Unified pH scale – from concept to applications

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https://analytical.chem.ut.ee/bechem_2024/

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Introduction

- pH is the best known parameter for expressing acidity

Activity of solvated proton

$$pH = -\log a(H^+, solvent)$$

- The pH scale in **water** is well established
  - Conventional pH ≡ IUPAC pH

IUPAC Recommendations 2002:
    R. P. Buck et al *Pure Appl. Chem.* 2002, *74*, 2169

Other solvents?   Mixed solvents?

- In water pH is established and clear
- In practice very often non-aqueous or mixed solvents

**The situation is much more complicated
with other solvents/media**

The standard state

- In every solvent (medium) the **activity of solvated proton** is linked to its **concentration** in *that solvent*

- The **standard state** is 1 m (or 1 M) solvated H^+ in *that solvent*

The conventional standard state is *concentration-based*

- **But:** The same concentration of protons **in different solvents have hugely different ability** to influence processes
  - Catalysis, protonation of bases, etc

Solvents differ by the ability to solvate H⁺

- By the ability of decreasing the **chemical potential** of H⁺
- Transfer free energies of H⁺ from water to solvents:

Solvent	$\Delta_{transfer}G°$ of H⁺ from H_2O (kJ/mol)
$MeNO_2$	95
MeCN	**46.4**
MeOH	10.4
Water	0.0
DMSO	**-19.4**
Pyridine	-28

One pH unit corresponds to 5.7 kJ/mol

The **same [H⁺]** leads to difference of more than **11 pH units**

- The same pH in different solvents refers to the similar H$^+$ concentration but to **different acidity in terms of chemical potential**

  - It is the chemical potential that matters (protonation of bases, catalysis, acidic hydrolysis, redox potential, ...)
  - **Every solvent (or mixture) has its own pH scale**
  - **Not comparable to other solvents**

Example:
pH 7.0 in water is neutral,
pH 7.0 in MeCN is strongly acidic

In mixtures: somewhere inbetween

As another Result ...

- The **pK_a** values of the same compound in different solvents **can be very different**

    - And it is the difference between pH and pK_a that controls ionization (charge state)
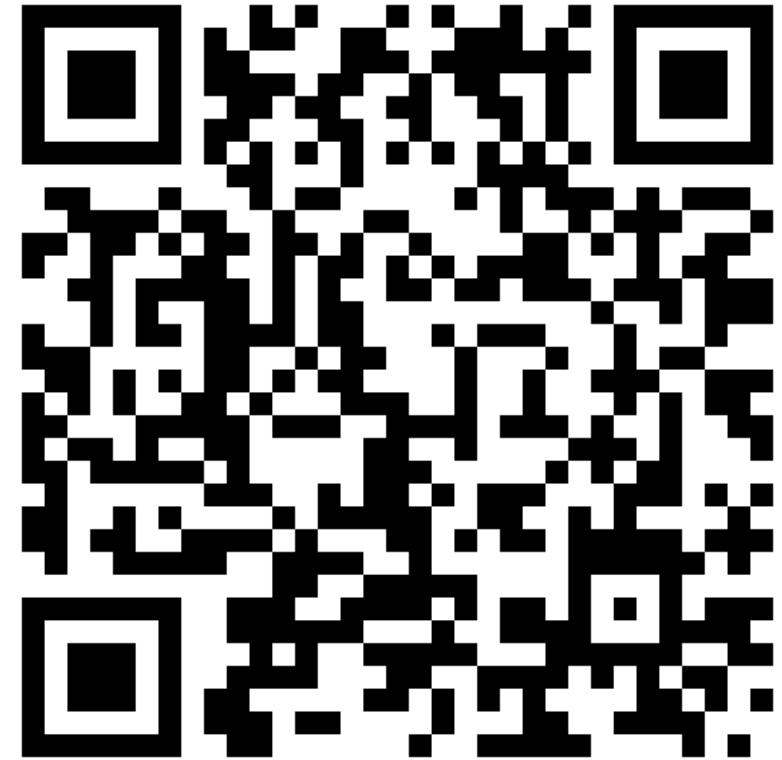
Example:

**pK_a of benzoic acid in water is 4.2,
pK_a of benzoic acid in MeCN is 21.5**

In mixtures: somewhere in between

Conclusion:

The conventional pH …

- … is **non-comparable** between solvents
  - Different solvents –> different standard states
  - The same pH in different solvents refers to different acidity

- … is **limited** to very few solvents
  - Essentially water, plus few more

Absolute/Universal pH possible? Yes: pH$_{abs}$

- pH$_{abs}$ values are linked to **absolute chemical potential of H$^+$**

  - Orignal standard state: 1 bar „proton gas"

  - „Aligned" to the aqueous pH scale: **in water pH$_{abs}^{H_2O}$ and pH are equivalent**

