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Comparison of the performance of forward fill/flush and reverse fill/flush flow modulation in comprehensive two-dimensional gas chromatography

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ABSTRACT

The performances of forward flow fill and flush (FFF) and of reverse flow fill and flush (RFF) in flow modulated comprehensive two-dimensional gas chromatography (GC × GC) using the same volume of the sampling channel have been studied and compared.

Sample models include a reference mixture of hydrocarbons at low concentration, a petroleum reformate product and the essential oil of *Rosa damascena* Miller. The latter samples contain solutes in different concentrations but some up to 30% allowing to study overloading phenomena in detail. For solutes injected at low quantity, the performance of FFF and RFF is similar. For solutes present in a sample at high quantity, RFF guarantees less broadening and spreading resulting in better quantitation.

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC), introduced more than two decades ago, is nowadays the most powerful and effective technique for analysis of volatile and semi-volatile solutes in complex samples [1–5]. GC × GC is far superior to any conventional one-dimensional gas chromatographic separation. In GC × GC, two columns of different selectivity are coupled in series. The sample is firstly separated on a first dimension (^{1}D) column and very small fractions of the effluent from the ^{1}D column are then continuously focused via a modulator. The focused and narrow fractions are subsequently injected onto a second (^{2}D) column in which a very fast separation is taking place within the selected modulation period (P_M). The most commonly used modulators that are also commercially available are based on cryogenic modulation or on flow modulation [4,5].

A cryogenic modulator traps the volatile compounds from the ^{1}D column effluent in a cold zone during a selected modulation time. The cold zone is then rapidly heated to flush trapped compounds via the carrier gas flow into the ^{2}D column [4–6]. A flow modulator collects and compresses the ^{1}D column effluent within a selected modulation period in a collection channel during sampling and then rapidly flushes the content of the channel using a very high carrier gas flow into the ^{2}D column during the injection period. The filling and flushing cycles of the collection channel are controlled by a fast-acting three-way solenoid valve [6]. In both cases, the effluent eluting from the ^{2}D column is monitored by a proper detector.

Without question, cryogenic modulation provides the highest peak capacity and sensitivity. However, the simplicity of flow modulators and in particular those based on the original device developed by Seeley et al. [7], in combination with their low cost and robustness makes them a very good choice for analysis of a large variety of samples in a routine environment [6]. Moreover, they can be designed and operated in fully flexible configurations [8,9]. The accumulation channel can be adjusted in terms of length and diameter e.g. to avoid its overloading when extended re-injection periods are applied or to obtain a secondary column volumetric gas-flow compatible with MS detection.

The flow modulator based on capillary flow technology (CFT) on a microfluidic plate was commercialized in 2006 by Agilent Technologies [10] and the forward fill/flush (FFF) dynamics described by Seeley et al. [7] are applied. Several papers have been published using FFF flow modulated GC × GC instrumentation for analysis of some complex samples [11–16]. The 2 D contour plots presented in

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these papers illustrate that FFF flow modulated GC × GC is an appropriate method for the analysis of samples where concentrations of constituents do not differ drastically. Highly abundant peaks, however, may cause solid streaks in the ^{2}D column [16–19]. This is a negative attribute of FFF flow modulation, since any tailing significantly reduces resolution in the second dimension and, moreover, is detrimental to quantitation.

A second generation flow modulator was described by Griffith et al. [17] and adopts a reverse fill/flush (RFF) flow procedure of the collection channel which substantially reduces the tailing of peaks in the ^{2}D column [17–19]. RFF flow modulation can be performed on one CFT plate (1-plate RFF) with carved collection channel, or on two CFT plates (2-plate RFF) with adjustable collection channels. The one CFT plate RFF version has recently been produced by Agilent Technologies and will be commercialized soon. The main difference between the FFF and RFF approaches is that the gas flow direction in the collection channel is reversed during the flushing step using an additional channel fill restrictor [17–19].

In this study, the performances of FFF and RFF using the available CFT microfluidic devices with integrated collection channel on 1-plate and of the same volume were evaluated and compared. Performances at modulation times in the interval 1–6 s are compared for C9-C12 *n*-alkanes, selected compounds present in reformate and in *Rosa damascena* Miller essential oil.

2. Experimental

2.1. Samples

Toluene, methylene chloride, *n*-hexane, *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane were obtained from Sigma–Aldrich, Buchs, Switzerland. Two mixtures containing 50 μg (Solution A) and 25 μg (Solution B) of toluene, *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane dissolved in 10 mL of *n*-hexane were used in this study. Sample of reformate produced by a petroleum-refinery reforming process was obtained from Testing Laboratories of Slovnaft Petrochemicals Bratislava, Slovakia. *Rosa damascena* Miller essential oil cultivated in Bulgaria (Rose Otto, LOT FLE 077, QO50815861) was purchased from Florihana, Les Grands Prés, 06460 Caussols, France.

