

Thermal-managed sputtered micro machined gas chromatography columns for oilfield applications

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ABSTRACT

Gas chromatography is a technique enabling the separation, identification and quantification of the different compounds in a gaseous mixture, and, thus, a first-rate technique for oilfield gas analysis. However, it is a bulky and expensive method which requires a long analysis time and a consequent power. A fully miniaturized gas chromatograph, including collective fabrication, is a solution for this issue. Yet, the fabrication of the micro column (the fundamental component enabling the separation) is hardly compatible with miniaturization and mass production. Thanks to the rerouting of the sputtering technique, a new micro columns fabrication process was developed, matching the criteria of industry-readiness. The separation performances of thermal-managed silica or graphite sputtered micro columns were investigated: a separation of light alkanes (C1 – C5) was completed in 9 s, and heavier alkanes (until C9), aromatic and cyclic hydrocarbons were also successfully separated.

Keywords: gas chromatography, sputtering, silica, graphite, thermal management.

1 INTRODUCTION

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which passes a gas stream (carrier gas). Upstream from the column, an injection system allows the introduction of the sample to analyze into the carrier gas stream. As the carrier gas sweeps the analyte molecules through the column, this motion is inhibited by the adsorption of the analyte molecules either onto the column walls or onto packing materials in the column. The rate at which the molecules progress along the column depends on the intensity of interaction with the stationary phase, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyte mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column. Thus, the different compounds initially present in the mixture can be identified and quantified (signal integration). In chromatography, column heating is a common method to weaken the intensity of the interactions with the stationary phase, and, thus, to shorten elution times in order to obtain the fastest analysis possible.

In the late 70s, Terry & al proposed a new method to miniaturize gas chromatography technique using silicon based micro fabricated separation systems [1]. Performances, in terms of separation speed and thermal management, are expected to be improved with miniaturization, owing to the reduction of the length and of the thermal capacity of the column. Such a fully miniaturized micro gas chromatograph would enable in-situ, cycled and real time analysis for various applications requiring continuous monitoring, low power consumption, and safety (oilfield, environment,...).

The main challenge in miniaturized gas chromatography consists in the reproducible and collective fabrication of micro columns. While it is rather easy to make serpentine channels of dimensions compatible with GC requirements into a silicon chip, the critical step of coating the inner walls of the column with the stationary phase is hardly compatible with miniaturization and mass production.

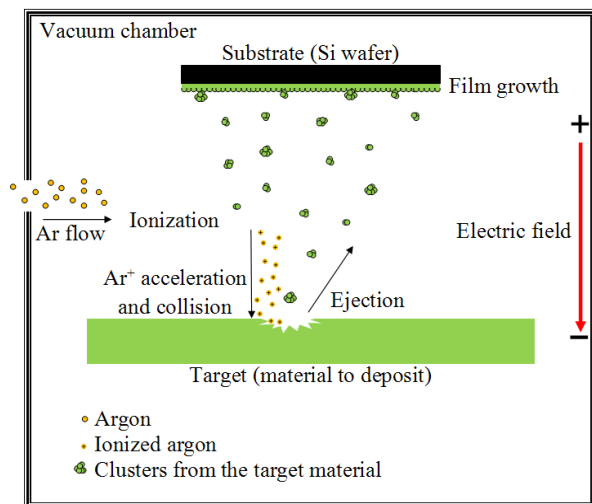


Fig. 1 : Scheme of the sputtering process. Collisions of the gaseous ions with the target induce ejection of target material clusters which are then deposited on the surface of the silicon wafer.

In a previous publication [2], we presented how the rerouting of the sputtering technique (fig.1) to coat columns with a thin film of silica was able to answer this issue (fig. 2, patent pending). We presented promising isothermal separations of light alkanes on silica sputtered micro columns (fig. 3, 5a). In order to go beyond the limits of isothermal separations in terms of analysis time, it is necessary to be able to provide controlled heating to the separation column [3].

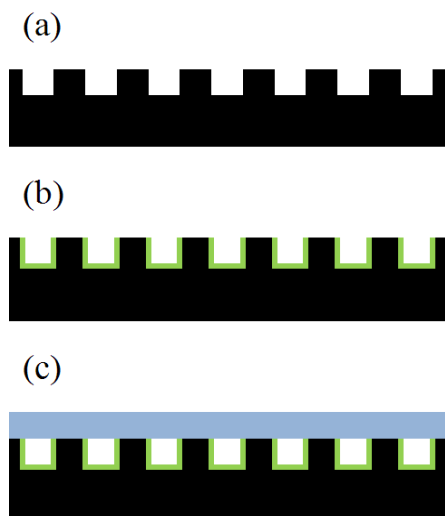


Fig. 2 : Cross-sectional view of the silicon substrate (wafer) showing the main fabrication steps of the column's micro chip : (a) etching by DRIE, (b) sputtering, (c) silicon-pyrex anodic bonding.

