



Optimizing loop-type cryogenic modulation in comprehensive two-dimensional gas chromatography using time-variable combination of the dual-stage jets for analysis of crude oil



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ABSTRACT

The enhanced chromatographic capability of the comprehensive two-dimensional gas chromatography (GC \times GC) has already found several applications in analytical chemistry comprising complex samples. However, setting the appropriate chromatographic conditions that maximize sensitivity and separation efficiency in GC \times GC may be more difficult than in conventional one-dimension gas chromatography, mainly due to the additional parameters strictly related to the modulation. Loop-type cryogenic modulators have been currently used for crude oil analysis using GC \times GC, requiring sometimes a laborious try-and-error procedure to properly tune the dual-jets elapsed times on modulation. In this work, the advantages of choosing a time-variable combination of cold and hot jets pulses in a loop-type cryogenic modulator is presented when performing the fingerprinting analysis of crude oils using GC \times GC-QMS, contrary to the conventional procedure based on a single combination for the dual-stage jets. A design of experiments approach is proposed to most effectively optimize the time-variable combination of the dual-jets elapsed times while modulating the wide hydrocarbons range along the GC \times GC analysis. The most abundant classes of hydrocarbons contained in the maltenes fraction of a crude oil sample, such as paraffins, aromatics, steranes and hopanes were successfully resolved.

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1. Introduction

Comprehensive two-dimensional gas chromatography (GC \times GC) has been widely used for analysis of samples that comprises an overwhelming number of compounds whenever appropriate separations cannot be achieved on conventional one-dimensional gas chromatography (GC) [1]. The higher analytical performance of GC \times GC is achieved due to the connection of two capillary columns containing orthogonal separation properties along with a modulation process. Modulators periodically concentrates an unresolved fraction of the effluents coming from the first column (1D) and rapidly reinjects this fraction for separation into the head of the second column (2D) as a narrower band, enhancing also detectability [2]. GC \times GC has found several prominent applications in petrochemistry [3], environmental [4] and food [5] chemistry, forensics [6] and metabolomics [7].

The GC setup while maximizing sensitivity and separation efficiency requires handling instrument parameter related mainly to the inlet (e.g.; temperature and split/splitless mode), column settings (e.g.; column dimensions and type of stationary phase), carrier gas flow, oven temperature and the total analysis time. For GC \times GC, even more parameter deserves attention; apart from the orthogonality properties of the columns, they are preferable to have dimensions that result in the optimal individual linear velocity for the carrier gas [8]. Beens et al. [9] have already demonstrated how the columns set dimensions affect the carrier gas velocities from the optimal value in each column for GC \times GC. Furthermore, parameters strictly from the modulator, such as modulation period and the transference of the effluent from 1D into 2D, also demand adjustments [10].

Different types of modulators have already been developed for GC \times GC [11]. Loop-type cryogenic modulators have been commonly used for crude oil analysis, due to the recognized capability of the dual-stage jets to modulate the wide range of hydrocarbons contained in crude oils [12–16]. Gaines and Frysinger [17] have already pointed out the importance on manipulating the cold and hot jet pulses temperatures in loop-type modulators when ana-

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lyzing the C_4 – C_{40} hydrocarbons range in a crude oil sample. The authors concluded that decreasing the cold jets flows along the chromatographic analysis is necessary to avoid inefficient remobilization of the less volatile effluents into 2D by the next hot jet pulse. Additionally, Tranchida et al. [18] discussed the importance of the carrier gas velocity at the point of reinjection into 2D for GC \times GC analysis using loop-type cryogenic modulators. Despite the carrier gas velocity is easily handled by appropriately setting its flow according to the columns set (1D + loop + 2D) dimensions, controlling the cold jet flow during cryogenic modulation has not been used, probably due to instruments limitations. Instead, an offset on the temperature of the hot jets can be established throughout the GC \times GC analysis to provide fast remobilization (see the aforementioned references). However, excessive cold jets can still persist and building the modulator becomes more complex.

This work presents the advantages of using time-variable combinations of cold and hot jets pulses in a loop-type cryogenic modulator to perform the fingerprinting analysis of a complex mixture such as crude oils, using two dimensional gas chromatography – quadrupole mass spectrometry (GC \times GC-QMS), contrary to the conventional procedure based on a single combination of the dual-stage jets. Herein, the temperature of the jets at the point of the modulation is intrinsically manipulated according to the (variable) elapsed time of the dual jets pulses. Furthermore, a design of experiments (DoE) approach is presented to more effectively handle the experimental parameters related to the jet pulses elapsed times during the modulation of the wide hydrocarbons range contained in the crude oils, without excessive number of trials. DoE is undoubtedly the most efficient strategy to extract the influence of instrumental parameters in chromatography, finding several successful application in conventional GC [19]. However, extending DoE concepts to GC \times GC has still found few applications, e.g.; assessing robustness aspects [20] and optimization of the overall chromatographic conditions when analyzing essential oils [21] and phenolic isomers [22]. In this work, the instrumental conditions for the GC \times GC-MS analysis related to the chromatographic separation (i.e.; columns set dimensions, carrier gas flow, inlet and oven settings) and the (quadrupole) MS detection (i.e.; ion source and transfer line temperatures, ionization energy, detector voltage) were carefully chosen according to the aforementioned literature. Moreover, the extracted DoE-optimized time-variable combination of the dual jets demonstrated that manipulating both cold and hot jets simultaneously on modulation extends possibilities for achieving narrow peaks in fingerprinting of complex samples using GC \times GC.

