Report of studying abroad

Department of Applied Chemistry, Akihiro TORIMOTO

Institute: Vrije Universiteit Brussel, Belgium

From October 25, 2024 to March 28, 2025

Research topic: Investigation of band broadening behavior on MOF-LC

1. Background

Chromatography is one of the most powerful tools for separation and analysis and a lot of separation modes have been developed until now. Metal–organic frameworks (MOFs) are porous compounds formed through self-assembly of metal ions and organic ligands, which have nano- or sub-nano-sized pores. Recently, MOFs have been used as the stationary phase in chromatography, showing high selectivity or/and unique separation trend enabled by well-designed and narrow channels of MOFs.[1]

To achieve high separation efficiency, detailed analysis of band broadening behavior is pivotal and band broadening behavior in reversed-phase chromatography has been investigated in detail by many researchers.[2] In liquid chromatography with MOF (MOF-LC), [1] heterogeneity of flow path due to non-sphere particle shape with wide distribution of particle size and [2] slow diffusion in narrow pore space can strongly affect separation efficiency, therefore analysis of band-broadening behavior is crucial. However, band broadening behavior in MOF-LC has rarely been investigated so far.

2. Objective

Based on background above, I aimed to unveil

(A) Whether analysis method for reversed-phase chromatography can also be applied to MOF-LC

(B) How characteristics of MOF-LC affect the band broadening behavior and separation efficiency

in this study.

3. Research

3.1 Experimental approach

3.1.1 Plate height measurement

Plate heights were measured using small test probes. MOF column showed significantly larger plate heights than reversed-phase column even in low velocity region, indicating huge contribution of eddy dispersion.

3.1.2 Peak parking measurement

Effective diffusion coefficients of small test probes were calculated by peak parking experiments. Obtained values (and effective diffusion coefficient divided by molecular diffusion coefficient) were smaller than previous results on reversed-phase column. Appropriate model equation enabled to compute intra-particle diffusion coefficient (and the value divided by molecular diffusion coefficient). The values were significantly small, providing high mass-transfer resistance.

3.2 Computational approach

Plate height curves were simulated for stationary phase with sphere particles and box-shaped particles. Intra-particle diffusion coefficient dependence was firstly investigated because peak parking experiments showed slow diffusion in MOF stationary phase. Slow diffusion in stationary phase provides extremely large slope in high velocity region, indicating that optimization of flow rate is highly important from the viewpoint of separation efficiency and total analysis time. Particle shape dependence was also investigated, but no significant difference was observed.

4. Conclusion

In this study, it was demonstrated that analysis technique for reversed-phase chromatography can be applied to MOF-LC. As expected, the diffusion in MOF stationary phase was very slow. Computational approach unveiled that this slow diffusion leads to huge plate height value especially in high velocity region.

5. Acknowledgements

I am grateful to Prof. Gert Desmet and staffs in Vrije Universiteit Brussel for great discussion and helping me in many situations like experiment, simulation, and data analysis. I am also grateful to Prof. Takashi Uemura, staffs in the University of Tokyo and my family for helping me in preparation for life in Belgium and supporting me when I had difficulty.

6. References

1) A. A. Kotova, *et al*., *Coord. Chem. Rev.* **2022**, *455*, 214364.

2) G. Desmet *et al*., *Anal. Chim. Acta* **2022**, *1214*, 339955.