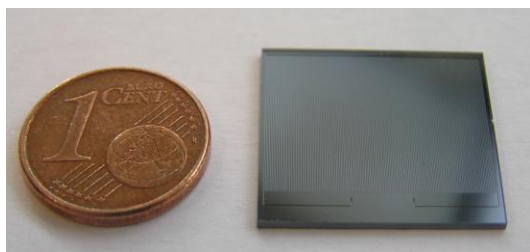


Fig. 3 : picture of the column's micro chip.

2 MATERIALS AND METHODS

2.1 Column fabrication

2 m x 100 μm x 100 μm columns have been fabricated on a double-sided polished silicon wafer (9 columns per wafer). To enable thermal management of the columns micro chips, two platinum resistive filaments per chip (one small resistance filament for dissipative heating, one high resistance filament for temperature reading) were deposited by sputtering on the back side of the wafer. Channels were etched to a chosen depth by deep reactive-ion etching (DRIE) using an anisotropic standard Bosch process. The

wafers were sputtered with a thin layer of silica or graphite using the appropriate target (fig. 1). The silicon wafer was anodically bonded to a Pyrex substrate (fig. 2). In a similar manner, inlet and outlet back access holes were etched on the back side of the wafer. After fabrication the wafer was diced to obtain ~2 cm x 2 cm micro columns (fig. 3). Two ~5-cm-long fused silica capillaries were plugged and glued on the inlet and outlet vertical holes on the back of the micro column silicon chip.

2.2 Analytical GC device

A conventional GC was used to evaluate the micro columns. Experiments were carried out on a Varian 3800. The chromatograph was equipped with a 1079 split-splitless injector and a flame ionization detection (FID) system. Helium was used as carrier gas.

2.3 Gas samples

Gas samples were prepared by filling a sampling bag with a 25 % methane, 25 % ethane, 25 % propane and 25 % n-butane mixture by Air Liquide. For species liquid at ambient temperature, gaseous samples consisted in vapors extracted from the headspace of the flasks. A glass syringe was used to sample the gas mixture and inject it into the GC injector.

2.4 Data acquisition

A commercial acquisition board was used to interface the Varian GC with a computer. Galaxie 1.9 was used as acquisition software. For experiments involving thermal management, a National Instruments Data Acquisition PAD USB 6008 OEM was used and ran with Labview.

2.5 Thermal block building

The reading filament was connected to the NI DAQ PAD board, through a voltage divider bridge and a small amplification circuit. The heating filament was connected to a 30 V power supply ; the column's chip was placed on a Peltier device (3.3 V power supply), itself placed on a dissipative radiator equipped with mini-fans (5 V), for the fast cooling of the chip. Solid-state relays (electronically controlled switches) were placed between the power supplies and the components, to enable real-time automate feedback control of the temperature of the chip by Pulse Width Modulation.

2.6 Column temperature calibration

The output analogical voltage recorded by the NI DAQ PAD was compared to the actual temperature of the chip measured with a Omega Datalogger thermometer, for temperatures between 10°C and 190°C, and the resulting calibration curve was found linear ($R^2=0.99$).

3 RESULTS

3.1 Thermal management

Heating rates, linear in the range 13°C to 220°C, and up to 20°C/s, were achieved (fig. 4). Above this temperature, the chip could be damaged. Power consumption to bring the chip's temperature from 13°C to 220°C was 13 W (at 5°C/s), 32 W (at 10°C/s), and 49 W (20°C/s). As much as fast heating of the chip, fast cooling was also a crucial requirement for cyclic applications. The thermal block (Peltier device, radiator and fans) allowed very fast cooling of the chip from 200°C to below ambient (30°C) in less than 60 s, with an average power consumption of 10 W.

