

This is a submitted version of the following article:

Zampolli S., Elmi I., Cardinali G.C., Masini L., Bonafè F., Zardi F., Compact-GC platform: A flexible system integration strategy for a completely microsystems-based gas-chromatograph (2020), Sensors and Actuators, B: Chemical, 305, art. no. 127444

# Compact-GC platform: a flexible system integration strategy for a completely microsystems-based gas-chromatograph

**Stefano Zampolli**<sup>1</sup>, Ivan Elmi<sup>1</sup>, Gian Carlo Cardinali<sup>1</sup>, Luca Masini<sup>1</sup>, Filippo Bonafè<sup>1</sup>, Federico Zardi<sup>2</sup>

<sup>1</sup>CNR-IMM, Via P. Gobetti 101, 40129 Bologna, Italy

<sup>2</sup>CNR-ISAC, Via P. Gobetti 101, 40129 Bologna, Italy

Corresponding author: Stefano Zampolli

Italian National Research Council - Institute for Microelectronics and Microsystems CNR-IMM

Via P. Gobetti 101, 40129 Bologna (BO), Italy

e-mail: [zampolli@bo.imm.cnr.it](mailto:zampolli@bo.imm.cnr.it)

tel: +39 051 639 9109

## Abstract

The increasing need for portable analysis systems to be used in field sensing applications with the quality and reliability of laboratory analyses, characterized by high sensitivity and specificity, calls for miniaturization and optimization of laboratory analytical techniques, as enabled by the use of micro-electro-mechanical-systems (MEMS) technology. This paper reports on an innovative all-on-MEMS platform for the implementation of miniaturized or portable multi-purpose gas-chromatographic (GC) systems. The use of a directly interconnected MEMS technology for all three main GC components, namely injector, purge&trap pre-concentrator and GC separation column, allows for a very efficient system integration and for a zero dead-volume and chemically inert analytical chain, which can be heated up to 200°C to avoid sample condensation. In this work, the analytical chain and the integration strategy will be reported, and several applications and analyses will be demonstrated using the compact-GC platform with both photoionization (PID) and thermal conductivity detectors (TCD).

**Keywords:** MEMS; gas-chromatography; miniaturized; portable; indoor air quality; natural gas; ethylene

## 1. Introduction

The selectivity required for reliable in-field analyses of gaseous samples can rarely be reached using partially selective stand-alone detectors. In many critical real-world applications, the complex sample matrix is typically composed of huge and varying amounts of interferents and trace amounts of the target gases to be detected. Furthermore, often those field analysis applications mandate for zero false positives, especially in the safety and security sector, where positives may indicate relevant health risks for the population, resulting in evacuations or other complex countermeasures.

The most established laboratory technique used for analyses of gases in complex mixtures is gas-chromatography, where the sample is pre-separated before detection by means of a gas chromatographic separation column. Laboratory GC systems are generally bulky, fragile and expensive, and not suitable to be used in field, unless installed inside mobile laboratories with limited portability and huge acquisition and

operation costs.

The difference between laboratory equipment modified for field usage and innovative systems designed from scratch to be portable, lightweight and cost effective, impacts in particular on sensor size, weight, constraints on power consumption, but also and most importantly on consumables and accessories, like carrier gas supplies, control and acquisition electronics, simplified user front-ends and packaging.

The use of micro-electro-mechanical-system (MEMS) technology for the miniaturization of gas-chromatographic equipment has been widely exploited in recent decades. The first publication on MEMS GC by Terry [1] in 1979 proposed and demonstrated an entire GC system on a MEMS wafer. While this excellent result inspired many research groups and started a long series of developments, the monolithic integration of all components on a single wafer is not a cost-effective solution, mainly because of the large silicon surface area necessary to integrate long GC separation columns. While some GC components like injectors and detectors can be miniaturized to the millimeter scale and require a rather complex fabrication procedure to implement mechanical and electrical functions, the GC separation column typically needs a few square centimeters surface and can generally be fabricated with a simpler process flow. Furthermore, the GC column must be functionalized with a suitable stationary phase, which often requires high temperature processes and chemical solutions which could damage the other parts of the system. For this reason, splitting the main MEMS components of a GC system into distinct devices is a more efficient and flexible solution.

