Journal of Chromatography A, 1216 (2009) 7301–7306

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Enhanced resolution comprehensive two-dimensional gas chromatography applied to the analysis of roasted coffee volatiles

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ARTICLE INFO

Article history:
Available online 23 June 2009

Keywords:
Comprehensive two-dimensional gas chromatography
GC × GC
Flow splitting
Roasted coffee
Solid-phase microextraction

ABSTRACT

The present research is based on the full exploitation of the separation power of a 0.05 mm internal diameter (ID) capillary, as a comprehensive two-dimensional (2D) GC (GC × GC) secondary column, with the objective of attaining very high-resolution second dimension separations. The aim was achieved by using a split-flow system developed in previous research [P.Q. Tranchida, A. Casilli, P. Dugo, G. Dugo, L. Mondello, Anal. Chem. 79 (2007) 2266], and a dual-oven GC × GC instrument. The column combination employed consisted of a polar 30 m × 0.25 mm ID column connected, by means of a T union, to a detector-linked high-resolution 1.1 m × 0.05 mm ID apolar analytical column and to a 0.33 m × 0.05 mm ID retention gap; the latter was connected to a manually operated split valve. As previously demonstrated, the use of a split valve enables the regulation of gas flows through both analytical columns, generating the most appropriate gas linear velocities. Comprehensive 2D GC experiments were carried out on Arabica roasted coffee volatiles (previously extracted by means of solid-phase microextraction) with the split-valve closed (equal to what can be defined as conventional GC × GC) and with the split-valve opened at various degrees. The reasons why it is absolutely not effective to use a 0.05 mm ID column as second dimension in a conventional GC × GC instrument will be discussed and demonstrated. On the contrary, the use of a 0.05 mm ID column as second dimension, under ideal conditions in a split-flow, twin-oven system, will also be illustrated and discussed.

1. Introduction

Comprehensive two-dimensional (2D) GC (GC × GC), a method which has been on the chromatographic scene since the beginning of the 90s, can be considered one of the most revolutionary inventions in the GC field [2]. The 2D technique enables a great increase in peak capacity, if compared to single-column GC separations. Typically, and briefly, GC × GC separations occur on two capillaries connected in series, and characterized by distinct selectivities. A transfer device, defined as modulator, is located between the two columns and has the fundamental function of cutting and concentrating first dimension column effluent bands; the latter, after the focusing stage, are injected onto a short micro-bore capillary. The whole process, which lasts typically 4–8 s, is carried out continuously throughout the GC × GC analysis. During the second-dimension run time, the modulator is engaged in the subsequent modulation process. Comprehensive two-dimensional GC has been thoroughly described elsewhere [3,4].

The combination of a long 0.25 mm internal diameter (ID) + a short 0.10 mm ID column, with thermal modulation, has always been by far the most preferred choice made by analysts in this field. However, the full potential of GC × GC is hardly ever expressed when using the conventional set-up because mobile phase velocities are generally satisfactory (usually near to optimum) in the first dimension and higher than ideal in the second dimension [1,5,6]. The main consequence is that in many GC × GC separations a great amount of the exploitable chromatographic space remains unoccupied.

In previous research, a GC × GC system, defined as "split-flow", was developed: a primary 0.25 mm ID column was connected to a short 0.10 mm ID secondary one and to a 0.3 m retention gap, by using a T press fit. The second-dimension analytical column passed through the modulator, while the retention gap outlet was linked to a manual split valve. The column flows were regulated in both

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doi:10.1016/j.chroma.2009.06.056

dimensions by simply adjusting the split valve [1]. The validity of the new approach was demonstrated by analyzing petrochemical and fatty acid methyl ester (FAME) samples.

The present research is based on the use of a 0.05 mm ID column as GC × GC secondary column, with the objective of attaining very high-resolution second dimension separations. However, such a micro-bore column has been employed rarely as second column [7,8] and never under optimized conditions. In order to achieve such an aim, a split flow, twin-oven, GC × GC system was employed, characterized by a 30 m (0.25 mm ID) polar primary column (located in GC1) connected to a 2 m segment of 0.25 mm ID retention gap (necessary for cryogenic loop-type modulation); the latter was connected, *via* a T-union, to a 1.1 m × 0.05 mm ID apolar analytical column and to a 0.33 m × 0.05 mm ID retention gap, both located in GC2. The outlet of the 0.05 mm ID retention gap was connected to a needle split-valve, situated in GC2. As demonstrated previously, column flows can be regulated at the conjunction point by adjusting the split valve. Conventional and split-flow GC × GC experiments were carried out on a very complex matrix, *viz*., roasted Arabica coffee volatiles, extracted by using solid-phase microextraction (SPME).

2. Experimental

2.1. Sample and sample preparation

The Arabica ground coffee was a commercially-available one, produced in Italy (the producer will not be reported for industrial secrecy reasons). No preliminary treatment was applied before the SPME process.

The C_{16} alkane and $C_{12:0}$ FAME, used for efficiency calculations, were supplied by Sigma–Aldrich (Milan, Italy). Solutions, at the 100 ppm level, were prepared in *n*-hexane.

