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Analytical Methods

On-line RPLC–GC analysis of terpenes using polydimethylsiloxane as a packing material

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Abstract

The effectiveness of absorbent polymers as packing materials alternative to adsorbents in the interface of the on-line coupling of RPLC to GC via PTV for the analysis of terpenes in orange juice was evaluated. To that aim, a comparative study of an absorbent (polydimethylsiloxane, PDMS), and an adsorbent (Tenax TA) was carried out. As a result, satisfactory repeatability was achieved from both packing materials obtaining relative standard deviation values lower than 10% in most cases. Regarding sensitivity, higher recoveries and far lower detection limits were however attained by using PDMS as the packing material inside the PTV injector. Specifically for PDMS the recoveries varied from 52% to 63% whereas in the case of Tenax TA values ranging from 10% to 22% were obtained. Detection limits varied from 1.5 to 1.9 ppb for PDMS and from 30 to 1900 ppb with Tenax TA. In addition to the sensitivity enhancement, PDMS proved to be more effective in the elimination of the solvent coming from the RPLC-pre-separation. Besides, PDMS is more thermally stable and, as a consequence, it results in lesser degradation products.

Keywords: RPLC–GC; Absorbent; PDMS; Adsorbent; Tenax TA

1. Introduction

The analysis of complex mixtures such as foodstuffs is generally rather difficult and tedious because of the great number of constituents occurring in them. Time-consuming and laborious analytical procedures are normally required prior to the chromatographic analysis to effectively isolate the compounds of interest from the matrix. The analyte isolation is even more complicated when chiral compounds are intended to be determined since each chromatographic peak can split at least into two signals increasing considerably the probability of overlapping.

In this context, the use of multidimensional systems can be especially worthwhile since the fraction of interest can be selectively separated from the rest of components in the first dimension of the system and transferred to the second one, increasing notably the analysis reliability. Specifically, the on-line coupling between high performance liquid chromatography (HPLC) and gas chromatography (GC) has proven to be a powerful technique for the analysis of samples formed by chemically different compounds. LC–GC coupling combines the effectiveness in the pre-separation provided by LC with the high chromatographic efficiency and sensitivity obtained by GC. The employment of LC as a replacement of the conventional sample preparation procedures offers various advantages such as the avoidance of a source of error, the lower overall analysis time and the no need for large organic solvent amounts (Grob, 1991; Grob, 1995; Vreuls, de Jong, Ghijsen, & Brinkman, 1994).

The great challenge of on-line LC–GC is encountered in the development of interfaces that enable two chromatographic techniques using incompatible mobile phases to successfully be coupled. This coupling becomes particularly tricky when working in the reversed phase mode, as the high polarity of the eluents commonly used may result in

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the irreversible damage of the gas chromatographic gas column. A few interfaces allowing the coupling LC–GC can be found in the literature. Most of them are however aimed for the use of normal phase in the pre-separation because of the lesser difficulty that it involves compared to the use of reversed phase (Cortes, Pfeiffer, & Richter, 1985; Goosens, de Jong, de Jong, & Brinkman, 1994; Grob & Li, 1989; Mol et al., 1993; Noroozian et al., 1987; Vreuls, Goudriaan, Brinkman, & de Jong, 1991).

