Journal of Chromatography A, 1216 (2009) 442–448

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Development of a novel high volume band compression injector for the analysis of complex samples like toxaphene pesticide

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ARTICLE INFO

Article history:
Available online 1 October 2008

Keywords:
Large volume injection
HVBC injector
Toxaphene
Sample preparation
"In situ" pretreatment of injected sample
Chromathermography

ABSTRACT

A new type of injector has been developed for gas chromatographic analysis. The injector has high volume and band compression (HVBC) capabilities useful for the analysis of complex samples. The injector consists essentially of a packed liner operated at room temperature while a narrow heated zone is used to axially scan the liner selectively desorbing the compounds of interest. The scanning speed, distance and temperature of the zone are precisely controlled. The liner is connected to an interface which can vent the solvent or any undesirable compounds, and transfer the analytes to an analytical column for separation and quantification. The injector is designed to be compatible with injection volumes from 1 to more than 250 μL. At a low sample volume of 1 μL, the injector has competitive performances compared to those of the "on-column" and "split/splitless" injectors for the fatty acid methyl esters and toxaphene compounds tested. For higher volumes, the system produces a linear response according to the injected volume. In this explorative study, the maximum volume injected seems to be limited by the saturation of the chromatographic system instead of being defined by the design of the injector. The HVBC injector can also be used to conduct "in situ" pretreatment of the sample before its transfer to the analytical column. For instance, a toxaphene sample was successively fractionated, using the HVBC injector, in six sub-fractions characterized by simpler chromatograms than the chromatogram of the original mixture. Finally, the ability of the HVBC injector to "freeze" the separation in time allowing the analyst to complete the analysis at a later time is also discussed.

1. Introduction

In the area of chromatographic sciences, two trends are observed with regards to the volume of sample that is introduced into the chromatographic system. The development of packed and open capillary columns in liquid chromatography requires more and more that small volumes of sample be injected. With these capillary columns, the injection volume must be small (nanoliters to picoliters) in order to maintain the efficiency of the chromatographic system [1–4]. However, in gas chromatography (GC), the need to significantly increase sensitivity in trace analysis requires that larger and larger volumes be introduced. Many research efforts are directed at the development of injection techniques that can satisfy the present needs.

Large volume injection (LVI) into a capillary or megabore GC column shows numerous advantages [5–10]. The introduction of large volume of sample allows an obvious gain in detection limit, an improvement in relative standard deviation (retention time or area) for trace components, a reduction in the time-consuming pretreatment-concentration of the sample and facilitates the coupling between liquid chromatography and gas chromatography. However, several drawbacks are also associated with LVI [5,7,10–13]. These are related to the presence of high amounts of solvent in liquid or gas phases, to the polarity of the solvent that affects its volatility, to the possible contamination of the pneumatic components and other cold spot area in the system, to the discrimination of compounds with different volatilities, and to the decomposition of some labile compounds due to catalytic effects of packing material present in some LVI systems.

Introduction of large volumes of liquid into the GC column is carried out either by the on-column injection–retention gap technique [14] or by the vaporizing chamber techniques [7,12,15]. The on-column techniques show important limitations for samples containing non-volatile constituents that cause contamination and affect the long term stability of the system [12–15]. The vaporizing chamber techniques overpass the previous limitations by the reten-

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doi:10.1016/j.chroma.2008.09.083

tion of the non-volatile matrix compounds and easier vaporization of the less volatile solvent.

The most used LVI techniques show conceptual differences in their design. Grob and Biedermann define on-column injection/transfer through the vaporization of the liquid sample from capillary tubing at oven temperature [7]. The introduction of the liquid sample is done at temperatures below the pressure-corrected solvent boiling point. By contrast, in vaporizing techniques, the introduction of the sample involves a temperature-controlled device maintained at temperatures higher than that of the GC oven [7]. The temperature profiles of the vaporizing chambers may involve isothermal or temperature programmed modes of operation [7,15]. To obtain the optimal performance from LVI injectors numerous optimizations must be made [16–18].

Several instrumental devices and operational modes have been proposed for LVI systems. Modified on-column (OC) injectors have been extensively tested in coupling liquid chromatography to gas chromatography (LC–GC). The modification of the OC injector involves the addition of an uncoated or coated capillary tube of various lengths and diameters between the injector and the column [10,14,19,20]. The system can be used in the early vapor exit mode [21] or with a partially concurrent evaporation mode [22]. Split/splitless injectors can be used to introduce hundreds of microliters of a liquid sample in capillary GC [23,24]. The injector is used with a packed liner and the overflow technique allows the injection of very polar solvents such as water [24].

