Multidimensional chromatography

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Currently, two opposing trends in the instrumental analysis of small organic molecules (up to about 2,000 Da) are observed. First, to cope with the ever increasing number of samples, faster analytical methods must be developed. Promising current developments here are, for example, immunoassays and the ambient desorption ionization methods (DESI, DART, etc.). Second, the demands on modern instrumental analysis are becoming greater. Therefore, the desire for decreasing detection limits and the comprehensive analysis of more complex samples (all possible constituents of a sample to be determined qualitatively and quantitatively) lead to increasingly sophisticated analysis platforms. Powerful analytical methods for such problems are, in addition to the classic and now very commonly used multidimensional chromatographic methods (e.g., heart-cut), comprehensive two-dimensional gas and liquid chromatography (GC×GC and LC×LC), each coupled to mass spectrometers.

In contrast to the conventional two-dimensional GC (GC-GC) developed in the late 1970s, GC×GC, which was introduced by Liu and Philip in 1991, is a two-dimensional method that captures all sample components in two dimensions. To realize this, typically a non-polar GC capillary is coupled to a very short polar capillary. Near this capillary connection unit, a modulator is

installed, which has the task of fractionating substance zones arriving at the end of the first capillary and transferring the individual fractions separately into the second capillary. Over the last two decades, several types of modulators have been developed, of which the cryogenic modulators are by far the most commonly used.

The beginning of comprehensive two-dimensional liquid chromatography (LC×LC) can be traced to two works that are 12 years apart. In 1978 Erni and Frei described the two-dimensional separation of a Senna-glycoside extract by GPC in the first and an RP column in the second dimension. The analysis time was 10 h in the first dimension and, with two sample loops (each about 1.8 mL), a total of seven 1.5-mL fractions were collected and transferred to the second dimension. Because of the long accumulation time, however, there was mixing within the sample loop, which led to a reduced first dimension separation.

Then, in 1990, Bushey and Jorgenson demonstrated the first truly comprehensive two-dimensional liquid chromatography separation, using a protein sample with a microbore cation-exchange column in the first and an SEC column in the second dimension. In this case, a platform similar to that of Erni and Frei, an 8-port valve with two 30-μL sample loops, was used. The flow rate in the first dimension was only 5 μL/min and in the second dimension, 2.1 mL/min. This publication initiated the interest in LC×LC, and, in recent years, because of two systems which are now commercially available (including software), a significant increase in publications is to be found.

Although both comprehensive two-dimensional separation techniques are almost 25 years old, no GC×GC or LC×LC application has yet been established as the standard analysis method by a regulatory authority, and only this is the ultimate indication of whether an analytical method has found wide acceptance in the community. In the opinion of the guest editors, however, both methods offer potential for broad applications. GC×GC has in this respect far more users. However,

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LC×LC has, particularly for polar substances and those not analyzable by GC (i.e., not vaporized without decomposition), great potential, for example in the fields of metabolomics, non-target analysis, and polymer analysis.

Therefore we are pleased that the topical collection in this issue of *Analytical and Bioanalytical Chemistry* demonstrates the separation power and usefulness of classical and comprehensive two-dimensional chromatography. We also hope that the readers of *ABC* will enjoy this paper collection.

We thank all authors for submitting their interesting contributions for this special paper collection, the referees for their on-time reviews with critical but also constructive comments, and the editorial team of *Analytical and Bioanalytical Chemistry* for their highly professional collaboration and encouragement.

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