2.2. SPME process

About 2 g of ground coffee bean were transferred to a 10 mL vial and then sealed. A Shimadzu autosampler (AOC-5000; Kyoto, Japan) was used for the headspace-SPME operations. The SPME triple phase 50/30 μm fiber (divinylbenzene/carboxen/polydimethylsiloxane) was purchased from Supelco (Milan, Italy). The fiber was appropriately conditioned before use. The extraction procedure was carried out according to previously optimized conditions [9]. Briefly, the samples contained in the vials were heated at 60 °C for 10 min (preincubation) and agitated (clockwise–anticlockwise alternate rotation) at 500 rpm. After this preliminary equilibrium procedure, the SPME needle was inserted in the sealed vial and the fiber exposed to the coffee for 40 min at the same temperature and agitation speed. After this process, the fiber was thermally desorbed in the GC injection port for 1.0 min at 250 °C in the splitless mode (after 1 min, a 100:1 split ratio was applied).

2.3. GC × GC-FID operational conditions

All comprehensive 2D GC applications were carried out on a Shimadzu GC × GC system consisting of two independent GC2010 gas chromatographs, and a flame ionization detector (FID) (280 °C). Data were acquired using the GCsolution software (Shimadzu). Bidimensional chromatograms were generated by using the ChromSquare software (Chromaleont, Messina, Italy). The two GC ovens were linked through a heated (280 °C) transfer line (Shimadzu). The primary GC (GC1) was equipped with an AOC-20i auto-injector and a split-splitless injector (280 °C). The primary column (situated in GC1), an Omegawax 250 30 m × 0.25 mm ID, 0.25 μm film thickness [poly(ethyleneglycol)], was connected to a 2 m × 0.25 mm ID retention gap segment (Supelco) by using an SGE SilTite mini-union (Ringwood, Victoria, Australia). The retention gap was passed through the heated transfer line and connected, by using a fixed outlet capillary column splitter (SGE), to a custom-made SLB-5ms 1.1 m × 0.05 mm ID, 0.05 μm film thickness (silphenylene polymer) capillary and to a 0.33 m × 0.05 mm ID retention gap (both columns, provided by Supelco, were located in the second oven, defined onwards as GC2). The outlet of the 0.05 mm ID retention gap was connected to a manually-controlled valve, namely an OSS-2 outlet splitter system (SGE). A scheme of the split-flow, twin-oven GC × GC instrument is illustrated in Fig. 1. The 2 m retention gap was used to create a double-loop, necessary for cryogenic modulation. The latter was carried out in GC2 and was applied every 6 s by using a dual-stage loop-type modulator (under license from Zoex Corporation, Houston, TX, USA). The duration of the hot pulse (325 °C) was 375 ms. The FID was operated as follows: H_2 flow: 50.0 mL/min; air flow: 400.0 mL/min; make up (He): 50.0 mL/min; sampling frequency: 125 Hz and 250 Hz in the split-flow and conventional GC × GC applications, respectively.

GC1 oven program was optimized elsewhere [9]; optimized conventional GC × GC: GC1 and GC2 temperature program: 60 °C (5 min) to 230 °C at 1.5 °C/min, to 280 °C (2 min) at 50 °C/min. Initial H_2 pressure (constant linear velocity): 614 kPa.

Optimized split-flow GC × GC: GC1 temperature program: 60 °C (5 min) to 230 °C at 1.5 °C/min, to 280 °C (2 min) at 50 °C/min. GC2 temperature program: a −20 °C offset was applied. Initial H_2 pressure (constant linear velocity): 292 kPa.

First-dimension chromatographic efficiency calculations for conventional and split flow GC × GC: a $C_{12:0}$ FAME 100 ppm solution

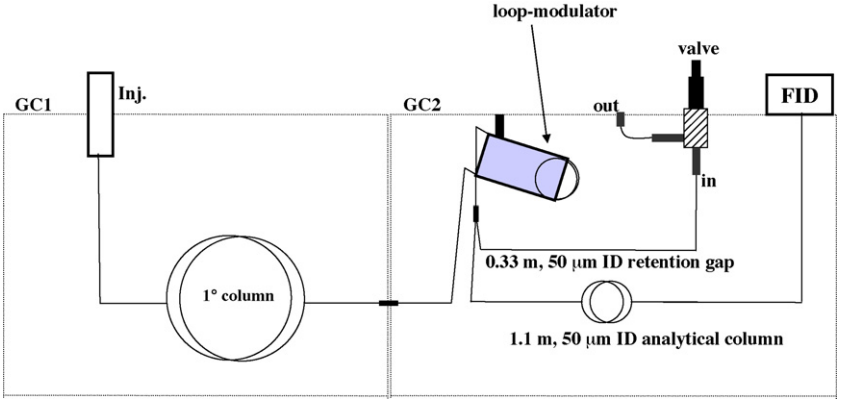

Fig. 1. Scheme of the split-flow, twin-oven GC × GC instrument.