In this respect, we have already proposed an interface for the direct coupling RPLC–GC based on the utilization of a programmed temperature vaporizer (PTV), which acts, in turn, as the injector of the gas chromatograph. As earlier discussed (Blanch, Ruiz del Castillo, & Herraiz, 1998), the performance of this interface is based on the effective elimination of the eluent coming from the RPLC-pre-separation by both the evaporative and non-evaporative modes, while simultaneously the solutes are retained in a packing material placed inside the PTV injector. In former works, adsorbent polymers, mainly Tenax TA, have mostly been utilized as packing materials. Nonetheless, although the use of these materials is in general advisable, they also possess some limitations, such as their thermal degradation and the low recoveries obtained in some cases. For this reason packing materials alternative to adsorbent polymers overcoming these drawbacks are still sought. On the basis of the usefulness of certain absorbents in a number of different sample preparation techniques (Baltussen, Cramers, & Sandra, 2002), we have recently reported for the first time the use of an absorbent polymer, i.e. polydimethylsiloxane, as a packing material inside the PTV injector for both the introduction of large sample volumes in capillary gas chromatography (Flores, Herraiz, Blanch, & Ruiz del Castillo, 2007) and on-line coupling RPLC–GC via PTV (Flores, Ruiz del Castillo, & Herraiz, 2007). As a result of these studies, the viability of this material has been demonstrated by using model solutions. However, the application of polydimethylsiloxane to the analysis of real-life samples by RPLC–GC via PTV and, therefore, the matrix effect on the retention of the compounds of interest has not been studied thus far.

The aim of this work was to develop a method based on the employment of absorbents as packing materials inside the interface of on-line coupling RPLC–GC via PTV to analyze complex matrices. A further purpose was to improve the recoveries obtained to date by using adsorbent materials instead. To that end, a comparative study of an absorbent material, i.e. PDMS, and an adsorbent material, i.e. Tenax TA, to determine certain terpenes in orange juice was accomplished.

2. Materials and methods

2.1. Samples and solutions

A standard solution containing a mixture of myrcene and γ-terpinene, as non-chiral terpenes, and limonene and α-pinene, as chiral terpenes, was employed for identification purposes. This solution was prepared by adding 4 μg of myrcene and γ-terpinene and 2 μg of each enantiomer in the case of limonene and α-pinene to 10 ml of methanol. All the standards were acquired from Fluka (Buchs, Switzerland). Methanol (HPLC grade) was provided by Lab Scan (Dublin, Ireland) and the water used was obtained from a Milli-Q water purification system (Millipore, Milford, MA).

Orange juice was purchased in the commercial market. Prior to its RPLC–GC analysis, it was only centrifuged (10^4 rpm, 10 min at 10 °C) and then directly introduced into the RPLC–GC system.

2.2. RPLC-pre-separation

The pre-separation of the investigated compounds was performed using a liquid chromatograph (Hewlett–Packard model 1050, Wilmington, DE). The HPLC system was composed of a manual injection valve (model 7125, Rheodyne, Cotati, CA) having a 20-μl sample loop, an ultraviolet (UV) detector operated at 205 nm and a 100 mm × 4.6 mm I.D., 5-μm-ODS2 column (Waters, Madrid, Spain) operated at 26 °C. Methanol/water was used as the mobile phase. Different eluent flow rates were set depending on whether one packing material or another was employed. Specifically the flows used were 0.5 ml/min for PDMS and 0.7 ml/min for Tenax TA. The initial eluent composition (methanol/water, 35:65, v/v) was maintained for 10 min and subsequently a linear gradient was applied within 5 min up to 100% methanol which was kept during the transfer of the selected cut from LC into GC. The LC equipment was adequately washed by passing methanol through the equipment between consecutive runs.

2.3. RPLC–GC transfer

The transfer of the terpenes of interest was performed through a 75-cm × 0.25-mm i.d. fused silica tube inserted into the septum of the PTV injector, which acted as the interface of the RPLC–GC system, filled with a packing material as detailed below. The transfer was carried out by switching from the waste position to the transfer position a multiport valve model 7060 (Rheodyne), placed immediately after the UV detector. As a consequence of the different eluent flow rates set according to the packing material used, different volumes were equally transferred. Specifically, the volumes of the transferred fractions were 630 μl for PDMS and 700 μl in the case of Tenax TA. Based on our previous experience (Flores et al., 2007), during transfer the injector was maintained at a fixed temperature (20 °C for PDMS and 5 °C for Tenax TA) to facilitate the retention of the studied compounds. As already reported (Blanch et al., 1998), the solvent elimination was promoted during the transfer step by removing the column end from the injector body while passing a helium flow through the PTV. As later explained in Section 3, the