Unified pH values of liquid chromatography mobile phases

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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

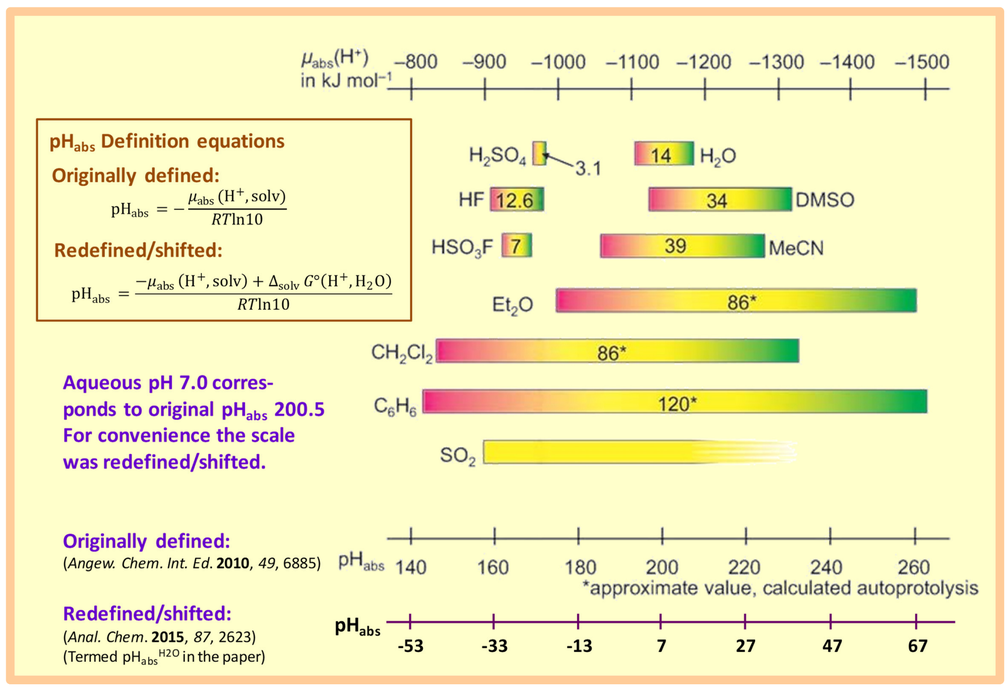
pH measurement of **LC mobile phases** is not trivial

pH measurement in mixed solvents is not well established, the most widespread approach is ${}^{w}_{w}\mathrm{pH}$

Is there a rigorous way?

There is the concept of Unified pH scale (pH_{abs}* scale)!

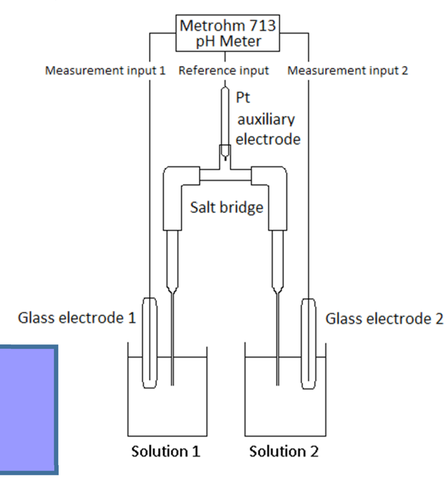
* Here we used pH_{abs} in the meaning of pH_{abs}^{H2O}, i.e. "aligned" with the aqueous pH scale [1]



How to measure that in practice?

Differential potentiometry[1]

[1] *Anal. Chem.* **2015**, *87*, 2623–2630, http://dx.doi.org/10.1021/ac504692m.

