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Supercritical fluid chromatography hyphenated to bidimensional gas chromatography in comprehensive and heart-cutting mode: Design of the instrumentation

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ABSTRACT

A new multidimensional chromatographic instrument has been developed to perform both SFC-GC × GC and SFC × GC × GC, in response to the challenge of complex matrices characterization. The design of this online system is fully described and enriched by theoretical and practical discussions. A new interface has been investigated: this interface allows the temporary storage of SFC fractions inside sampling loops before their quantitative transfer toward the GC × GC. This innovative design allows flexible and automatic hyphenated approaches such as single, multiple, total heart-cutting and comprehensive modes. An overview of the interfacing experimental conditions is also presented. Thanks to all the hyphenation possibilities of the three dimensions, this instrument opens up new prospects for the quantitative analysis of very complex matrices.

1. Introduction

Analytical chemistry has to face the increasing complexity of matrices. The complete identification and quantification of very complex matrices are challenging tasks. In order to respond, even partially, to this challenge, high-resolution analytical techniques must be implemented. For several years, multidimensional chromatographic systems [1] have been developed to circumvent the limiting peak capacity of one-dimensional chromatographic methods. Thanks to the use of dimensions corresponding to different physicochemical properties, analytes are scattered in a higher peak capacity space [2]. In two-dimensional chromatographic techniques, the heart-cutting mode leads to transfer and analysis of one or several parts of first dimension solutes, eluted into the second dimension. The comprehensive mode, on the contrary, allows the separation of the entire sample along both columns, which induces better global separation. In this case, peaks are scattered in a structured 2D contour plot, whose axes correspond to the properties of the separation dimensions. From a technical point of view, the realization of such systems can be very difficult, especially for what concerns the compatibility between dimensions. Therefore, the application of comprehensive modes is essentially limited to the most complex matrices. Among the various chromatographic modes (LC × LC [3–5], LC × GC [6–8], SFC × GC [9], SFC × SFC [10] or SFC × LC [11]), GC × GC [12–14] is still, by far, the most used. Thanks to its powerful modulation systems and to the access to efficient quantitative detectors, GC × GC [13] has gained ground in many domains, like food industry, biology or environment. However, even working in GC × GC mode, dealing with the most complex samples can still be a difficult task. This problem has been highlighted while working on diesel fuels [15], but mostly during analyses of heavy petroleum fractions, like vacuum gas oils (VGOs) [16,17]. Because of the high number of different molecules (more than 1 million in case of VGOs), strong co-elutions can occur and bias the group type quantification. Clearly, the peak capacity of a conventional GC × GC is not enough for some matrices. Separation systems with higher dimensionality are necessary: therefore, the addition of an extra dimension to a GC × GC was considered.

An obvious approach is the implementation of a specific detector to monitor the analytes of interest. For this purpose, MS detections [18] (TOF-MS or qMS) have proven to be a powerful way, as far as identification is concerned. Besides, the hyphenation of GC × GC with a heteroatomic specific detector can serve a quantitative purpose, for instance in case of sulfur [19] or nitrogen-containing compounds [20,21].

Concerning the quantitative analysis of hydrocarbons, though, chemical group types cannot be specifically monitored by a

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quantitative detector. In order to resolve high co-elutions on 2D contour plots, an extra-physical separation must be implemented in case of heavy matrices [17] and even of some diesels [15]. This implies a few specific practical or theoretical considerations, especially regarding interfaces and modulators [22]. Unlike GC × GC, the "on the fly" approach is more complicated in case of three-dimensional systems, because of running time considerations and because of the need to select optimum conditions for each dimension. Three-dimensional gas chromatography, GC–GC × GC [23], has been successfully employed for the analysis of the olefins contained in petroleum samples. However, the thermal stability of GC stationary phases represents a real problem for the selection of different selectivities. GC × GC × GC with a two six-ports diaphragm valves interface was recently described [24]. In this case, a real time operation was preferred, even if it was difficult to obtain optimum kinetic conditions, due to the difference of columns geometry. The choice of truly orthogonal dimensions for a GC × GC × GC analysis is not straightforward, even if the recently introduced ionic liquid stationary phases seem to open up new prospects [25]. Nevertheless, a separation dimension operating in a dense phase (LC or SFC) appears to be more complementary to GC × GC systems. In fact, it provides higher selectivities compared to a gas phase dimension, thanks to numerous possible choices of solvent/solutes/stationary phase interactions. Besides, a GC × GC dimension proves to be complementary to a dense phase, because it provides high peak capacity and offers wide possibilities of hyphenation with some quantitative detectors.

Concerning the hyphenation of a LC dimension with a GC × GC, the offline mode is obviously the simplest to be implemented. It is often used for analytical explorations, including those of heavy petroleum samples [26–29]. In case of online approaches, the technical key point is the evaporation of the LC mobile phase, which must induce a limited reinjection band broadening. Thanks to its flexibility, the stop-flow mode is generally preferred via adapted valve-based or syringe-based interfaces [30,31]. Despite the remarkable results obtained for edible oils [31] and petroleum samples [30], the total running time of such an analysis remains the major issue.

