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Comprehensive two-dimensional gas chromatography (GC×GC) retention time shift correction and modeling using bilinear peak alignment, correlation optimized shifting and multivariate curve resolution

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ABSTRACT

A combination of peak alignment methods and multivariate curve resolution (MCR) is proposed for handling retention time shifts and modeling of comprehensive two-dimensional gas chromatographic (GC×GC) data in the case of univariate detection systems such as in flame ionization detection (FID) or in total ion current mass spectrometry (TIC-MS) detection. A new bilinear peak alignment (BPA) method, based on MCR, is first proposed to correct for progressive within run retention time shifts in GC×GC due to temperature programming effects on second chromatographic dimension. The performance of the proposed peak alignment method is compared to that of the correlation optimized warping (COW) method. In addition, Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) method, under proper constraints, is also proposed to analyze the augmented GC×GC data matrix for the resolution and quantification of target compounds in complex samples when incomplete separation and co-elution problems exist. For those difficult cases in which large between GC×GC run retention time shifts exist in both dimensions, a preliminary between runs first dimension peak alignment method by Correlation Optimized Shifting (COShift) is used to preserve the bilinearity model assumption needed for MCR-ALS application. The results showed the successful application of the proposed strategy for resolution and quantification of some target compounds in GC×GC analysis of simulated and of real samples.

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1. Introduction

In recent years, comprehensive two-dimensional gas chromatography (GC×GC) has been accepted as a powerful technique with high resolving power (peak capacity) and high sensitivity for the analysis of complex mixtures such as petrochemical, biological, food and environmental samples [1–3]. In GC×GC experiments, the separation process is based on two orthogonal chromatographic dimensions with different separation mechanisms (i.e. the stationary phase of the first dimension is non-polar whereas that of the second dimension is polar). The two dimensions are connected with a suitable interface, so-called modulator, located between the two chromatographic dimensions. The modulator acts as an on-line injector that produces very narrow injection pulses (down to 50 ms peak width) on the second dimension head, accounting for a fast sampling of compounds eluting from the first dimension. The entire first dimension chromatogram is thus "sliced" following a modulation period (P_M) of a few seconds and re-injected into second dimension for a fast GC-type separation. In addition, the modulator is operated at such a frequency that each compound being eluted from the first dimension is sampled frequently enough (at least three times for each elution peak) to maintain the first dimension separation [4]. Finally, the linear signal from the detector (e.g. flame ionization detector (FID), electron capture detector (ECD) or mass spectrometer (MS)) is converted to a series of secondary chromatograms stored in a data array, which facilitates visualization of the elution process as two-dimensional (2D) contour plots (corresponding each dimension to the chromatographic separation in one of the two dimensions). However, one of the main challenges in GC×GC is related to the analysis and interpretation of the data obtained in these cases. In this context, resolution, identification and quantification of target compounds in the presence of interferences are issues which have a great importance and not totally solved yet [5,6]. Data from GC×GC analysis of multiple samples using univariate detectors such as FID, ECD or MS in total ion current (TIC) or selected ion monitoring (SIM) modes, can in theory be organized in a three-way data array with two retention time axes (ways, modes) and one sample axis. In an ideal case,

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this three-way data array could be considered to conform to a trilinear model if there would no significant changes in retention times within (for single sample) and between (for multiple samples) runs. However, due to the change in instrumental conditions (e.g. temperature and pressure changes), stationary phase degradation, matrix effects and manual injection, retention times may shift in both dimensions from sample to sample (between runs shift) [7]. Up to now, different methods have been proposed to correct retention time shifts between GC×GC runs such as rank alignment [8,9], correlation optimized shifting (COShift) [10], two-dimensional correlation optimized warping (2D-COW) [11], and dynamic time warping (DTW) [12]. However, a more serious problem can be occurred when retention time changes within the same GC×GC run [13]. In most GC×GC experiments, in order to have a fast enough chromatographic separation and an acceptable chromatographic resolution, the temperature of the second dimension is rapidly changed in relation to that of the first dimension and this causes significant changes in retention times of the elution peaks of the same component from slice to slice, when sample is passed from the first dimension to the second dimension (within run shift). Surprisingly, the within run retention time shifts in GC×GC analysis have been little investigated [13], although it can cause a clear deviation from bilinear model assumption and degrades chemometric quantitative results. Additionally, when within run retention time shifts and co-elution problems coexist at the same time, peak alignment methods for conventional chromatography such as dynamic time warping (DTW) [14,15] or correlation optimized warping (COW) [16–18] do not produce reliable results. This is due to the procedure used by these techniques of choosing a peak reference and aligning the target chromatograms to it. This strategy of peak reference selection cannot work in the case of the simultaneous presence of within run shifts and co-elution problems in the second dimension. Therefore, there is a need to develop a new strategy to handle retention time shifts within the same GC×GC run and to discriminate the shift problem from the co-elution problem in the chromatographic analysis of samples with complex matrices. Moreover, simpler and more flexible resolution and quantification methods are required to be less sensitive to retention time shift problems between GC×GC runs compared to Generalized Rank Annihilation Method (GRAM) [14] or PARAllel FACtor analysis (PARAFAC) [15] methods, frequently used for GC×GC analysis. In this context, the Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) method [16–18] can also be used advantageously for GC×GC analysis of multiple samples. In some circumstances, PARAFAC2 [19,20] can be also used for GC×GC data analysis as a more flexible version of PARAFAC. However, PARAFAC2 is computationally more complex and expensive, and it does not allow for the application of constraints like non-negativity or unimodality in one of the data mode and therefore unreasonable negative values and multimodal peaks appear in the results. Also, selecting the application of constraints only to some selected components is not possible.

