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Back-flushing and heart cut capillary gas chromatography using planar microfluidic Deans' switching for the separation of benzene and alkylbenzenes in industrial samples

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ABSTRACT

Planar microfluidic devices coupled with modern electronic pressure control have allowed gas chromatography (GC) practitioners to easily manipulate chromatographic systems to achieve heart cut and back-flushing configurations. These planar microfluidic devices have enhanced the connectivity between different components of GC instrumentation and have improved the inertness and minimised system dead volumes compared to classical chromatographic unions and valves. In the present contribution the setup and configuration of two multidimensional GC (MDGC) platforms is described for achieving the separation and quantification of trace level target C_6–C_8 alkylbenzenes in styrene monomer and Isoparaffin™ solvents, using flame ionisation detection (FID). The performance of these MDGC platforms indicated excellent retention time (0.2% relative standard deviation, RSD) and peak area repeatability (1% RSD) for all analytes of interest. The limit of detection (LOD) was 0.8 mg kg^{-1} for benzene in styrene monomer, and 2.4–2.8 mg kg^{-1} for C_6–C_8 alkylbenzenes such as benzene, toluene, ethylbenzene and xylene in Isoparaffin™ solvent.

1. Introduction

Back-flushing and heart cutting are important approaches in capillary gas chromatography (GC) achieved by manipulating the net direction of carrier gas flow at the confluence of two or more capillary columns. Contemporary back-flushing and heart cutting approaches build on the work Deans described 50 years ago [1,2]. These once seemingly complicated approaches are readily accessible today using precise electronic pressure control (EPC) [3] and advanced capillary column connectivity using planar microfluidic devices [4–10]. Planar microfluidic devices feature low connection void volumes that enhance carrier gas flow and pressure equilibration response times compared to classical setups. The thermal mass of each device is kept low to reduce the potential for thermal hysteresis during temperature programming, and these devices are chemically deactivated to ensure inert surface chemistry, which prevents chemical activity during GC analysis.

Planar microfluidic devices are particularly useful when coupled with modern electronic pressure control, which is able to rapidly achieve and maintain accurate and precise pressure settings. Instrument control software can determine the pressures required to deliver user defined carrier gas flow rates after compartment temperatures, column dimensions, and connectivity between injector modules, microfluidic devices, and detector modules has been entered. Electronic pressure control and event control have enabled fast and simple implementation of column back-flushing, heart cutting or comprehensive two-dimensional GC configurations, minimising the need for laborious iterative system optimisation [9,11].

Multidimensional GC (MDGC) is increasingly required to address the complexity of samples to permit accurate compound identification and quantification. By utilising the stationary phase selectivity of two columns it is possible to reduce the probability of false-positive or false-negative results arising from peak co-elutions which enhances the confidence in solute identification based on retention time [12,13]. The present investigation uses planar microfluidic Deans' switching to achieve MDGC for the separation and quantification of trace levels of benzene in styrene monomer, and C_6–C_8 alkylbenzenes in Isoparaffin™ solvent. It is important to monitor styrene and Isoparaffin™ solvent for alkylbenzene content to ensure that these compounds are not incorporated into final products, since these compounds have

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health and hygiene implications that affects the quality of household, industrial, and automotive products [14–16].

Styrene monomer is an important industrial chemical that is for the production of synthetic rubber. Styrene is synthesised industrially from benzene, and residual benzene can be found in crude styrene, intermediate process products, or as an undesirable impurity in purified styrene. Analysis of benzene in styrene is normally performed using long, polar stationary phases, such polyethylene glycol (PEG), as specified by ASTM Method D5135-14 [17]. However these methods are not ideal for process monitoring and trace level quantification due to the high probability of false positive measurements arising from incomplete separation, and poor long-term method stability. The upper temperature limit (250 °C) for PEG phases limits the ability to elute high molecular weight compounds that are present in styrene and petroleum derived samples.

Isoparaffin™ solvents are light petroleum products that are derived from petroleum feedstock. They are industrially useful due to their high chemical stabilities, well-defined boiling points, low surface tensions, low freezing points and low electrical conductivities. They are used extensively in industrial applications during fuel refinery, process chemistry and are further used as cleaning agents, functional fluids, and fuels. The analysis of benzene and C_6–C_8 alkylbenzenes in Isoparaffin™ solvent is complicated by numerous peak co-elutions that are typical of one-dimensional separations. For this reason GC coupled with mass spectrometry (GC–MS) operated in the selective ion monitoring mode (SIM) is often utilised for the analysis of benzene and the alkylbenzenes [18]. GC–MS with SIM alleviates the need for complete temporal separation prior to detection, and reduces the possibility of false positive results. Unfortunately GC–MS systems have a high cost of ownership, which precludes them from being implemented universally; therefore other methods should be explored to complement GC–MS for routine analysis. An alternative MDGC method for the analysis of aromatic compounds in finished gasoline using FID is the ASTM D5580 method which uses a polar 1,2,3-tris (cyanoethoxy)propane (TCEP) column to selectivity trap aromatic compounds, which are then eluted to a polydimethylsiloxane (PDMS) column for additional separation. While this method is effective for the separation of a range of aromatic compounds, the temperature stability of the TCEP phase is limited (145 °C) and prone to contamination by high molecular weight compounds making this method not ideal for routine analysis.

