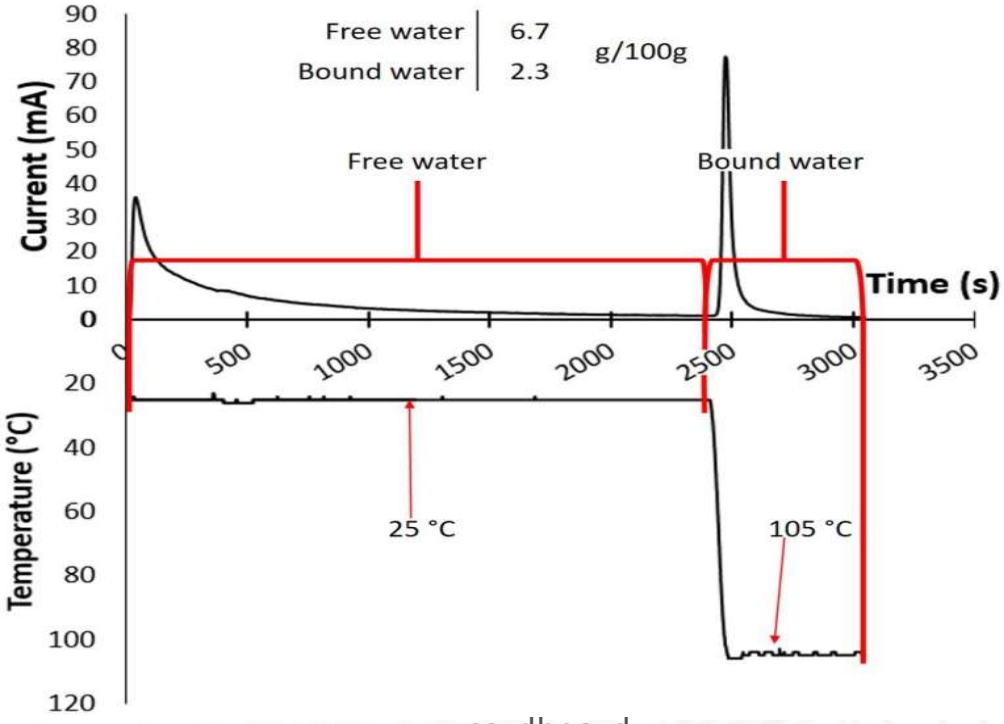
Humidity measurement at CETIAT (4/10)

Reference method: Evolved Water Vapour – EVW (TC)

- Water bonding forms



kaolinite clay



cardboard

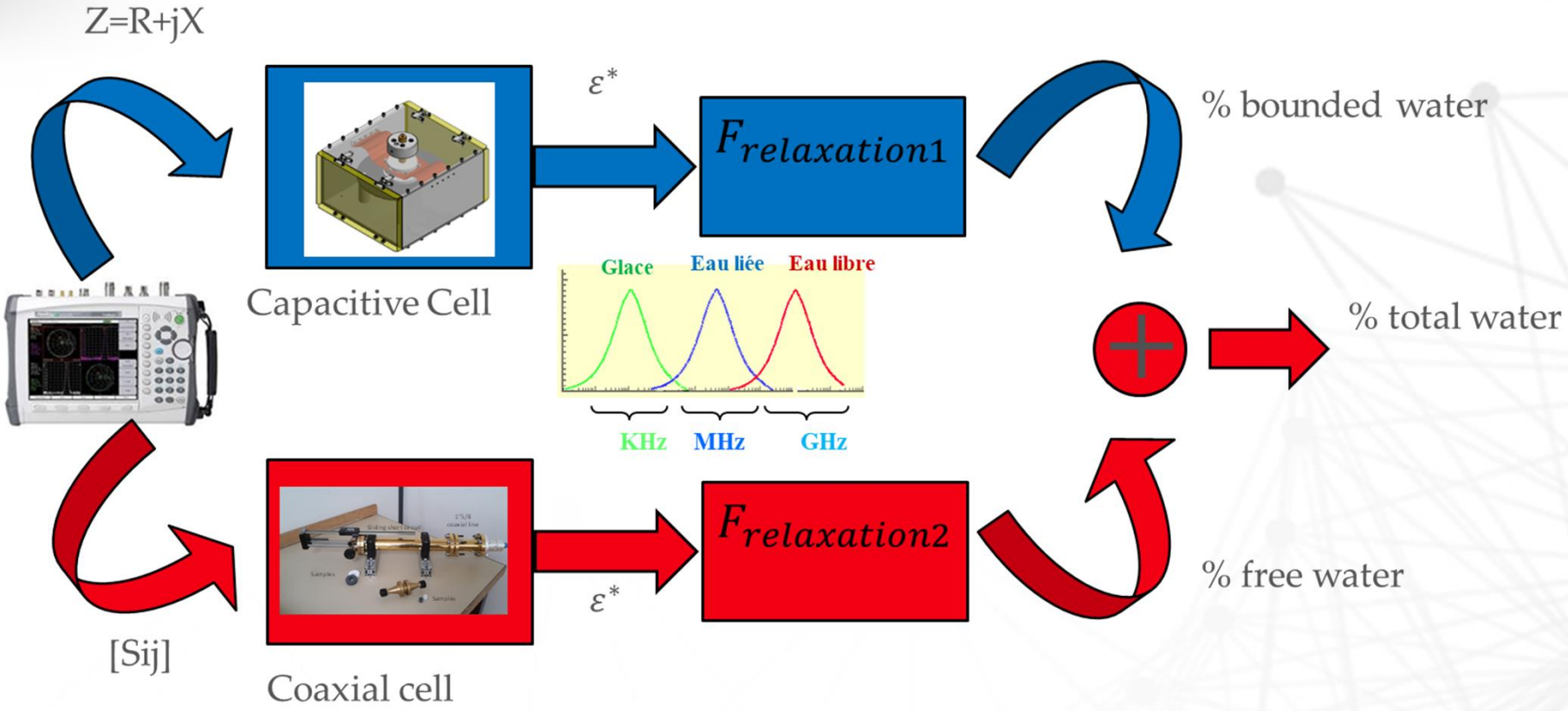
Humidity measurement at CETIAT (5/10)