    - pH$_{abs}^{H_2O}$ 7.0 corresponds to $\mu_{abs}(H^+)$ -1144 kJ mol^{-1}

- **pH$_{abs}^{H_2O}$ values in any solvent/medium are comparable**
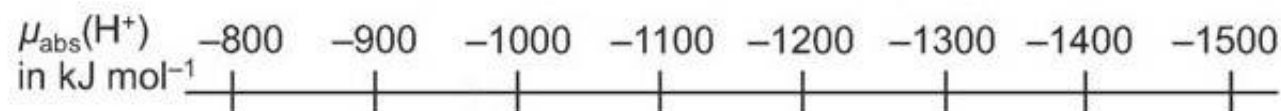
$$pH_{abs}^{H_2O} = \frac{-\mu_{abs}(H^+, solv) + \Delta_{solv}G°(H^+, H_2O)}{RT\ln 10}$$

D. Himmel et al *Angew. Chem. Int. Ed.* 2010, *49*, 6885

What does „Aligned to the aqueous pH scale" mean?

Example: $pH_{abs}^{H_2O}$ 7.0
measured in any solvent/medium
has the same acidity as
aqueous solution with (conventional) pH 7.0

$pH_{abs}^{H_2O}$ values are comparable
between different solvents!

The original development was (mostly) computational

Can $pH_{abs}^{H_2O}$ be measured?

Yes!
Using differential potentiometry
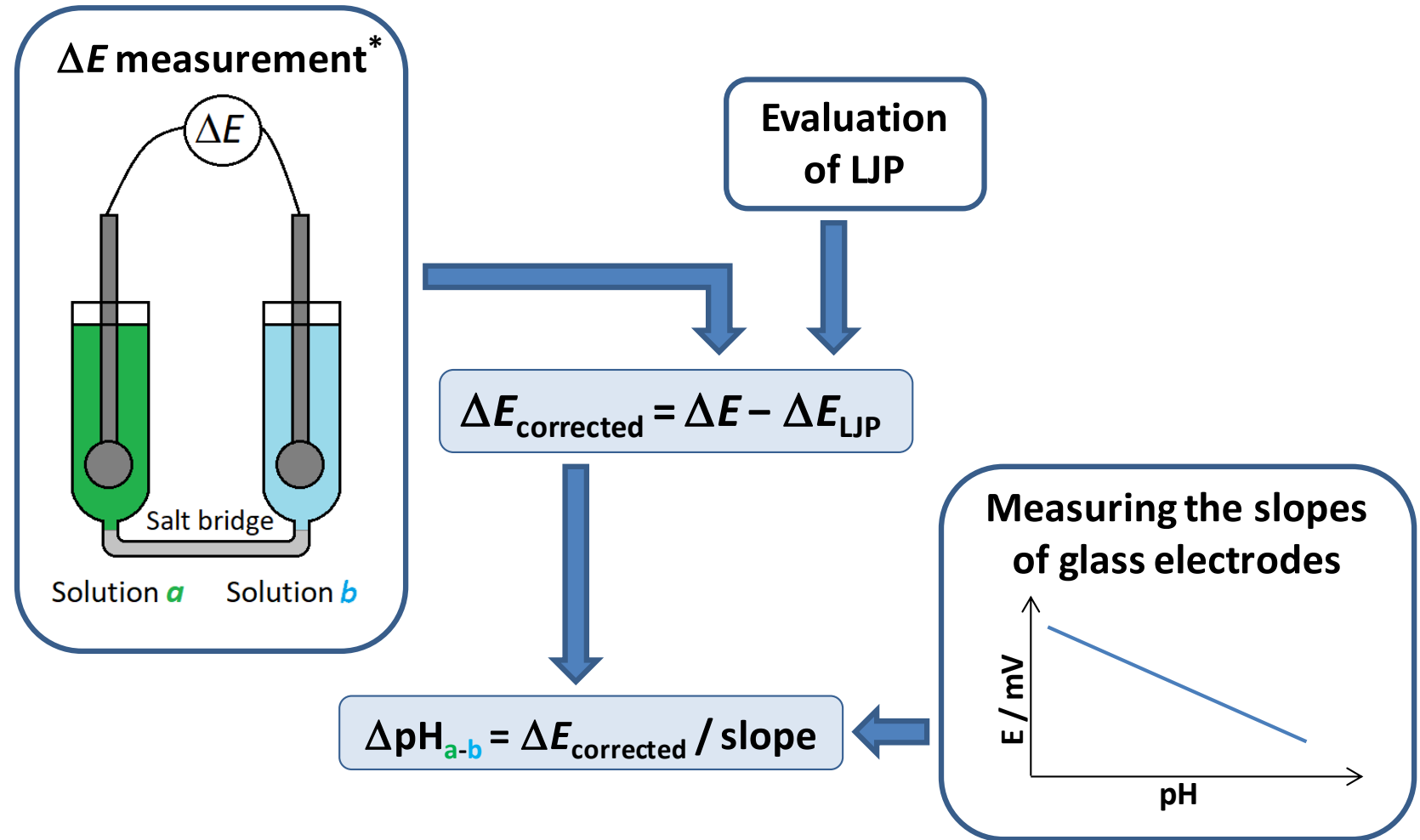
A. Suu et al *Anal. Chem.* **2015**, *87*, 2623-2630
A. Heering et al *Symmetry* **2020**, *12*, 1150
V. Radtke et al *Pure Appl. Chem.* **2021**, *93*, 1049
A. Heering et al *Analyst* **2024**, *149*, 1481
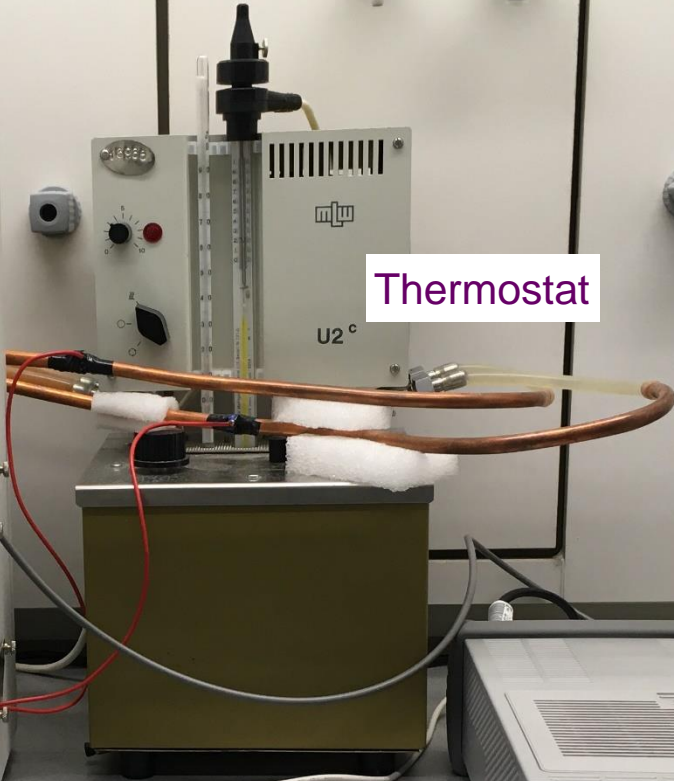
Principle of measurement: ΔpH