A successive relevant publication is the work of 2004 by Dziuban [2], which reports on microfabricated membrane injectors and thermal conductivity detectors for a portable gas chromatograph. With similar components, commercial devices were proposed by Varian (CP-4900), Agilent (490 Micro GC) and Inficon (Fusion). In these systems, only the injector and detector are MEMS devices, and standard fused silica capillary GC columns are used. Furthermore, since these systems allow for loop injections and use thermal conductivity detectors (TCD), which have a comparatively low sensitivity, the detection limits are in the ppm range. Use of purge&trap pre-concentration would allow for an increased sensitivity, but is not implemented in these commercial devices.

The Microchemlab by Sandia National Laboratory was reported in several versions during the last two decades, and in [3] the trade-off between monolithic integration of the components and system flexibility is addressed. Mainly targeting military applications, Microchemlab uses innovative multiple detection techniques and integrates pre-concentration capabilities to enhance the sensitivity.

The research groups at University of Michigan [4] and Virginia Tech [5] have demonstrated several MEMS based analytical sensing systems targeting portable applications. Both works require inert carrier gas supplies for operation, and [5] successfully integrates a helium discharge detector into the MEMS GC chip. With reference to advances in the development of MEMS GC columns, [6] reports on the use of pillar density modulation in a semi-packed GC column, yielding increased separation efficiency at reduced pressure requirements, while [7] proposes zone heating of MEMS GC columns, aiming at a decrease of power consumption per analysis while maximizing the separation efficiency.

Regarding sample pre-concentration, which is used to reduce the detection limits of the sensing systems, a recent paper [8] reports on an innovative MEMS device for passive pre-concentration, aiming at completely eliminating any power consuming pumping device during the generally long sampling stage of the chemical analysis.

In [9] an exhaustive review of existing micro-gas analyzer systems is reported. Most of the reported devices offer application-specific solutions, where generally MEMS technology is used only for some of the devices composing the analytical path (mainly micro-columns and detectors), and are assembled by hybrid integration with conventional modules and interconnections using tubes or capillaries. [10] is a recent review of micro-GC technology, with particular reference to the challenges of integration of MEMS components, and reporting an exhaustive comparison of micro GC columns. Furthermore, guidelines for the comparative evaluation of column performances are recommended, since papers often use different metrics and different test mixtures for the evaluation of the GC separation capability.

This paper reports on an innovative all-on-MEMS GC platform designed to be possibly flexible, general-purpose and easily re-configurable, by using different kinds of injections (either loop injection or elution from a purge&trap pre-concentrator), different kinds of MEMS GC separation columns (micro-packed or wall-coated open tubular), different kinds of carrier gases (micro-cylinders with inert gases like Helium or Nitrogen, or generated carriers like filtered air) and suitable to be interconnected to detectors based on different technologies. More precisely, the detector is not part of the reported compact-GC platform, which

is suitable to be used for sample enrichment and gas-chromatographic pre-separation upstream of any commercial or innovative gas detection technology.

Furthermore, the analytical circuit of the injector is designed to be driven by as few as two external pilot valves, and the three MEMS components are directly interconnected by means of micro-O-Rings, thus minimizing the dead-volume while lowering the assembly complexity and overall cost of the GC system.

The proposed system uses an active pre-concentrator, where a pump drives the sample through the purge&trap cartridge during the pre-concentration step, as opposed to the passive device reported in [8]. While electrical power is necessary to drive the sampling pump, this enables to flexibly implement different pre-concentration strategies. As examples, fast high-volume sampling with high performance pumps enables to decrease the analysis cycle time, while slower pumping results in measurements reporting the average concentration over longer sampling times. On the other hand, many applications require a fast sample acquisition by means of a sampling port, which has to be inserted inside the volume to be analyzed.

Furthermore, different pre-concentrator geometries are currently under development for the compact-GC platform, allowing for tailoring the sample volume to the pre-concentrator break-through volumes and adjusting the flow impedance of the packed MEMS device.

To the best of our knowledge, this is the first portable GC system where all three analytical components of the analytical chain (pre-concentrator, injector and GC separation column) are fabricated in MEMS technology and directly interconnected at assembly level, without the use of tubes or fluidic manifolds. This enables an extreme reduction of dead volumes together with a reduction of sample, detection and carrier gas volumes, while maximizing analytical performance and portability and enabling flexible reconfiguration. Furthermore, the whole analytical chain is based on silicon MEMS devices and is therefore suitable to be operated at high temperatures (up to 200°C), as necessary for a multi-purpose system capable of analyzing also low volatility compounds.