Reference methods

METHOD	SELECTIVE	REPEATABILITY	TURNAROUND TIME	MAINTENANCE
TC	Yes	Average	Average	Simple
LoD	No	Good	Long	Simple
O-cKF	Yes	Average	Short	Complex

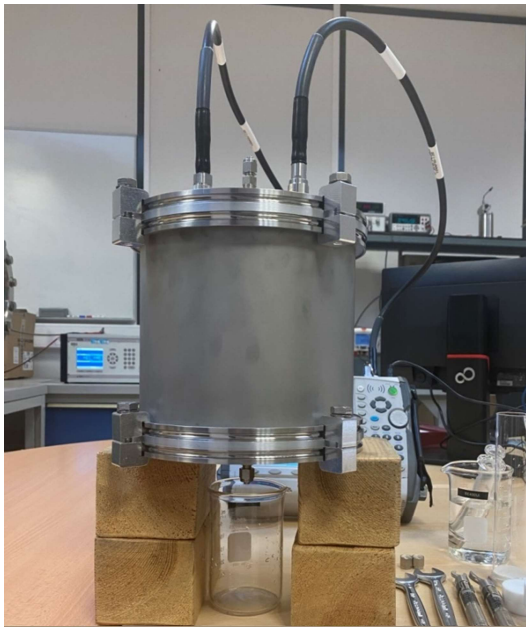
Humidity measurement at CETIAT (6/10)

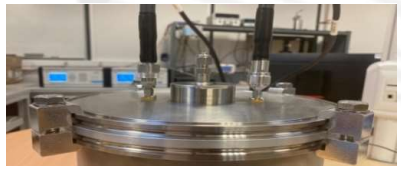
Secondary methods



Humidity measurement at CETIAT (7/10)

Secondary methods

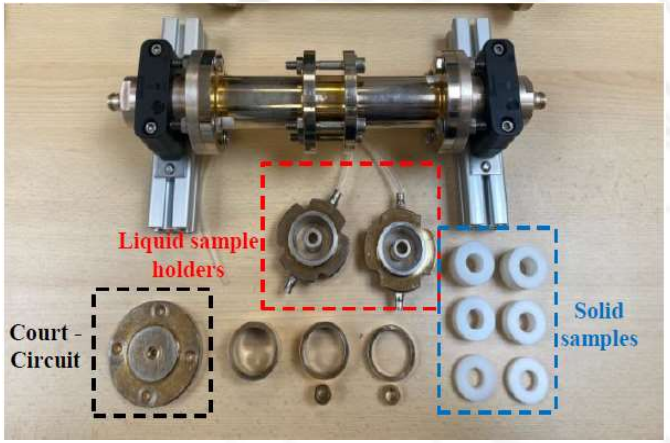




CETIAT
ensemble, innover et valider

Humidity measurement at CETIAT (8/10)