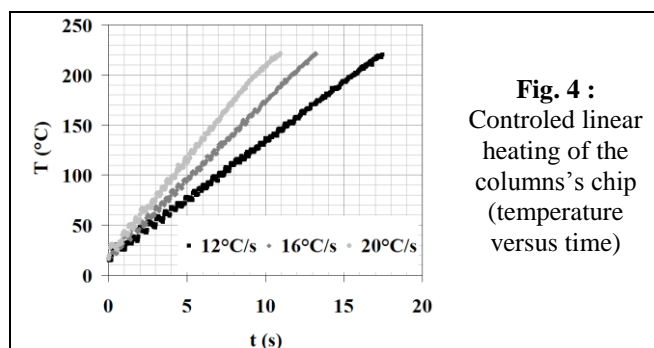


Fig. 4 :
Controlled linear heating of the columns's chip (temperature versus time)

3.2 Separations on silica-sputtered columns

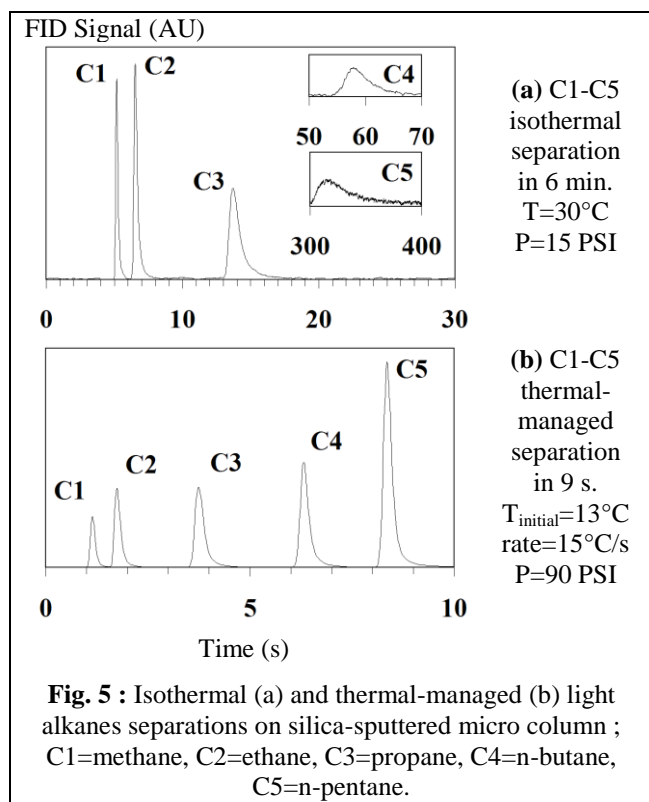


Fig. 5 : Isothermal (a) and thermal-managed (b) light alkanes separations on silica-sputtered micro column ; C1=methane, C2=ethane, C3=propane, C4=n-butane, C5=n-pentane.

As shown in figure 5, thermal management of the chip shortens considerably analysis time. Whereas isothermal separation of light alkanes (from methane to pentane) took 6 minutes, thermal-managed separation of the same light alkanes took only 9 seconds, using a heating rate of 15°C/s. A preliminary cooling ($T_{\text{initial}}=13^{\circ}\text{C}$, instead of $T_{\text{amb}}=30^{\circ}\text{C}$) allowed to use a higher pressure (90 PSI instead of 15 PSI) without losing the quality of the methane – ethane resolution, and, thus, to obtain an even shorter separation.

As shown in figure 6, thermal-managed silica-sputtered micro columns were also able to separate various oilfield-related compounds, such as heavier linear alkanes (from C6 to C9) in 15 seconds (fig. 6a), cycloalkanes (cyclopentane and cyclohexane) in 10 seconds (fig. 6b), and aromatic compounds (benzene and toluene) in 26 seconds (fig. 6c)