Temperature programmable (PTV) injectors are another alternative for LVI [25]. PTV injectors have been used under various modes of operation [11]. In the split mode of operation [25,26], the sample is injected in a packed liner. The split exit of the injector is open and the temperature of the injector is below the boiling point of the solvent. The PTV injector can also be used in the splitless mode. In this instance, the large volume of sample is introduced at temperatures below or close to the pressure-corrected boiling point of the solvent. In this injection method, the analyte and the solvent are vented via the analytical column. A third mode of PTV used for LVI is the vapor overflow technique. The sample is rapidly injected into a packed liner maintained at high temperature. The split exit is closed but the septum purge outlet is open. A fourth mode of the PTV injector is called adsorption/thermal desorption mode [27]. This technique has been used with aqueous samples. It involves the use of a packed liner filled with adsorbent material that retains the analyte of interest. The dissolved sample is feed through the system with a high flow of carrier gas. After drying, the analyte is thermally desorbed and transferred to the analytical column. A latter mode of PTV injection for LVI is the AT-column injection technique [9]. AT-column injection is based on solvent evaporation in an empty liner with solvent vapor overflow via the split line.

On-column injection–retention gap techniques or the vaporizing chamber techniques make easier LVI injections into GC systems. However, alternative approach [28] to these LVI injectors could be developed from Russian works done in the early fifties. Zhukhovitskii and co-workers have explored a variant of the chromatographic technique called chromathermography [29]. In this technique, a moving thermal gradient (a mobile oven) migrates along a straight chromatographic column at a constant rate. This movement and the distribution of temperature in the oven, induce a heat-field gradient in space and in time. An appropriate selection of the displacement speed and temperature of the heating device allows for eliminating the evaporation of large solvent volumes. Moreover, an effect of the heat gradient is to reduce the broadening of the initial chromatographic band [30,31].

The present work describes a new versatile injector with high volume and band compression (HVBC) capabilities. This injector consists of a packed liner operated at room temperature for the injection (Fig. 1). Following injection, a narrow thermal assembly, that we shall name MOVEN for MObile OVEN in this study, is scanned alongside the liner at different controlled temperatures. This heating procedure allows the venting of the solvent and helps to vaporize and transport the analytes of interest to be transferred to the analytical column for subsequent analysis. The injector that can be operated in several modes allows LVI of hundreds of microliters, sample pretreatment and multidimensional gas chromatographic discrimination of the components of complex samples amenable to GC analysis.

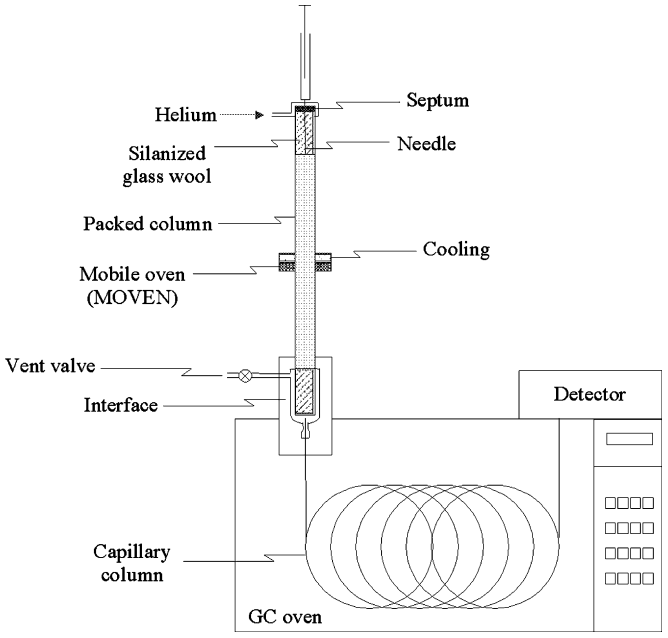

Fig. 1. Simplified schematic diagram of the high volume band compression injector.

2. Materials and methods

2.1. Instrumentation

A model Fisons 8160 gas chromatograph equipped with a flame ionization detector (FID) and interfaced to a CHROM CARD data station (Fisons) was used in the study. Sample introduction was done either by means of an OC injector, a split–splitless (SPL) injector or using a first generation prototype of the HVBC. All GC separations were performed on a methyl silicone megabore GC column (SPB-1, 0.53 mm i.d. × 30 m; 0.5 μm film thickness). The packed liner of the HVBC injector was filled with Supelcoport support coated with 3% methyl silicone phase SP-2100 on 80–100 mesh particles (Supelco). Other packing support could however be used.

Fig. 1 shows a simplified drawing of the prototype injector used in this study [28]. It has an entry port, operated at room temperature, where the syringe needle penetrates the septum. The port is connected to the vector gas inlet (helium) and to a liner or a small column (1 mm i.d.) packed with a stationary phase (20 cm bed) restrained between glass wool end plugs. A small heating device, the MOVEN, is mounted on a tread and move up or down along the packed column to allow the vaporization of the compounds introduced and the transfer of the analytes to the interface. The displacement (distance and speed) of the MOVEN along the column is precisely controlled by a step motor and a motion controller. The heating zone used consists of a handicraft-heating element (Watlow H01901987A, Zesta Engineering Ltd., Ville St-Laurent, Canada)