- It is a relative measurement

- ΔpH of two solutions is measured

ΔE measurement*

ΔE

Salt bridge

Solution *a*   Solution *b*

Evaluation of LJP

$\Delta E_{corrected} = \Delta E - \Delta E_{LJP}$

Measuring the slopes of glass electrodes

E / mV

pH

$\Delta pH_{a-b} = \Delta E_{corrected} / slope$
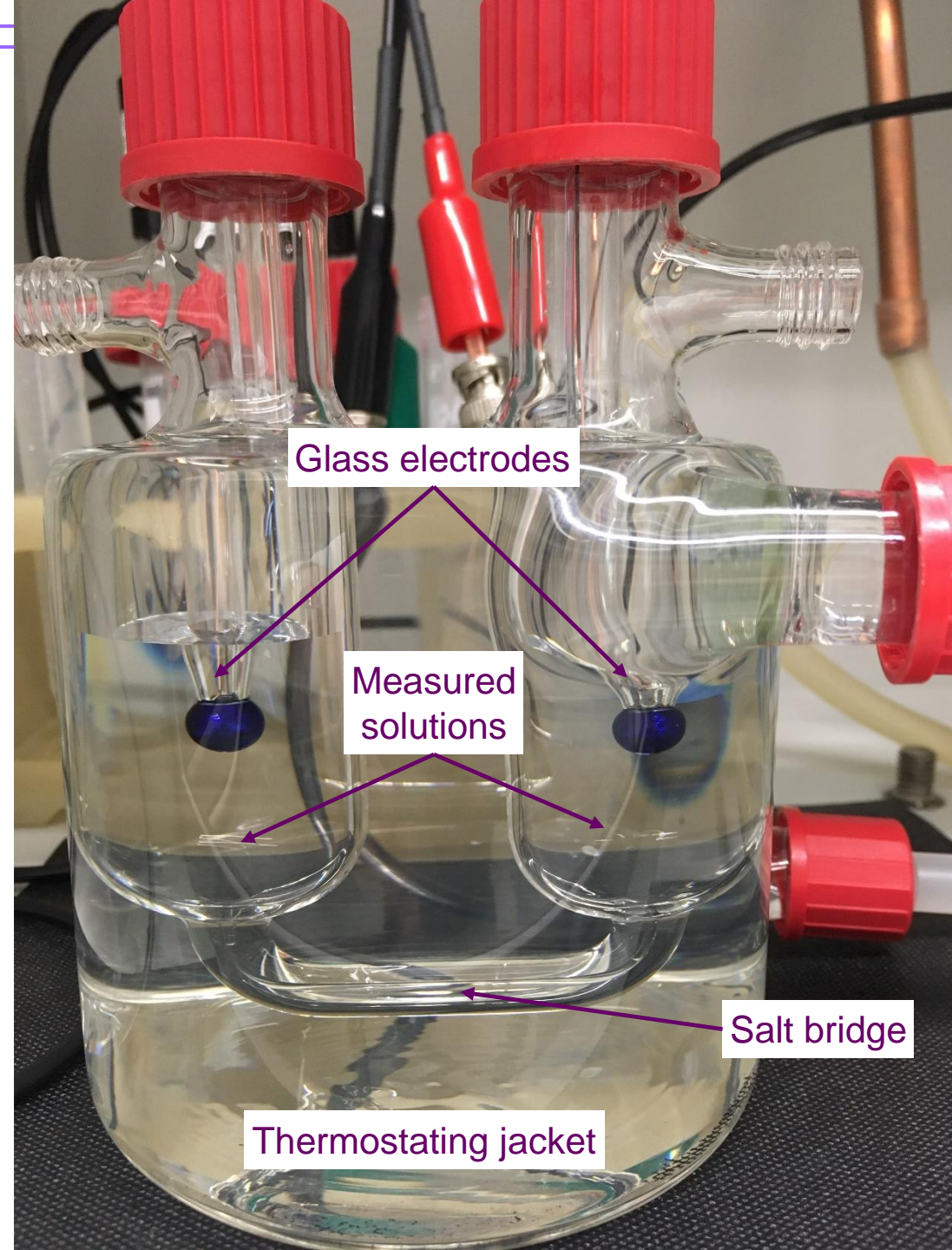
Faraday cage