## 2. Materials and methods

### 2.1. The fluidic circuit

The main characteristic of the reported platform is the use of a silicon fluidic motherboard (FMB) to interconnect the MEMS pre-concentrator with the MEMS GC column, while the same FMB acts as also injector (INJ), using integrated micromachined externally piloted micro-membrane-valves [12]. The fabrication process of the MEMS pre-concentrator and MEMS GC column is reported elsewhere [11, 13].

The use of all fluidic components, including the FMB/INJ, fabricated in form of silicon MEMS devices capable of withstanding high temperatures, allows using integrated thin film heaters to operate the whole GC circuit at high temperatures, up to at least 200°C, to avoid condensation of high-boiling target analytes. As a matter of fact, the three MEMS components are interconnected by means of miniature O-Rings, preferably made of Viton® or Calrez® material, which are also suitable for high temperature operation, and also the sample inlet manifold can be actively heated to a programmable setpoint. To avoid condensation phenomena which would compromise the detection capability and result in carry-over effects between analyses, in conventional laboratory GC systems the entire analytical chain is generally operated at temperatures higher than the boiling point of the analysis targets. The temperature of the GC column at the beginning of the separation step is lower than that of the other parts of the GC system, followed by the temperature ramp on the GC column providing analyte separation. As an example, in most benchtop GCs all sampling and transfer lines are heated, as is the detector housing, and the injector is a robust multi-port valve heated by means of electrical power. On the other hand, most portable micro-GC systems reported up to date implement the sample injection using miniaturized electro-valves, which can rarely be heated to temperatures higher than 60°C. This compromises their use for analyses of high boiling molecules, like typically encountered in safety and security applications.

Furthermore, the injection circuit is implemented using 5 normally open micro-valves grouped in two sets, each set being pressure-actuated by a single external pilot valve, thus requiring a minimal set of external

components.

A schematic representation of the fluidic circuit, representing the two operational states (sampling/eluting and injection) as well as the segmentation between the three MEMS and the position of the O-Ring interconnections, is shown in Figure 1. The interconnection ports shown in Figure 1 and throughout the rest of the paper are defined as follows: “-dP” is to be connected to a under-pressure source, e.g. a sampling pump, which is used to drive the sample through the pre-concentrator. “+dP” is the input for the carrier gas source, which must be at over-pressure as required to drive the flow through the GC column and through the pre-concentrator (PC) during injection. “Sample in” and “To detector” are the sample inlet and the output to the detector respectively.

The device is designed to inject a pre-concentrator during its thermal desorption phase, acting as enriched loop to increase the GC sensitivity. Optionally, the device can be used to inject a conventional sample loop, in two of the following ways: i) by using an empty, non-packed pre-concentration MEMS; ii) by using a modified FMB/INJ implementing an integrated microliter sample loop.

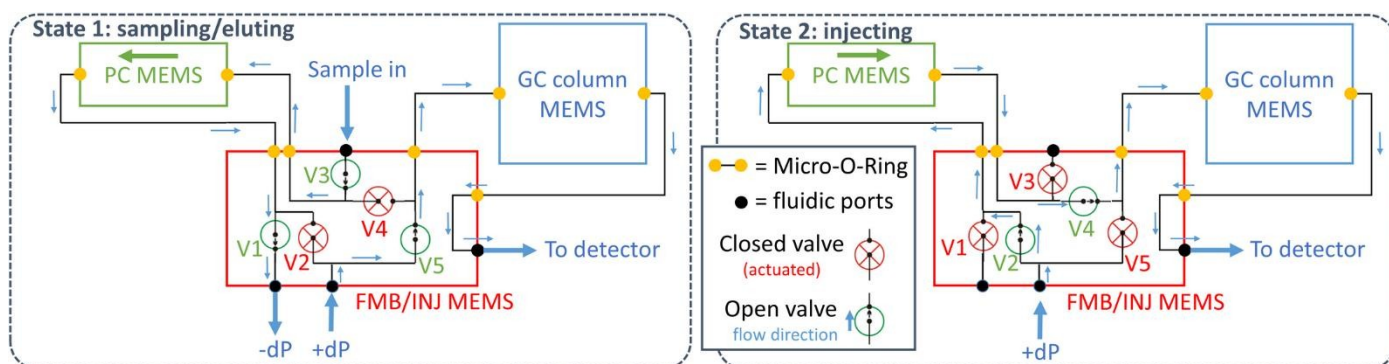


Figure 1: block diagram of the compact-GC platform in the two functional states: sampling/eluting and injecting. The state of the micro-valves and the flow directions inside each path are also shown.