MDGC with a combination of non-polar PDMS columns and highly polar PEG or ionic sorbent PLOT columns can be effective at separating benzene and C_6–C_8 alkylbenzenes in styrene monomer and petroleum derived samples which lessens the need for expensive MS detection [19–22]. This approach enabled the quantitation of trace levels of C_6–C_8 alkylbenzenes compounds in styrene monomer and Isoparaffin™ solvent while using low cost flame ionisation detection. The approach is fast and robust, with potential for deployment in field quality control laboratories where time, space and resources are limited.

2. Experimental

2.1. Instrumentation

2.1.1. Measurement of benzene in styrene monomer

An Agilent 7890A gas chromatograph (Agilent Technologies, Wilmington, DE, USA) equipped with a Spilt/Splitless injector, Agilent 7683B series Automated Liquid Sampler, two FID modules, and an auxiliary Pressure Control Module (PCM) was used for benzene analysis in styrene monomer.

A highly inert, non-polar VF-1ms column coated with 100% dimethylpolysiloxane phase, 30 m × 250 μm ID × 1 μm d_f (Agilent, #CP8913), was connected between the injector and was connected to the central port of a planar microfluidic Deans' switch (Agilent, #G2855A). A polar VF-WAXms column coated with PEG phase, 30 m × 250 μm ID × 1 μm d_f (Agilent, #CP9206), was connected between the Deans' switch and FID 1. An 80 cm long, 100 μm ID piece of deactivated fused silica capillary (Agilent, #160-2635-5) was used as a transfer line and flow restrictor between the Deans' switch and FID 2.

The inlet was set to a temperature of 250 °C, and operated with a split ratio of 10:1. An Ultra Inert Liner (Agilent, #5190-2295) and Molded Thermogreen LB-2 septum (Supelco, Bellefonte, PA, USA) were incorporated into the injector and the sample injection volume was 1 μL for all samples. The carrier gas was helium (Air Liquide, Edmonton, Canada) and the first-dimension column was operated at a flow rate of 1.6 mL min^{-1} with an initial head pressure of 34.55 PSI for 8 min, after which the column was back-flushed at −2 mL min^{-1} for 7 min. The second-dimension column was operated at a constant flow of 3 mL min^{-1} with an initial pressure of 25.91 PSI for 8 min, after which the flow rate was increased to 5 mL min^{-1} for 7 min during the back-flush cycle. The oven was temperature programmed from an initial temperature of 40 °C, which was held for 1 min, and then ramped at 15 °C min^{-1} to 250 °C. The total analysis time was 15 min. A three-way switching valve (Agilent, #G2399-60600) was installed in-line with the PCM and Deans' switch enabling redirection of first-dimension column effluent to either the transfer line or the second-dimension column. The valve was actuated between 6.3 and 6.6 min to transfer benzene to the second-dimension column. The FID 1 and 2 were each held at a temperature of 250 °C and operated at a data sampling rate of 20 Hz. Data were collected and processed with ChemStation software (Agilent) version B.04.03SP1.

2.1.2. Measurement of C_6–C_8 alkylbenzenes in Isoparaffin™ solvents

An Agilent 6890 gas chromatograph (Agilent Technologies) equipped with a Spilt/Splitless inlet, Agilent 7683B series Automated Liquid Sampler, two FID modules and an auxiliary PCM was used for analysis of C_6–C_8 alkylbenzenes in Isoparaffin™ solvents.

A low polarity CP-Sil8 CB Low Bleed/MS column coated with 5 phenyl/95% dimethylpolysiloxane polymer, 30 m × 250 μm ID × 1 μm d_f (Agilent, #CP5862), was used as the first-dimension separation column which was connected between the injector and a Deans' switch (Agilent PN# G2855A). A high-polarity CP-Lowox column containing an ionic sorbent based stationary phase, 9 m × 530 μm ID × 10 μm d_f (Agilent, #CP8587), was connected between the Deans' switch and FID 1. A 63 cm × 250 μm ID deactivated fused silica capillary (Agilent, #160-2255-5) was used as a transfer line between the Deans' switch and FID 2. A three-way switching valve (Agilent, #G2399-60600) was installed in-line with the PCM and Deans' switch enabling redirection of first-dimension column effluent to either the transfer line or the second-dimension column.

The inlet incorporated a Molded Thermogreen LB-2 septum (Bellefonte, #28678-U, PA, USA) was used temperature was 250 °C, and a split ratio of 1:20, with a 1 μL injection volume into an Ultra Inert Liner (Agilent, #5190-2295). The carrier gas was helium (Air Liquide, Edmonton, Canada), which was held at a flow rate of 2 mL min^{-1}. The PCM was operated in the constant pressure mode at 4.6 PSI for flow switching. The oven was temperature programmed from an initial temperature of 60 °C, which was held for 0.2 min, and then ramped at 15 °C min^{-1} to 165 °C, and then ramped at a rate of 30 °C min^{-1} to 260 °C with a final hold time of 5 min. The total analysis time was 15 min. Four retention time windows were transferred from the first-dimension column to the second-dimension column by activating the three-way switching valve: benzene 2.90–3.05 min, toluene 3.95–4.10 min,