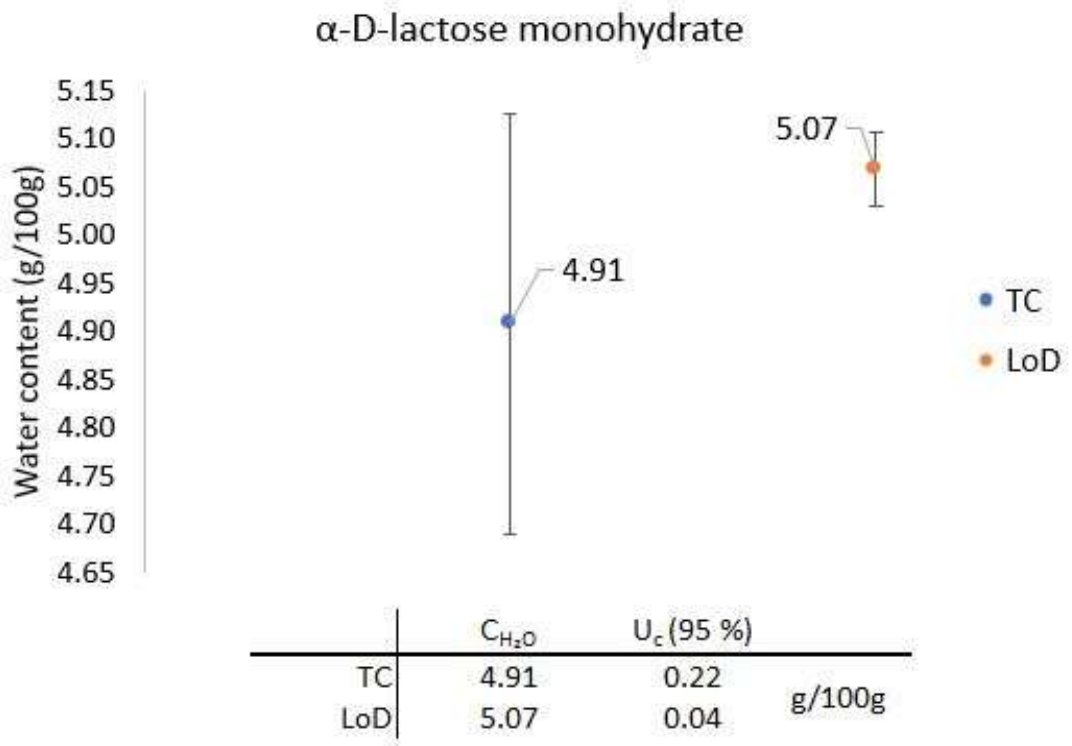
Secondary methods



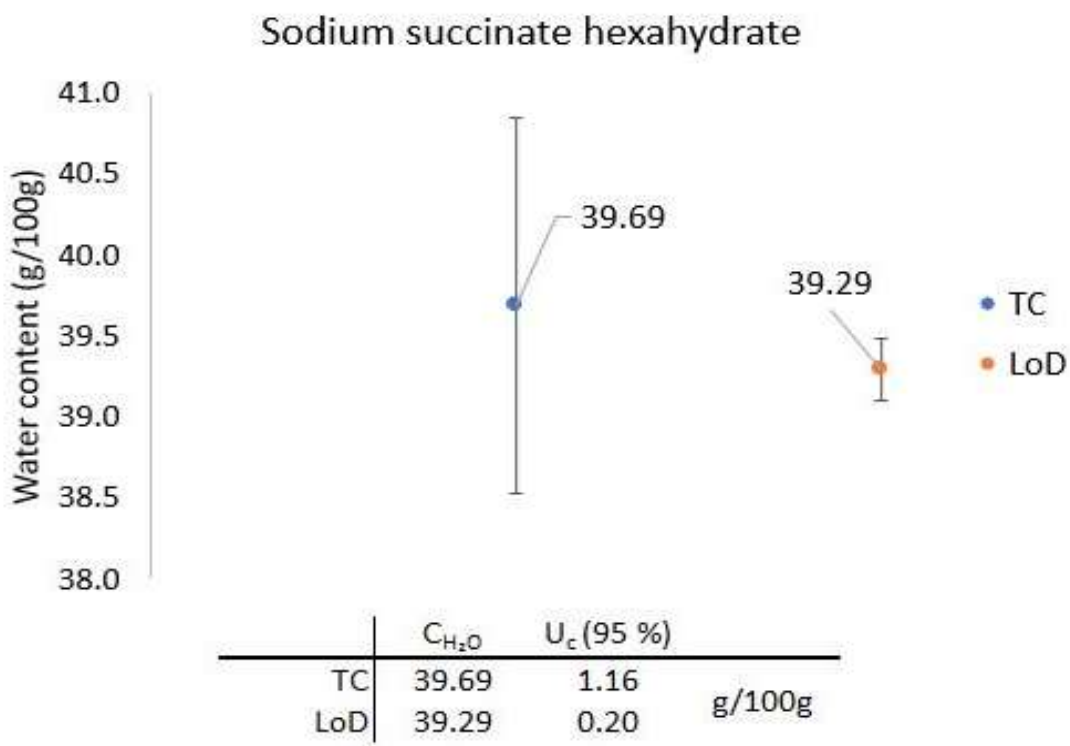
Humidity measurement at CETIAT (9/10)