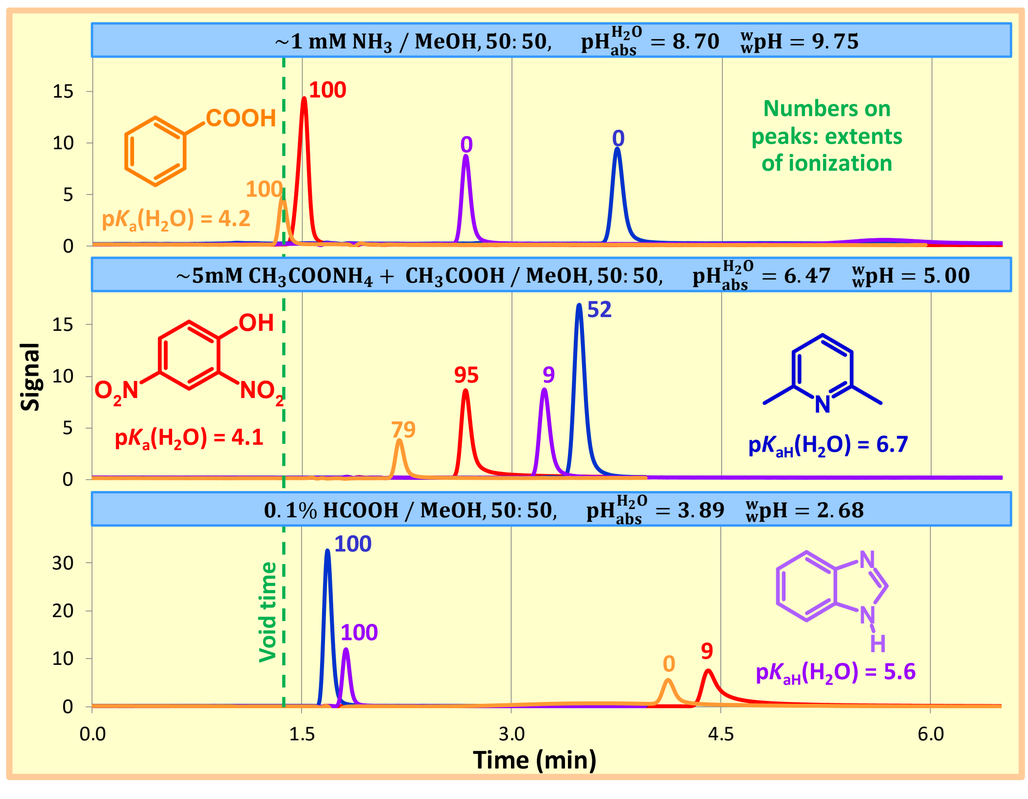


pH_{abs} of mobile phases?

Mobile phase	$pH_{abs}^{H_2O}$	${}^{w}_{w}\mathrm{pH}$
MeCN/ 1 mM NH_3 80/20	10.47	9.75
MeCN/ 1 mM NH_3 50/50	10.07	9.75
MeCN/ pH 5 80/20	8.93	5.00
MeOH/ 1 mM NH_3 80/20	8.89	9.75
MeOH/ 1 mM NH_3 50/50	8.70	9.75
MeCN/ pH 5 50/50	7.50	5.00
MeOH/ pH 5 80/20	7.49	5.00
pH 7 (diluted)	7.22	7.16
MeOH/ pH 5 50/50	6.47	5.00
MeCN/ 0.1% HCOOH 80/20	5.37	2.68
MeOH/ 0.1% HCOOH 80/20	4.79	2.68
MeCN/ 0.1% HCOOH 50/50	4.39	2.68
pH 4 (diluted)	4.09	4.15
MeOH/ 0.1% HCOOH 50/50	3.89	2.68

Possible in **any mobile phase**
Anchoring: **Aqueous std buffers**

Which works better in practice, ${}^{w}_{w}\mathrm{pH}$ or pH_{abs}?



Degree of ionization: **pH_{abs} is better with bases, ${}^{w}_{w}\mathrm{pH}$ with acids**
Retention: **Neither is perfect**

This work was supported by the EMPIR programme (project 17FUN09, UniPHied) co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme, by the EU through the European Regional Development Fund (TK141) and by Institutional Funding IUT20-14 from the Estonian Research Council.