The SFC dimension, with CO_2 as a mobile phase appears to be more compatible with a gas phase dimension than the LC dimension. The technical key point is indeed reduced to the expansion step, that removes the supercritical phase without any loss of solutes. Besides, SFC separations generally provide higher selectivities and can be carried out faster than LC separations [32]. The hyphenation of a SFC with a GC dimension has already been reported and includes the decompression of the supercritical fluid via a restrictor inserted into the GC injection port [33]. This was applied to SFC-GC [34], SFC × GC [35,36], and recently to SFC-GC × GC [37]. In the last case, a diesel sample was separated in two fractions, which were directly transferred into two distinct GC × GC column sets. However, SFC fractions were not controlled by a special interface.

In order to extend the interactions possibilities by performing SFC × GC × GC, it is necessary to go beyond the simple direct transfer of one SFC fraction into one GC × GC instrument. Therefore, a new interface must be implemented. Increasing the number of SFC fractions for one GC × GC requires several practical considerations. Based on the GC × GC running time, it is clear that analysis by SFC × GC × GC would be very slow. In order to reach a fully comprehensive mode, at least three samplings are necessary across each first dimensional peak [38]. If the SFC separation provides a high peak capacity, a comprehensive SFC × GC × GC could not be performed rapidly, considering the running time of GC × GC. For instance, if a SFC column separates 30 peaks, this would mean GC × GC must run 90 times. This corresponds to more than three days long analyses, if we consider that the classical GC × GC run lasts 1 h! Actually, it is more realistic to consider SFC × GC × GC as a multiple SFC-GC × GC of the entire sample.

Hence, each hyphenating possibility was reviewed in case of an SFC-GC × GC mode. Concerning a real-time route, the entire interconnection of the dimensions running time is required. Usually, each first dimension fraction is focused by a valve or a trapping modulator, while the previous one is analyzed by the following dimension. In order to fulfill the Murphy's criterion (i.e. at least three modulations by peak), the total running time (t_R) of each dimension must be much longer than the following one: ${}^1t_R \gg {}^2t_R \gg {}^3t_R$. A real time route has been already reported for SFC × GC [35], in a similar "on the fly" approach of GC × GC (i.e. same mobile phase in each dimension). However, the obtained separations were less efficient because of the use of CO_2 in the GC dimension. On the other hand, the SFC-GC × GC mode cannot be rationally implemented. The running time of a SFC separation usually ranges from 5 to 60 min, i.e. in the same range of time of the GC × GC run. The SFC separation can be slowed down, but this could induce undesired consequences, since it increases longitudinal diffusions. Another solution is the "fast" GC × GC [24,25]: using the valve approach, the first dimension can be approximately 5 s and the second dimension can be approximately 200 ms, corresponding to a 2D peak capacity of 20–30.

In the stop-flow mode, the first dimension flow rate is stopped for the time necessary to analyze the previously transferred fractions in the following dimension. This mode is widely used for LC × GC [6] or LC × GC × GC [22]. Time constraints for the second dimension are totally removed, which allows achieving an efficient second dimension separation. A slight increase of the first dimension band broadening could occur during repeated stop-flow operations, due to low diffusion coefficients in liquids. On the contrary, the diffusion coefficients in supercritical fluids are higher, and even much higher in gases. Thus, the stop-flow mode is less appropriate for SFCs or GCs in the first dimension. However, stop-flow SFC × GC has been proposed by Venter et al. for oil samples analyses [9]. In this case, a very fast GC dimension allowed the limitation of high band broadening. However, in the case of SFC to GC × GC hyphenation, this approach would induce a great loss of SFC resolution due to strong longitudinal diffusions.

Another way to perform a chromatographic coupling is the online intermediate collection of first dimensional fractions. This is usually carried out using sampling loops, but it is almost limited to LC first-dimensional separations like those for LC × LC experiments [39]. In this case, running times of each dimension are disconnected. This provides the time necessary for the implementation of the next dimensions during the temporary storage, without increasing longitudinal diffusions, since the first dimension is operated without interruptions. However, the main drawback is the restricted number of transferred fractions, which is directly related to the number of loops. Since the total running time of a separation cannot reasonably last more than one day, ten SFC fractions should be considered as a maximum. Besides, the intermediate collection leaves the possibility to choose fractions that should be transferred to the GC × GC dimension.

In our work, we have developed an intermediate collection of SFC fractions by sampling loops between a first SFC dimension and GC × GC. The design of the new flexible instrument is described in the first part and its application to the analysis of heavy petroleum fractions is discussed in the second part [40].

2. Experimental details

2.1. Samples and chemicals

A synthetic test mixture of model compounds (100–400 ppm) in heavy petroleum fractions range was prepared in carbon