



Multidimensional gas chromatography for the characterization of permanent gases and light hydrocarbons in catalytic cracking process

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ABSTRACT

An integrated gas chromatographic system has been successfully developed and implemented for the measurement of oxygen, nitrogen, carbon monoxide, carbon dioxide and light hydrocarbons in one single analysis. These analytes are frequently encountered in critical industrial petrochemical and chemical processes like catalytic cracking of naphtha or diesel fuel to lighter components used in gasoline. The system employs a practical, effective configuration consisting of two three-port planar microfluidic devices in series with each other, having built-in fluidic gates, and a mid-point pressure source. The use of planar microfluidic devices offers intangible advantages like in-oven switching with no mechanical moving parts, an inert sample flow path, and a leak-free operation even with multiple thermal cycles. In this way, necessary features such as selectivity enhancement, column isolation, column back-flushing, and improved system cleanliness were realized. Porous layer open tubular capillary columns were employed for the separation of hydrocarbons followed by flame ionization detection. After separation has occurred, carbon monoxide and carbon dioxide were converted to methane with the use of a nickel-based methanizer for detection with flame ionization. Flow modulated thermal conductivity detection was employed to measure oxygen and nitrogen. Separation of all the target analytes was achieved in one single analysis of less than 12 min. Reproducibility of retention times for all compounds were found to be less than 0.1% ($n=20$). Reproducibility of area counts at two levels, namely 100 ppm_v and 1000 ppm_v over a period of two days were found to be less than 5.5% ($n=20$). Oxygen and nitrogen were found to be linear over a range from 20 ppm_v to 10,000 ppm_v with correlation coefficients of at least 0.998 and detection limits of less than 10 ppm_v. Hydrocarbons of interest were found to be linear over a range from 200 ppb_v to 1000 ppm_v with correlation coefficients of greater than 0.999 and detection limits of less than 100 ppb_v.

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1. Introduction

The characterization of oxygen, nitrogen, carbon monoxide, carbon dioxide (permanent gases) and light hydrocarbons is an important analysis for petrochemical and chemical industries [1–5]. These compounds are often encountered in various critical chemical processes like catalytic cracking for example [6–8]. Gas chromatography is a technique of choice due to the high degree of volatility of the compounds involved. Unfortunately, without the employment of cryogenic chromatography, no single chromatographic stationary phase is capable of adequately separating all of these analytes [9]. For instance, on a porous polymer based

stationary phase like divinyl benzene, oxygen, nitrogen, and carbon monoxide are perfectly co-eluted. Hydrogen, oxygen, nitrogen, methane, and carbon monoxide can be well separated using a molecular sieve stationary phase; however carbon dioxide and heavier hydrocarbons are irreversibly adsorbed. The presence of water in the sample as vapor can also deactivate the stationary phase. Carbon molecular sieve or carbon black has been used to separate these analytes, but inadequate separation was encountered for oxygen and nitrogen especially when the concentrations of the two compounds are at the percent level [10–12]. Further, there is evidence of elevated reactivity of the adsorbent toward double and triple bond hydrocarbons like propylene, methyl acetylene, and 1,3-propadiene.

To compensate for the lack of an appropriate stationary phase for the characterization of permanent gases and light hydrocarbons, a common chromatographic practice involves the use of a series of multi-port switching valves to selectively transfer the

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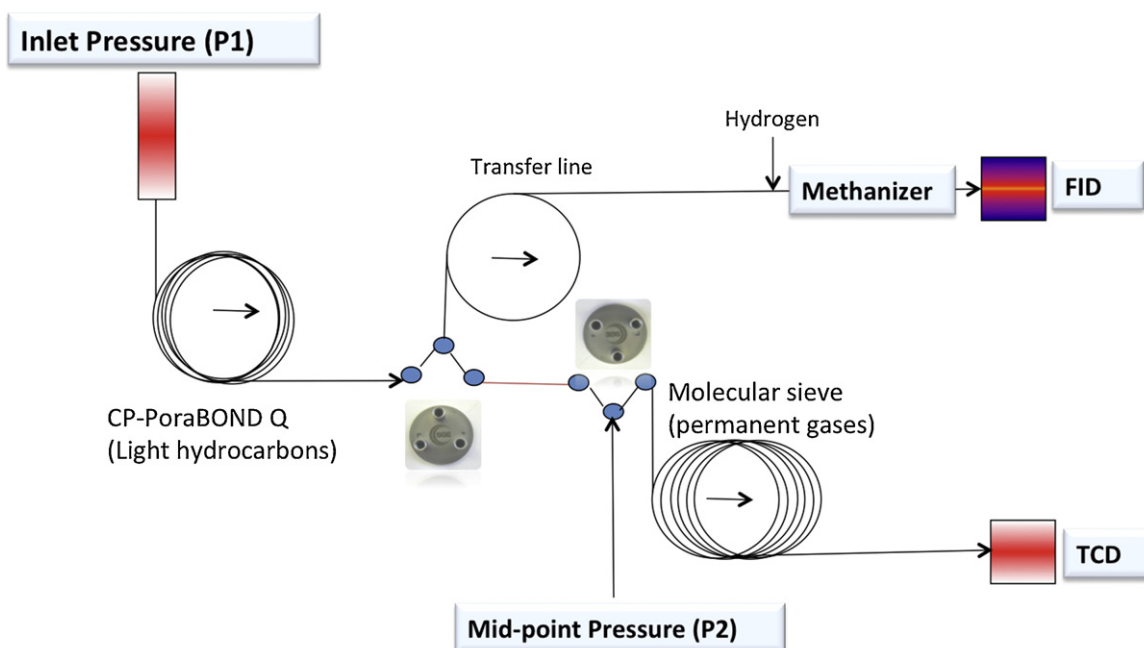