Thermostat

Potentiostat/
potentiometer

- This is one possible cell

- A number of different designs have been used

Gallery at: https://www.uniphied.eu/

Glass electrodes

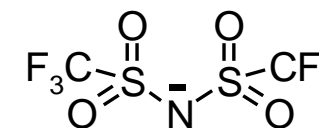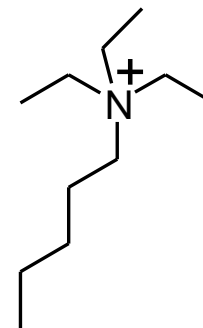Measured solutions

Salt bridge

Thermostating jacket

Liquid Junction Potential …
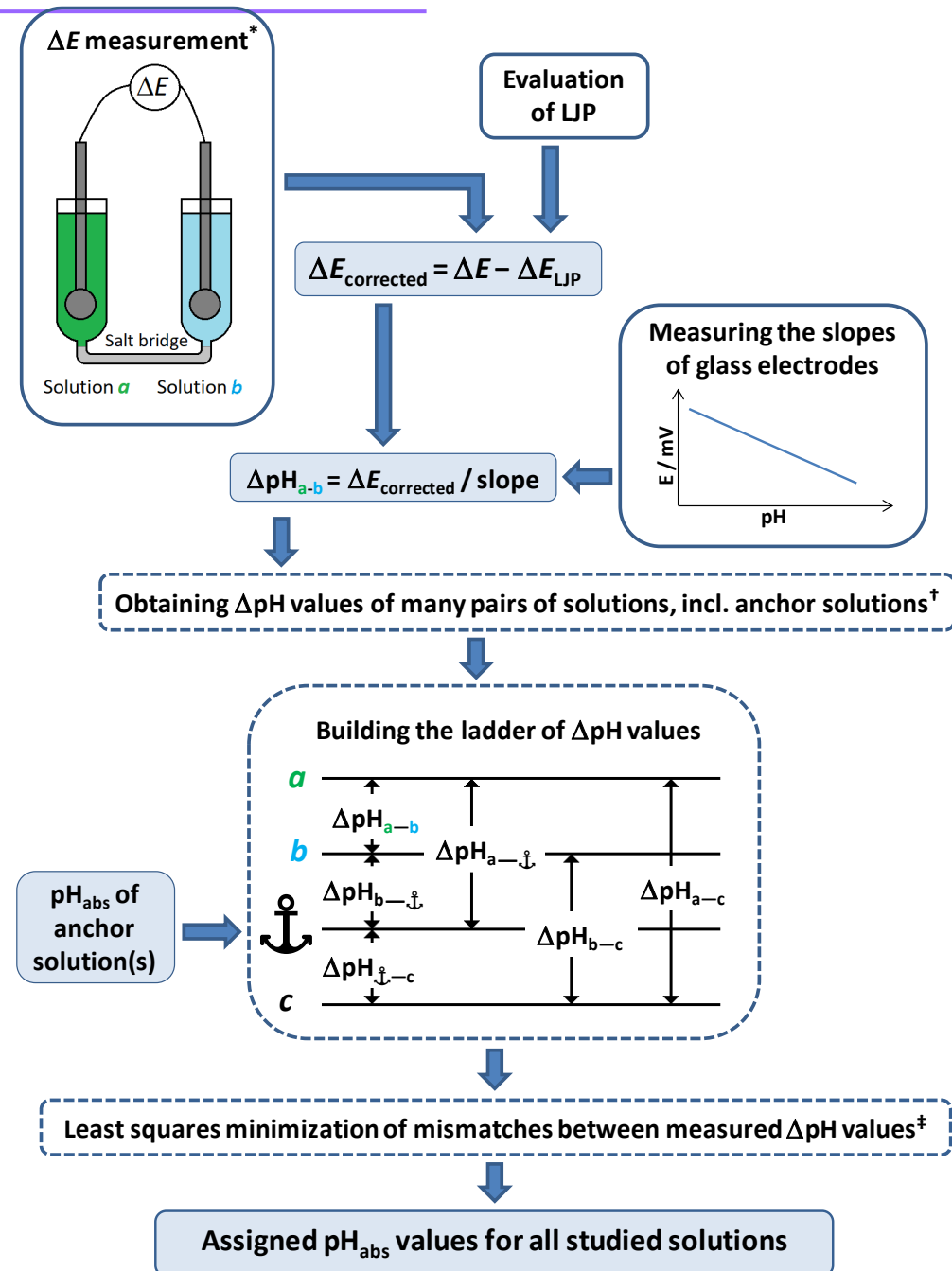
- … emerges at the interfaces:
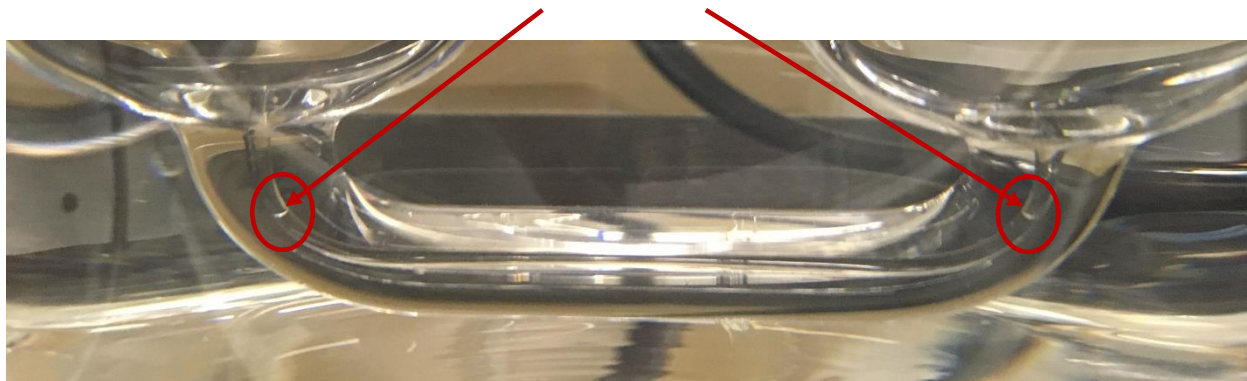
- Ionic liquid (IL) for salt bridge (SB), with specifically chosen IL
  - Very similar mobilities and solvation energias of ions

- enables **to cancel the LJP**, even between diferent solvents

$$[N_{2225}][NTf_2]$$

A. Ermantraut et al *Angew. Chem. Int. Ed.* 2018, *57*, 2348
V. Radtke et al *Chem. Eur. J.* 2022, e202200509

Principle of measurement: „ladder" and anchoring

- A „ladder" is built from a number of overlapping ΔpH_{abs} measurements

- The „ladder" is anchored to standard solutions
  - Typically aqueous standard buffers