2. Experimental

2.1. Sample preparation

The asphaltenes were firstly removed from the crude oil sample to extract the (maltenes) fraction that can be analyzed by GC [23]; a total amount of 100.0 (± 0.5) mg of the crude oil was added to 7.0 mL *n*-pentane in a centrifuge tube. The tube was vigorously shaken and centrifuged at 300 rpm ($t = 5$ min), and the supernatant was separated. This process was repeated 5 times to maximize the extraction yield. Then, the *n*-pentane was evaporated under gently nitrogen flow, next re-suspending the maltenes to 20 mg/mL using *n*-hexane.

2.2. Two-dimensional gas chromatography – quadrupole mass spectrometry (GC \times GC-QMS)

The maltenes were analyzed using a lab-made GC \times GC-QMS prototype based on a GC-2010+ chromatograph containing a

split/splitless injector and a GCMS-TQ8030 QqQ mass-analyzer (Shimadzu Corp., Kyoto, Japan). The cryogenic lab-made modulator operated with N_2 (g) cold jets frozen in liquid nitrogen ($p = 5$ psi) and N_2 (g) hot jets at $T = 380^\circ\text{C}$ and $p = 105$ psi. The N_2 (g) jet pulses were controlled by solenoid valves (ASCO, Florham Park, NJ – USA) connected to an Arduino[®] board that set the elapsed time of each pulse throughout the analysis. The GC first dimension was equipped with a capillary column (30 m \times 0.25 mm i.d. \times 0.25 μm) containing 5% phenyl methyl polysiloxane as stationary phase (RTX-5 ms) connected to a similar column (0.85 m \times 0.25 mm i.d. \times 0.25 μm) as the loop. The second dimension was a capillary column (1.0 m \times 0.15 mm i.d. \times 0.15 μm) containing 50% diphenyl – 50% dimethyl polysiloxane as the stationary phase (Rxi[®]-17Sil MS). The modulation period (MP) was set to 5.0 s, with the jet pulses elapsed times adjusted according to the DoE-approach detailed in Section 2.3. The analyses conditions were an injection volume of 1 μL , split mode 1:60, at $T = 300^\circ\text{C}$ and purge flow 2 mL min⁻¹, the oven ramp was set at 70°C to 325°C at 3°C min^{-1} . Hydrogen was used as carrier gas at initial flow of 0.93 mL min⁻¹, resulting in averaged linear velocities of 40 cm s⁻¹, 67 cm s⁻¹ and 287 cm s⁻¹ in 1D, loop and 2D, respectively [8]. Despite the averaged linear velocity of the carrier gas in the loop and its length would suggest a shorter MP for appropriate modulation, no wrap-around occurred in the optimized two-dimensional chromatograms, probably due to efficient trapping/refocusing by the cold jet and the stationary phase retaining the effluents also herein. Deactivated columns as the loop were easily disrupted due to the consecutive dual-stage jets during the analysis, thus they were avoided. The MS were acquired using the single quadrupole (Q3) full scan mode, in the m/z range 60–500 at 40 Hz, transfer line temperature at 300°C , ion source temperature at 230°C , detector voltage at 1.5 kV and electron ionization at 70 eV.

2.3. Design of experiments to optimize the modulations conditions in the GC \times GC-QMS analysis of the crude oil

Face-centred factorial designs (FCD) [19] were proposed to evaluate three factors related to the combination of the cold and hot jets pulses elapsed time (C and H , respectively) for each modulation period (MP): i) the fraction of the total elapsed time of the dual-jets ($C + H$) in relation to the MP (i.e. factor 1 = $[(C + H)/MP]$), ii) the initial proportion of C over ($C + H$) (factor 2 = $[C/(C + H)]$) and iii) the influence of a time-variable combination of the cold and hot jets pulses along the chromatographic analysis (factor 3 = $[jet\ ramp]$). The first two factors handled the efficiency in which effluents are trapped/refocused and remobilized in the loop. Meanwhile, the $[jet\ ramp]$ relied on adjusting the appropriate temperatures of the dual jets when modulating high molecular weight (MW) effluents prone to be excessively trapped/refocused whether modulation conditions remains the same for the lower MW counterparts. The levels of each factor for this FCD is depicted in Table 1. Herein, the decoding of the factors levels to the initial cold and hot jets elapsed times is done by firstly assessing the $[(C + H)/MP]$ level and next attributing C and H individually, according to the proportions from the corresponding $[C/(C + H)]$ level. Two **y**-responses vectors were used for each experiment, corresponding to the averaged second dimension peaks width at half height ($w_{1/2}$) for C_{12} – C_{22} (**y1**) and C_{23} – C_{32} (**y2**) hydrocarbons ranges. The decision for a two-responses DoE, contrary to a single **y**-response vector comprising the overall peaks, avoided biased dual jets optimization for lower- or higher MW hydrocarbons. The **y1**-response for each sample was computed for only the most relevant peaks that were chosen above a common peak-height threshold, totaling in 40–60 peaks corresponding to C_{12} – C_{22} saturated and aromatic hydrocarbons in general. The exact number of selected peaks in each chromatogram depended

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