Fig. 1. Analytical system configuration with two SilFlow three-port planar microfluidic devices for permanent gases and light hydrocarbons analysis.

effluent of one column to another, or bypass certain columns at various stages in the analysis to prevent the columns from being contaminated by the analytes in the matrix as in the case of carbon dioxide or water on a zeolite stationary phase like molecular sieve. Under such a scheme, it is common for a system to have three to five multi-port rotary or slider valves and a number of packed or micropacked columns or porous layer open tubular columns involved to achieve the separation required [13–15]. While this approach performs adequately, there are some important constraints, like the requirement of a dedicated gas chromatograph as a custom-built analyzer. The use of multi-port switching valves can lead to degraded chromatography due to excessive void volume encountered from connections and tubing, the lack of inertness along the sample flow path, and port-to-port cross leaks from valve rotor wear. The requirement for an additional external oven to house the valve assemblies, and the need for a highly accurate pneumatic system to minimize valve-timing shifts over the course of normal use are further complicating factors. These constraints can substantially add to the overall cost of ownership and have a negative impact on reliability and availability of the instrument for analysis.

In the present article, we introduce a practical and effective integrated gas chromatographic system for the measurement of permanent gases and light hydrocarbons in one single analysis with the capability of addressing the above mentioned shortcomings. The system employs an arrangement involving the use of two three-port planar microfluidic devices in series of each other with built-in microfluidic gates and a mid-point pressure source to perform critical in-oven chromatographic tasks like column isolation and backflushing.

2. Experimental

An Agilent 6890N gas chromatograph (Agilent Technologies, Wilmington, Delaware, USA) was used for all analyses. The chromatograph was equipped with one split/splitless inlet (operated at 150 °C), one flame ionization detector (operated at 250 °C), and

one flow modulated thermal conductivity detector (operated at 150 °C), a nickel based methanizer (operated at 375 °C) to convert carbon monoxide and carbon dioxide to methane, and a three-channel auxiliary pressure module. Two SilFlow three-port planar microfluidic devices, part number 123722 (SGE Analytical Science, Ringwood, Australia) were incorporated into this gas chromatograph as illustrated in Fig. 1 for the column isolation, flow diversion, and back-flushing in the analysis of permanent gases and light hydrocarbons. An Agilent universal, low pressure drop Ultra Inert liner part number 5190-3165 was used throughout. Injection volume was 1.0 mL and a split ratio of 2:1 was employed. Helium carrier gas was supplied to the column inlet using programmed pressure mode (30 psig (hold 8 min) – 2 psig (hold 4.5 min) @ 99 psig/min). The column midpoint pressure was also provided in programmed pressure mode (7.5 psig (hold 3.5 min) – 10 psig (hold 4.5 min) @ 99 psig/min then – 20 psig (hold 4 min) @ 99 psig/min). Detector gases were FID: hydrogen 45 mL/min, air 450 mL/min, nitrogen 25 mL/min; TCD reference flow 10 mL/min, make-up flow 3.5 mL/min.

Columns used involved a 50 m × 0.32 mm id × 5 μm CP-PoraBOND Q and a 15 m × 0.32 mm id × 25 μm Molecular Sieve 5A. A 5 m × 0.25 mm id, deactivated, uncoated fused silica tubing was used to connect the first three-port fluidic device to the methanizer while a 60 cm × 0.25 mm id deactivated, and uncoated fused silica tubing was used to connect the two three-port fluidic devices as described in Fig. 1.

A Hewlett-Packard desktop computer equipped with a Pentium Core-Duo 2.5 MHz processor, 3 gigabytes of RAM, and 500 Gb hard drive with Windows XP Professional SVP-3 as operating system was used to host the software and process the data obtained. Data was collected with ChemStation software B.04.03SP1.

Carrier and utility gases such as helium, nitrogen, hydrogen, and air used for system performance studies were acquired from Air Liquide (Edmonton, Canada). Primary gas standards were purchased from BOC (Edmonton, Canada). Secondary standards over a range from 100 ppb_v to 1000 ppm_v for hydrocarbons, and from 5 ppm_v to 1% for oxygen and nitrogen were prepared from the primary standards by serial dilution. Samples for analysis were collected

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