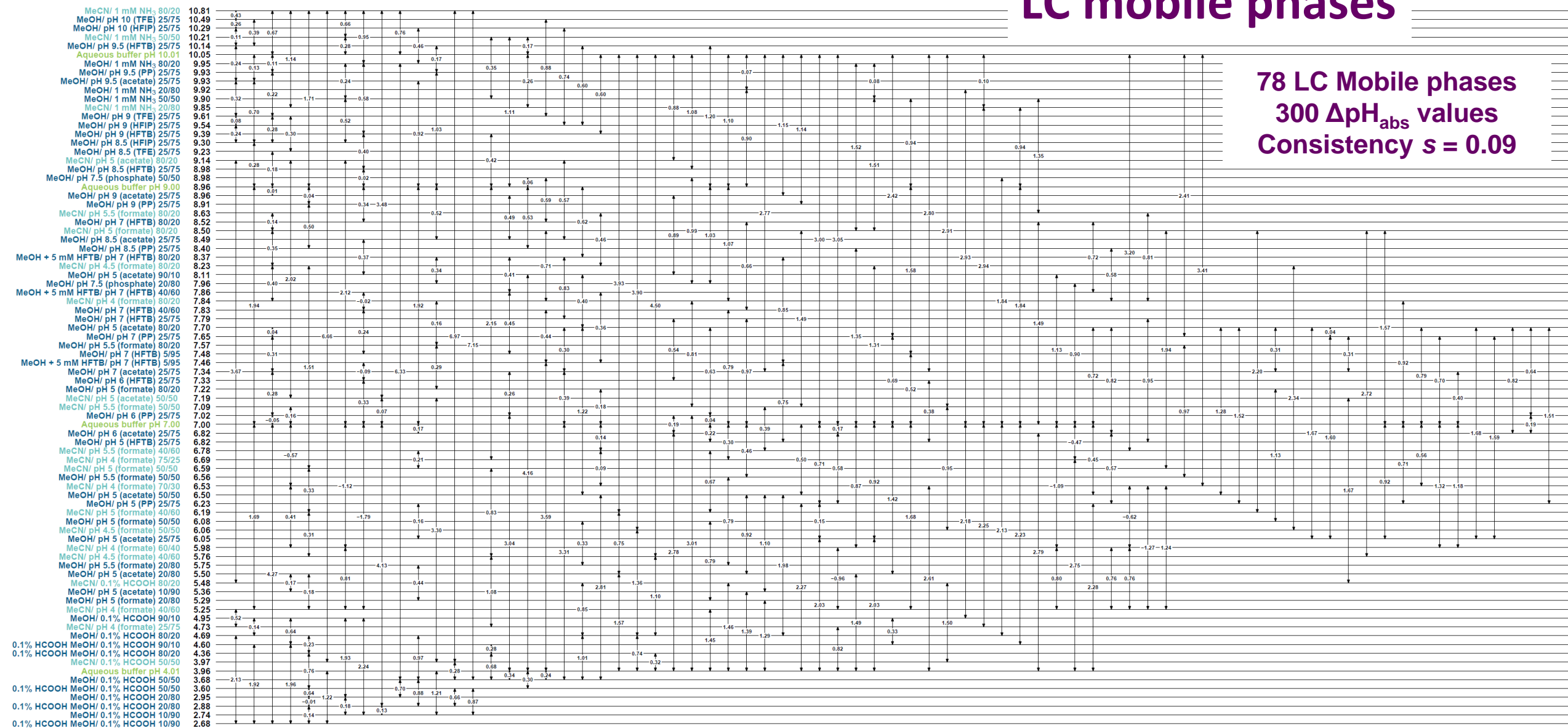ΔE measurement[*]

ΔE

Salt bridge

Solution a Solution b

Evaluation of LJP

$\Delta E_{corrected} = \Delta E - \Delta E_{LJP}$

Measuring the slopes of glass electrodes

E / mV

pH

$\Delta pH_{a\text{-}b} = \Delta E_{corrected}$ / slope

Obtaining ΔpH values of many pairs of solutions, incl. anchor solutions[†]

Building the ladder of ΔpH values

a

ΔpH_{a-b} $\Delta pH_{a-⚓}$

b

$\Delta pH_{b-⚓}$ ΔpH_{a-c}

ΔpH_{b-c}

$\Delta pH_{⚓-c}$

c

pH_{abs} of anchor solution(s)

Least squares minimization of mismatches between measured ΔpH values[‡]

Assigned pH_{abs} values for all studied solutions

UnipHied

16

78 LC Mobile phases
300 ΔpH_{abs} values
Consistency s = 0.09

Example: LC mobile phases

| Mobile phase	$pH_{abs}^{H_2O}$
MeCN/ 1 mM NH$_3$ 80/20	10.81
MeOH/ pH 10 (TFE) 25/75	10.49
MeOH/ pH 10 (HFIP) 25/75	10.29
MeCN/ 1 mM NH$_3$ 50/50	10.21
MeOH/ pH 9.5 (HFTB) 25/75	10.14
Aqueous buffer pH 10.01	10.05
MeOH/ 1 mM NH$_3$ 80/20	9.95
MeOH/ pH 9.5 (PP) 25/75	9.93
MeOH/ pH 9.5 (acetate) 25/75	9.93
MeOH/ 1 mM NH$_3$ 20/80	9.92
MeOH/ 1 mM NH$_3$ 50/50	9.90
MeCN/ 1 mM NH$_3$ 20/80	9.85
MeOH/ pH 9 (TFE) 25/75	9.61
MeOH/ pH 9 (HFIP) 25/75	9.54
MeOH/ pH 9 (HFTB) 25/75	9.39
MeOH/ pH 8.5 (HFIP) 25/75	9.30
MeOH/ pH 8.5 (TFE) 25/75	9.23
MeCN/ pH 5 (acetate) 80/20	9.14
MeOH/ pH 8.5 (HFTB) 25/75	8.98
MeOH/ pH 7.5 (phosphate) 50/50	8.98
Aqueous buffer pH 9.00	8.96
MeOH/ pH 9 (acetate) 25/75	8.96
MeOH/ pH 9 (PP) 25/75	8.91
MeCN/ pH 5.5 (formate) 80/20	8.63
MeOH/ pH 7 (HFTB) 80/20	8.52
MeCN/ pH 5 (formate) 80/20	8.50
MeOH/ pH 8.5 (acetate) 25/75	8.49
MeOH/ pH 8.5 (PP) 25/75	8.40