Comparison LoD vs EWV (TC)

- At LNE CETIAT



	C_{H_2O}	U_c (95 %)	
TC	4.91	0.22	g/100g
LoD	5.07	0.04	

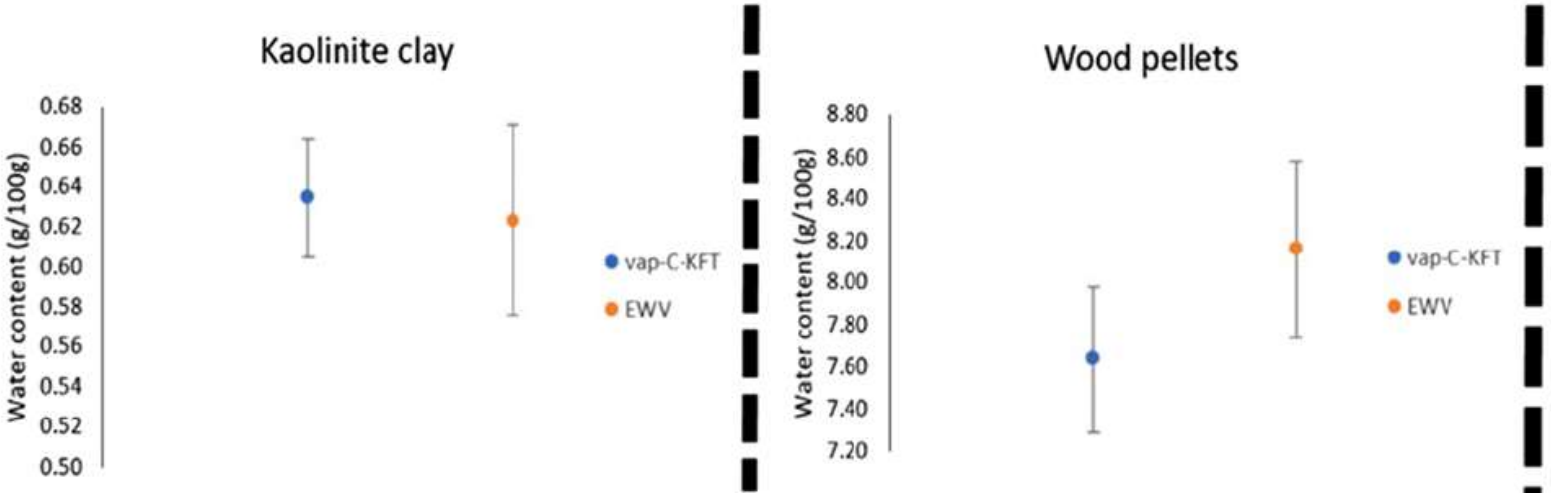


	C_{H_2O}	U_c (95 %)	
TC	39.69	1.16	g/100g
LoD	39.29	0.20	

Humidity measurement at CETIAT (10/10)

Comparison vap-cKF vs EWV

- University of Tartu and LNE-CETIAT



Kaolinite clay

	C_{H_2O}	U (k=2)	
vap-C-KFT	0.63	0.03	g/100g
EWV	0.62	0.05	

Wood pellets

	C_{H_2O}	U (k=2)	
vap-C-KFT	7.64	0.35	g/100g
EWV	8.16	0.42	

International Journal of Thermophysics (2020) 41:113
https://doi.org/10.1007/s10765-020-02697-6

Check for updates

Moisture in Solids: Comparison Between Evolved Water Vapor and Vaporization Coulometric Karl Fischer Methods

Rudolf Aro[1,2,3] · Mohamed Wajdi Ben Ayoub[2,4] · Ivo Leito[1] · Éric Georgin[2]

Conclusion

Moisture measurement present many technical aspects

- Measurand (moisture vs water content), water bonding forms, measurement technics, traceability routes

Traceability to S.I. unit

- Reliability and comparability

At LNE-CETIAT

- Implementation of reference methods: LoD, EWV, O-cKF
- Development of secondary methods (transfer standard) based on RF and MW measurements

Within BiofMET

- Reference methods will ensure the traceability of the transfer standard

CETIAT

ensemble, innover et valider

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