A simplified schematic representation of the cross-section of a part of the MEMS FMB/INJ with two membrane-valves is shown in Figure 2. It consists of a stack of 3 silicon wafers, each 0.3mm thick, processed by multiple deep reactive ion etching steps and attached by means of an adhesive bonding process using 10µm thin SU-8 photoresist as adhesive. The valve membranes are made of the same SU-8 layer used for the bonding of the top and middle wafer. Between the middle and the bottom wafer, the analytical/fluidic layer provides the interconnections between the different valves and the in- and outlets, which are through holes in the bottom wafer.

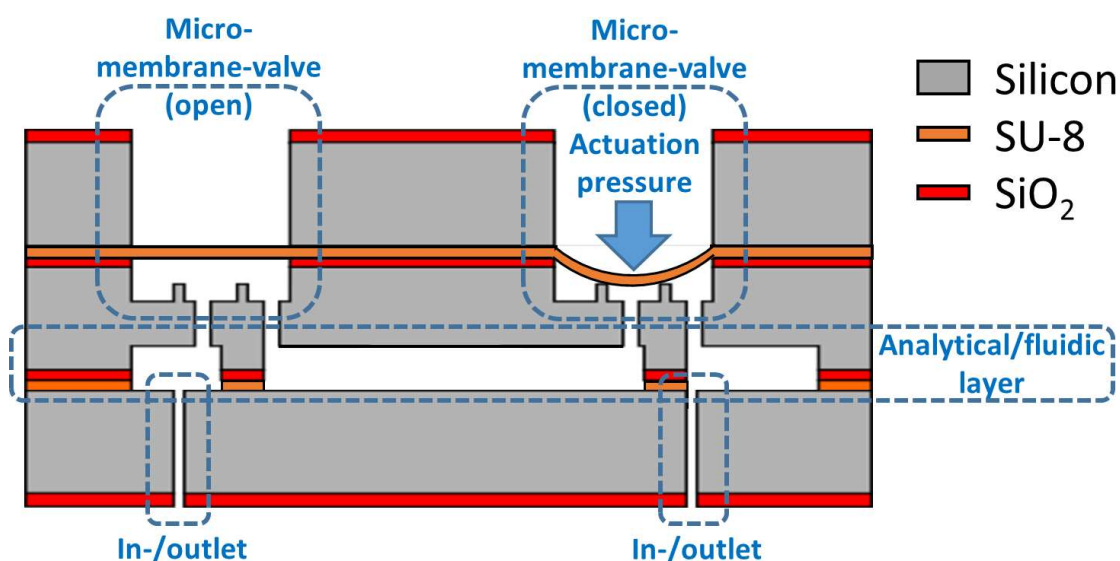


Figure 2: Simplified schematic representation of the cross-section of the 3-wafer MEMS stack implementing the injector used in this work.

Compared to previously reported MEMS-based membrane valve injectors, the use of spin-coated SU-8 as membrane material results in a simplified clean-room wafer-level fabrication technology not requiring lamination processes, while the reduced thickness and increased flexibility of the thin membrane yields smaller valve structures and thus reduced dead volumes and higher packing density. Furthermore, the SU-8 based micro-valves have proven to be robust and reliable, showing no damage after operation for several hours at temperatures up to 200°C.

Photographs and micrographs of FMB/INJ MEMS chips are reported in the supplementary material, Figures S1 and S2.

## 2.2. Direct on-assembly integration using micro-O-Rings

Simplified cross-sectional views of the assembly between the FMB/INJ, the pre-concentrator (PC) and the GC column using micro-O-Rings, together with the support manifolds and the pilot valve location applying the actuation pressures are shown in Figure 3. The system is assembled by using screws pulling the manifold 1 and manifold 2 together, and both manifolds are machined with calibrated spacers resulting in a correct and symmetrical compression of all O-Rings once the screws are perfectly tightened.

Unlike all other O-Rings shown in Figure 3, the O-Rings drawn without filling have only the mechanical function of pressing the GC and PC MEMS devices onto the FMB/INJ, and are thus not used to seal any gas flows. The upper part of the system as shown in Figure 3 is the analytical part, meaning that the sample gas, the carrier gas and the pre-concentrated and pre-separated sample flow through this part of the system. The lower part is the actuation side, and only an externally piloted gas flows on this side of the system to actuate the membrane valves. This means that the gas flowing in the lower part of the system does not need to be clean or analytical grade, as opposed to the gas flowing into the upper part.