A. Heering et al *Analyst* 2024, *149*, 1481
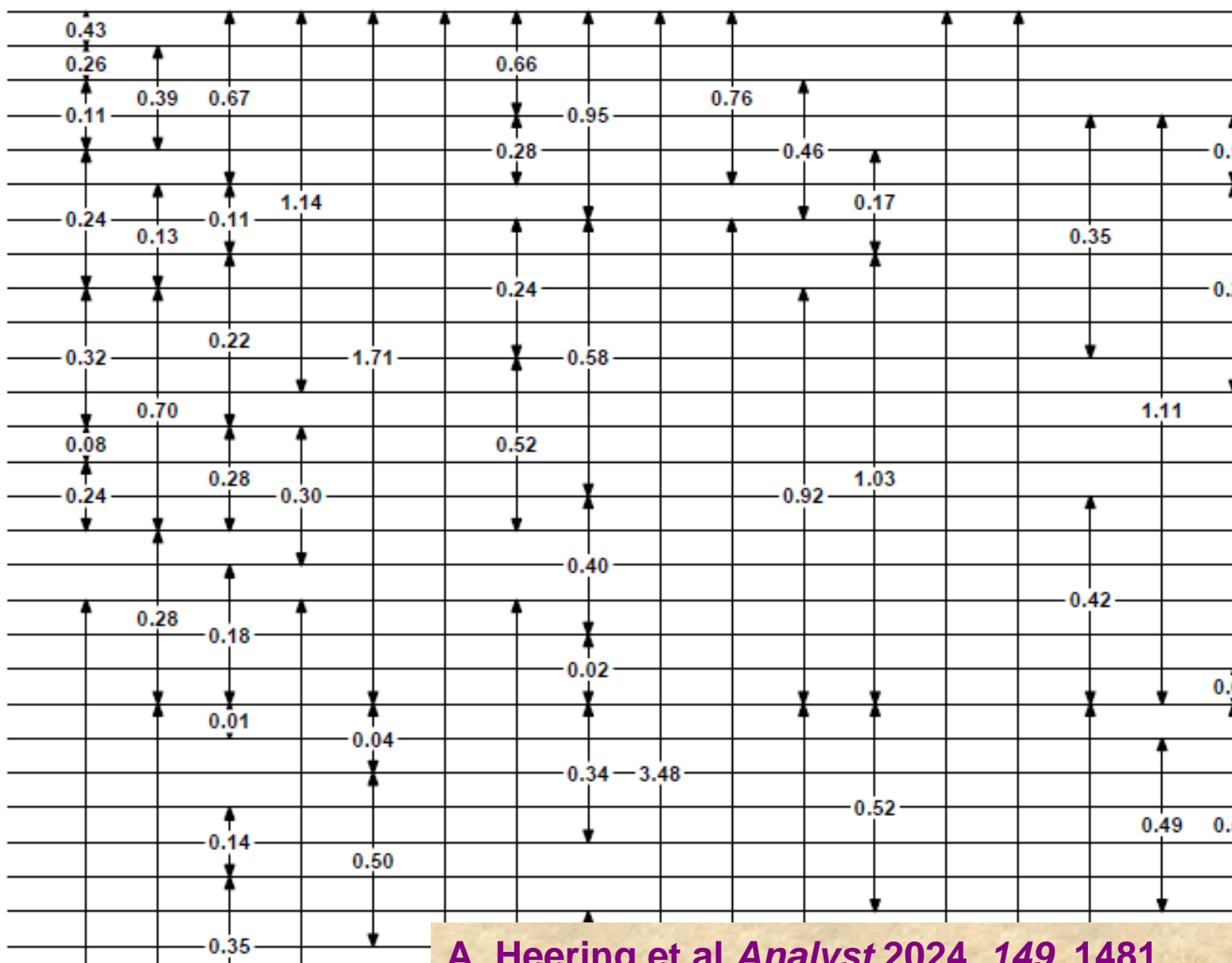
Example: Extreme acidities in low-polarity solvents
(in 1,2-dichloroethane)

- $\varepsilon = 10$
- Anchor point:
Solution of **Tf$_2$NH**

$$pH^{H_2O}_{abs} = -9.7$$
(Computational)