2.2. Capillary columns

The flow modulated GC × GC experiments were performed on two column series.

Series 1 consisted of a DB-5 ms column coated with 5%-phenyl–95%- methylpolysiloxane (30 m × 0.25 mm i.d., 0.25 μm d_f) as primary column and an HP-INNOWax column coated with polyethylene glycol (5 m × 0.25 mm i.d., 0.15 μm d_f) as secondary column. Both columns were purchased from Agilent Technologies, Folsom, CA, USA.

Series 2 was composed of a Rt-βDEXse chiral column coated with 2,3-di-*O*-ethyl-6-*O*-*tert*-butyldimethylsilyl-β–cyclodextrin added into 14% cyanopropylphenyl/86% dimethyl-polysiloxane (30 m × 0.25 mm i.d., 0.25 μm d_f) as primary column and an HP INNOWax column coated with polyethylene glycol (5 m × 0.25 μm i.d., 0.15 μm d_f) as second column. The first column in this set was purchased from Restek, Bellefonte, PA, USA.

2.3. GC × GC-FID instrument equipped with differential flow modulator

Flow modulated GC × GC-FID experiments were performed on an Agilent 7890A GC (Agilent Technologies, Wilmington, DE, USA) equipped with both FFF and RFF flow modulators and flame ionization detector (FID). Details on the instrumental GC × GC-FID set-up used in this study have been described earlier [13].

2.3.1. Forward flow fill/flush (FFF) differential flow modulator operational principle

The schematic of the GC × GC set-up with FFF flow modulation is presented in Fig. 1A and B. The one-plate FFF flow modulator No. G3486A (Agilent Technologies) was used in this study. A planar metal structure contains an internal collection channel etched in the plate that is connected via two metal branches to a three-way micro solenoid valve, which receives a controlled gas supply from an auxiliary electronic pressure control (EPC) module. The primary column (^{1}D) is connected to the split/splitless injector and the secondary column (^{2}D) to the detector. The collection channel is filled periodically with primary column effluent when the solenoid valve is in the load mode (Fig. 1A FFF Loading). During the loading time the effluent from the ^{1}D column is accumulated in the collection channel. The accumulated effluent is then rapidly injected by changing the flow direction from the modulation valve delivering a very high volume flow rate of He (Fig. 1B FFF Injecting) onto the ^{2}D column. The analytes are then quickly separated on the second column and the modulator is ready for the next modulation cycle. The modulation period (sampling plus injecting time) was varied within 1–6 s in this study. Both the FFF and the one plate-RFF modulators have equal volume of channel (19.6 cm length × 0.535 mm i.d.), which corresponds to a volume of 44 μL. Both channels were deactivated in the same way as all Agilent CFT devices.

2.3.2. Reverse flow fill/flush (RFF) differential flow modulator operational principle

The schematic of GC × GC instrument equipped with RFF flow modulator presented in Fig. 1C and 1D has three-ports for connection of the first and second dimension columns and a restrictor capillary. The collection channel in RFF is etched similarly as in the FFF flow modulator into the one-plate itself. The ^{1}D column effluent flow rate enters at the center port of the modulator plate (flow labeled with red color in Fig. 1C RFF Loading) and fill the fixed size collection channel which is connected to the restrictor capillary port (bottom port). This occurs during a sampling time at a first dimension column flow rate. The restrictor capillary enables the carrier gas to pass through the accumulation capillary during the fill cycle and allows a reversal of flow direction during the flush cycle. 5 m × 250 μm, 5 m × 100 μm or 10 m × 100 μm silanized fused silica capillaries (Supelco, Bellefonte, Pa, USA) were used in this study as restrictors connected to a second detector. The effluent flowing out of the capillary restrictor was monitored by FID2, allowing to monitor breakthrough of analytes. After the loading of the collection channel, the three-way solenoid micro valve switches the EPC module flow to the bottom position and the channel is flushed for typically 0.10–0.20 s in the reverse direction of the fill flow labeled in blue color into the ^{2}D column connected to the detector at a suitable volumetric flow (Fig. 1D, RFF Injecting). The band enters into the ^{2}D column where components present in this band are separated during selected modulation time. The modulation cycle is then repeated.

2.3.3. Flow modulated GC × GC working conditions

All experiments were performed in the constant flow mode. Injections executed by an automatic liquid sampler (HP 7673 Autosampler) were 0.1 μL using a 0.5 μL syringe or 1 μL using a 10 μL syringe. The injector was operated in the split mode at 250 °C. FID1 and FID2 were heated at 250 °C. Air, hydrogen and nitrogen (make-up) flows for FIDs were 450, 20 and 40 mL/min, respectively. The sampling rate of both FIDs was 100 Hz.

GC-FID as well as FM GC × GC-FID data were converted to ASCII format through the use of a file export option, and exported