Another schematic representation with the top and bottom views of the relative positions of the 3 MEMS, analytical ports and valve grouping is reported in the supplementary material Figure S3.

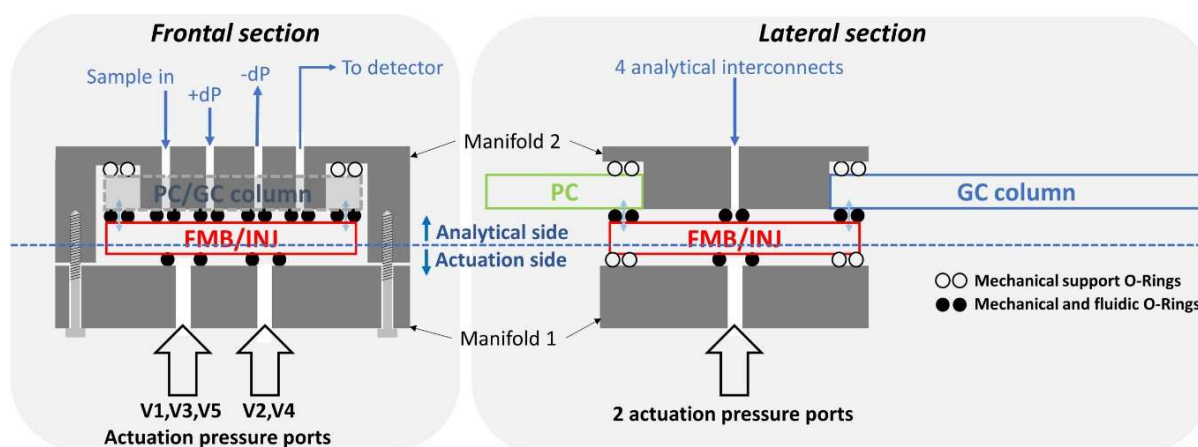


Figure 3: Simplified cross-sectional views of the system integration between the three MEMS components and the external parts.

## 2.3. The prototypes used for this work

A simplified 3D rendering with transparent parts showing the analytical core of the compact-GC module, namely the three MEMS devices, the support manifolds, O-Rings and pilot valves, is shown in Figure 4. The integrated heaters and temperature sensors on the MEMS GC and pre-concentrator can be easily disclosed, while only a part of the FMB is visible (rendered in orange color), buried between the other system parts. The heaters and temperature sensors on the pre-concentrator and on the GC separation column allow for a fast and precise temperature control, which is necessary during the chemical analysis cycle: during pre-concentration, the pre-concentrator is cooled by several miniature fans, to promote the absorption of the target gases. During injection, the pre-concentrator is rapidly heated to desorption temperature, which may

be as high as 350°C depending on the sorbent material and carrier gas used. The custom designed electronics allow for heating ramps as fast as 100°C/s on small pre-concentrator chips.

Regarding the GC separation column, usually controlled temperature ramps are applied, where the first part of the chromatogram is acquired with the GC column close to room temperature, followed by a temperature increase up to 325°C depending on the stationary phase and carrier gas. Heating ramps on GC columns are usually slower than for the pre-concentrator desorption, although FAST-GC applications may require ramps from room temperature to maximum temperatures in less than 2 minutes.