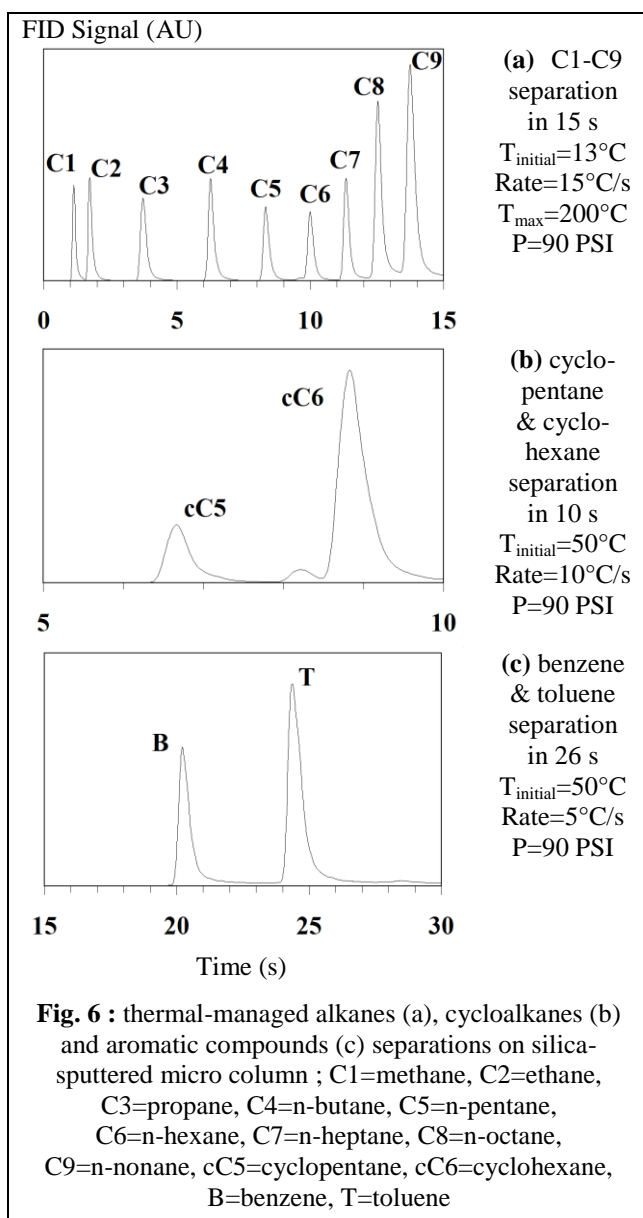


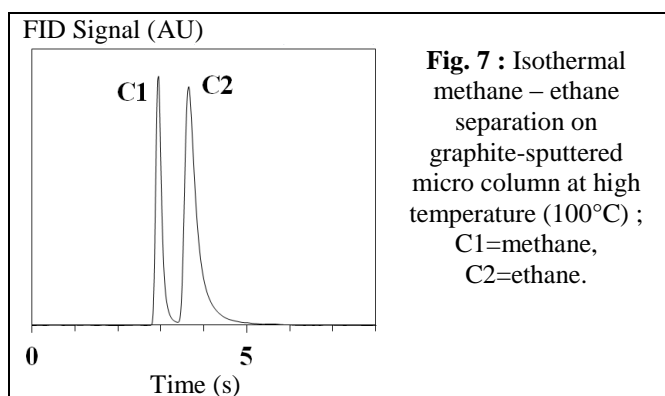
Fig. 6 : thermal-managed alkanes (a), cycloalkanes (b) and aromatic compounds (c) separations on silica-sputtered micro column ; C1=methane, C2=ethane, C3=propane, C4=n-butane, C5=n-pentane, C6=n-hexane, C7=n-heptane, C8=n-octane, C9=n-nonane, cC5=cyclopentane, cC6=cyclohexane, B=benzene, T=toluene

3.3 Graphite-sputtered columns

Previous thermal-managed separations on silica-sputtered micro columns showed a fair methane – ethane separation but only thanks to the low ambient temperature (30°C) and / or to a preliminary cooling (13°C). As oilfield monitoring is a potential application for such columns, the eventuality of high ambient temperatures (between 50°C and 150°C) must be considered.

In this case, silica as a stationary phase might be not retentive enough to provide a fully resolute methane – ethane separation, even with a preliminary cooling. As graphite is known to be a highly retentive stationary phase for alkanes [4], graphite-sputtered micro columns were fabricated and tested.

As shown in figure 7, graphite-sputtered micro columns were able to separate methane and ethane with a good resolution at a high temperature (100°C).



4 CONCLUSION

We have developed and fabricated micro gas chromatography columns through a collective, reproducible and industry-ready fabrication process, including the steps of sputtering deposition of the stationary phase and of the metallic filaments for resistive heating. These columns were coupled with a thermal management system allowing fast linear heating of the column's chip up to 20°C/s, and fast cooling (from 220°C to 30°C in less than 1 minute). Thermal-managed silica-sputtered micro-machined columns enabled fast separation of light alkanes (C1-C5) in 9 seconds. Separation of heavier linear alkanes (C6-C9) was carried out in 15 seconds, cycloalkanes (cyclopentane-cyclohexane) in 10 seconds, and aromatic compounds (benzene-toluene) in 26 s. Average power consumption was lower than 50 W. Graphite-sputtered micro columns were used to enable full separation of methane and ethane at high temperature (100°C). Thus, such columns could easily match the requirements of an oilfield monitoring sensor based on a gas chromatography method (safety, mud logging), in terms of fabrication process, separated compounds, fast thermal management, low power consumption, and good versatility.

Moreover, the design and fabrication of the up- and downstream components of a micro gas chromatograph (i.e. a micro injector [5], and a micro thermal conductivity detector [6]), also through conventional silicon micro machining techniques, have already been reported. Although some critical steps remain to be done (air-methane separation, quantitative analyses, tests on genuine samples, packaging, and carrier gas providing), the framework and the proof of concept of the essential components of a GC-based oilfield monitoring sensor are henceforth present.

5 ACKNOWLEDGEMENTS

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