- Potentiometry is difficult but doable
  - Experiments are in progress

	$pK_{ip,r}$	$pK_{a,r}$	$pK_{a,DCE}$	$pH^{H_2O}_{abs}$
TfOH	-11.4	-11.3	33.7	-9.0
C$_6$H$_5$SO(=NTf)NHTf	-11.5	-11.7	33.3	-9.4
TfCH(CN)$_2$	-11.6	-11.5	33.5	-9.2
Br-TCNP	-11.8	-11.8	33.2	-9.5
[C(CN)$_2$=C(CN)]$_2$NH	-11.8	-12.0	33.0	-9.7
3,5-(CF$_3$)$_5$-C$_6$H$_3$-TCNP	-11.8	-12.0	33.0	-9.7
Tf$_2$NH ^{f}	-11.9	-12.0	33.0	-9.7
4-Cl-C$_6$H$_4$SO(=NTf)NHTf	-12.1	-12.3	32.7	-10.0
Cl-TCNP	-12.1	-12.1	32.9	-9.8
(C$_3$F$_7$SO$_2$)$_2$NH	-12.1	-12.3	32.7	-10.0
(C$_4$F$_9$SO$_2$)$_2$NH	-12.2	-12.4	32.6	-10.1
CN-CH$_2$-TCNP	-12.3	-12.4	32.6	-10.1
(C$_2$F$_5$SO$_2$)$_2$NH	-12.3	-12.4	32.6	-10.1
CF$_3$-TCNP	-12.7	-12.8	32.2	-10.5
HClO$_4$	-13.0	-12.8	32.2	-10.5
CF$_2$(CF$_2$SO$_2$)$_2$NH	-13.1	-13.1	31.9	-10.8
4-NO$_2$-C$_6$H$_4$SO(=NTf)NHTf	-13.1	-13.3	31.7	-11.0
HB(CN)$_4$	-13.3	-13.3	31.7	-11.0
(FSO$_2$)$_3$CH	-13.6	-13.6	31.4	-11.3
Tf$_2$CH(CN)	-14.9	-15.0	30.0	-12.7
2,3,4,5-tetracyanocyclopentadiene	-15.1	-15.1	29.9	-12.8
CN-TCNP	-15.3	-15.3	29.7	-13.0
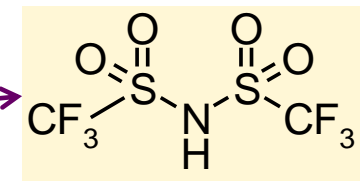
Work underway and future directions

- **Liquid chromatography**

  A. Heering et al *Analyst* **2024**, *149*, 1481

  - Predicting and interpreting retention

- **Low-polarity media**

  J. P. Samin, J. Saame, A. Heering, *In preparation.*
  E. Paenurk et al *Chem. Sci.* **2017**, *8*, 6964

  - Negligible concentration of solvated H^+, very low conductivity

- **Biphasic pK_a values**

  A. Leesment et al, *Anal. Chem.* **2022**, *94*, 4059

  - Low-polarity medium (1-Octanol) at equilibrium with water

  - Extendable to cell membranes, chemical sensors, extraction

- **Electrocatalysis**

  J. Saame, A. Heering, T. Hamann et al, *In preparation.*
  Y. Matsubara *ACS Energy Lett.* **2017**, *2*, 1886

  - Interplay between catalysis and acidity of the medium (CO2 reduction, ammonia splitting)

- **Replacing the H_0 scale**

  A. Heering, I. Krossing et al, *In preparation.*

  - pH_{abs} appears to be better than H_0 for strongly acidic meedia

Thank you for your attention!
Thanks to all contributors!

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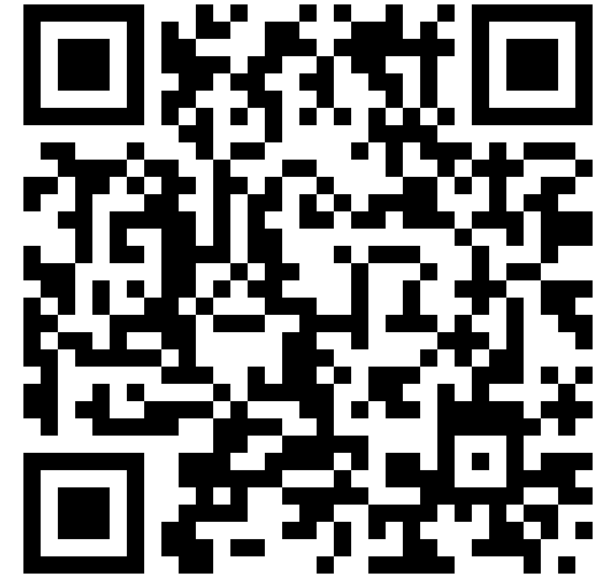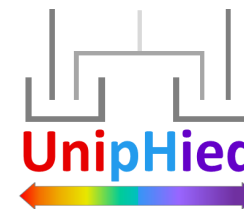
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LNE — Le progrès, une passion à partager   BUDAPEST FŐVÁROS KORMÁNYHIVATALA   CZECH METROLOGY INSTITUTE   DFM Danish National Metrology Institute   IPQ   SYKE Finnish Environment Institute   PTB Physikalisch-Technische Bundesanstalt Braunschweig und Berlin   TÜBİTAK UME   ((•)) ANB Sensors   Ciências ULisboa   UNI FREIBURG   UNIVERSITAS TARTUENSIS