For MCR-ALS analysis of GC×GC data from multiple samples, the data matrix is augmented column-wise, with first dimension elution times in columns and second dimension elution times in rows. This data matrix arrangement relaxes significantly the need to correct for the larger between GC×GC runs second dimension retention time shifts (see below).

In the present study, a new bilinear peak alignment (BPA) method is first proposed to correct for within run second dimension retention time shifts and its performance is compared to the COW [21–23] method. The three-way GC×GC data obtained in the analysis of different samples is unfolded in a column-wise manner and MCR-ALS method is then applied for the resolution and quantification of the target compounds from the analyzed samples. However, for cases in which large retention time shifts still exist between GC×GC runs in both dimensions, COShift is used to correct them in one dimension to preserve the required bilinear structure needed for MCR-ALS application.

In this work, a new strategy is proposed to handle GC×GC retention time shifts allowing the proper resolution and quantification of coeluted compounds for GC×GC univariate detection, including GC×GC-TOFMS-TIC analysis of polycyclic aromatic hydrocarbons (PAHs) mixtures and GC×GC-FID analysis of aromatic compounds mixtures in gasoline samples.

In the whole paper, and in accordance with the notation usually used in GC×GC studies, first dimension refers to measurements in the first chromatographic column and second dimension refers to measurements in the second chromatographic column.

2. Methodology

In GC×GC analysis, two different situations can be encountered. A first situation is encountered for the case of GC×GC coupled to multivariate detection, such as time of flight mass spectrometry (GC×GC-TOFMS) in full scan mode. In this case, peak shift correction is not needed because retention time shifts within and between GC×GC runs can be handled directly by MCR bilinear modeling of the proper column-wise augmented data matrix having the reproducible *m/z* spectral mode in its columns. This strategy has been successfully used for resolution and quantification of PAHs in the aromatic fraction of a heavy fuel oil sample (see our previous work [24]). A second completely different situation is encountered when GC×GC is coupled to univariate detection system, such as in flame ionization detection, FID, or in total ion current (TIC) mass spectrometric detection. This is the case studied in this paper, in which the absence of a spectral mode makes more difficult the proper identification, resolution and quantification of target compounds due to the retention time reproducibility problems.

2.1. Bilinear peak alignment (BPA) method

Bilinear modeling methods are based on the mathematical decomposition of a measured mixed signal into their 'pure' (factor) contributions [25]. The general equation for the bilinear model can be written as follows:

$$\mathbf{X} = \mathbf{Y}\mathbf{Z}^{\mathrm{T}} + \mathbf{E} \quad (1)$$

where for GC×GC data, $\mathbf{X}$ (I, J) is the data matrix having the experimental data measured by the chromatographic detector (e.g. FID or MS-TIC intensity measurements) ordered according to second dimension elution times in the matrix rows and according to first dimension elution time in the matrix columns. $\mathbf{Y}$ (I, N) is the matrix of pure second dimension elution profiles, $\mathbf{Z^T}$ (N, J) is the matrix of pure first dimension elution profiles, $\mathbf{E}$ (I, J) is the residual matrix with the data variance unexplained by the bilinear model $\mathbf{YZ^T}$, I is the number of elution times in second dimension, J is the number of elution times in first dimension, and N is the number of factors, or chemical components in this case.

As mentioned before, each "slice" in GC×GC has the chromatogram in the second chromatographic dimension from the automatic modulator injection of a small fraction of sample eluted in the first chromatographic dimension. For example, for a single chromatographic peak in the first dimension there are at least three sampling times in the modulator and therefore, three second dimension "slices". In GC×GC experiments, due to the within run retention time shifts between different slices taken from the first dimension, the data matrix is not bilinear and the number of significant singular values will be larger than the number of eluted components. In the literature there is a method named shifted factor analysis (SFA) [26–28] based on factor analysis to handle factor shifts. SFA incorporates shift (or time lag) variation as a part of the model's latent variable parameters. For GC×GC data due to the presence of two types of retention time shifts, first, there is need to a method to correct

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