

UNIFIED pH OF LIQUID CHROMATOGRAPHY MOBILE PHASES

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The mobile phase pH is a crucial factor in chromatographic separation of ionisable compounds, but measurement of mobile phase pH is not straightforward. One can measure the pH of water phase before the addition of organic solvent or the pH of the mixture. Both have advantages and disadvantages. The first approach does not describe the actual mobile phase and the second one needs calibration standards in the appropriate water-organic solvent mixture, which are difficult to obtain. There is a third option: to measure the pH of mobile phase, but calibrate in water. None of these approaches enable comparison of pH values of mobile phases made with different organic solvent composition.

This work presents the possibility of measuring the pH of the actual mobile phase in terms of thermodynamic activity of the proton. It is based on the unified acidity scale concept introduced by Himmel et al.¹, which enables comparison of acidities of any solutions, whatever is the solvent. The first experimental realisation of this concept was carried out by determining the acidities of liquid chromatography mobile phases. The measurement method is based on comparing pH of two solutions using differential potentiometry, where the potential difference of two metal-contact glass electrodes, immersed in these solutions, is measured². The unified pH values of several different mobile phases containing different proportions of water and acetonitrile or methanol were measured. It was found that the ionization behaviour of basic analytes can be better interpreted in terms of the unified pH values as compared to the conventionally used values (i.e. pH of the aqueous buffer before adding the mobile phase).

In conclusion, this work presents for the first time directly comparable acidities of liquid chromatography mobile phases prepared in different solvents, leading to better estimation of retention. If the pH of mobile phases is known, the analyst can compare mobile phases with similar acidities and pick the one with the most suitable properties for the intended analysis.

References

1. Himmel, D.; Goll, S. K.; Leito, I.; Krossing, I. *Angew. Chemie Int. Ed.* 2010, 49, 6885–6888.
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