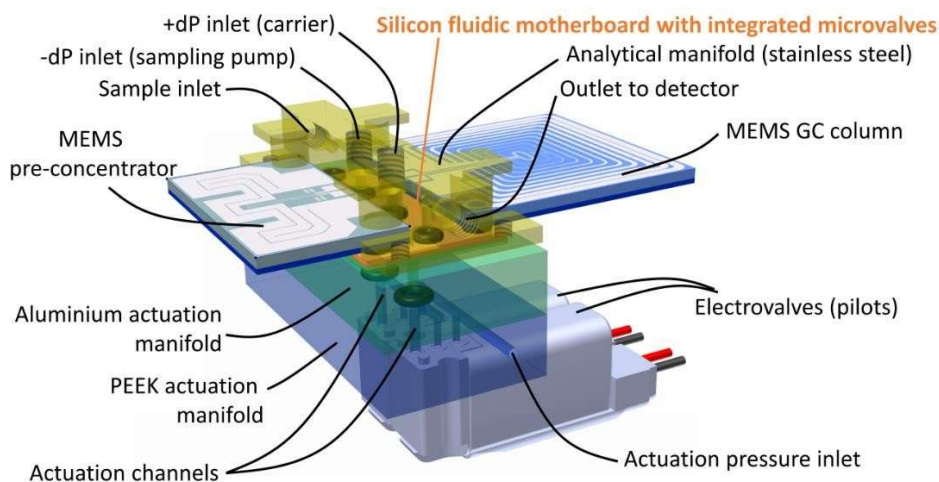


Figure 4: simplified 3D rendering of the compact-GC analytical core.

In gas-chromatography, the injector is usually kept at a fixed temperature, close to the maximum temperature of the GC ramp. This is currently achieved by two flexible polyimide/copper heaters in contact with the FMB/INJ MEMS (not shown in the simplified rendering of Figure 4), although integrated heaters will be designed and implemented in future versions of the compact-GC hardware.

This analytical core is common to all the applications and tests reported in section 3, while different detectors and different types of carrier gases were used. The following table 1 lists the different applications demonstrated in this work and the main compact-GC implementation details: injector type, carrier gas and detector technology.

TABLE I. COMPACT-GC: DEMONSTRATED PROTOTYPES

Application	Compact-GC components		
	Injector	Carrier	Detector
Natural gas analysis	Sample loop (integrated in the FMB/INJ)	Helium from cylinder	CNR-IMM Micro-TCD [14]
VOCs and benzene	Pre-conc. with graphitized carbon sorbent	Filtered ambient air	Mini-PID 2 HS (Ion Science)
Ethylene monitoring	Pre-conc. with molecular sieves	Filtered ambient air	Mini-PID 2 HS (Ion Science)

In the tests reported in section 3, two types of detectors were used at the outlet of the GC separation column: Thermal conductivity detectors (TCD) and photoionization detectors (PID).

TCDs rely on the difference in thermal conductivity between the carrier gas and the target gas species eluting from the GC column. In particular, TCDs are generally used with Hydrogen or Helium as carrier gases, which are characterized by a very high thermal conductivity compared to most target gas species ( $0.1805 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$  and  $0.1513 \text{ W}\cdot(\text{m}\cdot\text{K})^{-1}$  respectively). To enhance the detection sensitivity and the signal-to-noise ratio, TCDs

are generally composed by 4 heaters in a Wheatstone bridge configuration, where two heaters on one diagonal of the Wheatstone bridge (referred to as analytical branch of the TCD) are exposed to the outlet of the GC column, while the other two (referred to as reference branch) are exposed to pure carrier gas. As a chromatographic peak elutes from the GC column into the TCD chamber, the two heaters on the analytical branch are exposed to a gas mixture (carrier gas and eluting peak gas) with lower thermal conductivity compared to the pure carrier gas, and thus increase their temperature, resulting in a voltage difference on the diagonal of the Wheatstone bridge. The MEMS TCDs used in this work were designed and fabricated at CNR-IMM, and were reported previously together with the custom designed control and acquisition electronics [14]. In our implementation, the pure carrier gas for the reference branch is provided through an additional inlet on the TCD support manifold and a T-split on the carrier gas inlet, while the analytical branch is connected to the outlet of the GC column.

Photoionization detectors rely on the ionization of the target molecules by ultraviolet radiation (UV) generated by a UV lamp typically emitting at energies up to 10.6eV. As target gases with ionization potentials up to 10.6eV are ionized by the UV radiation, an ion current is measured between two polarized electrodes. In particular, commercially available “mini-PID 2 HS” devices by Ion Science (Fowlmere, UK), featuring patented fence electrode technology, were used in this work.

Figure 5 shows some photographs of the three MEMS components (a), of the complete compact-GC/TCD analytical core module (b) and of a complete compact-GC/PID device including all control electronics (c,d). It is noteworthy that the entire analytical core (Figure 5b) occupies a volume of less than 150 cm<sup>3</sup>.

Unless otherwise specified, all gas samples were provided through an automated gas mixing system using mass flow controllers (MKS Instruments) connected to certified cylinders of target gases at known concentrations (SIAD S.p.A. and SAPIO S.r.l., Italy) and diluted in high purity gas chromatographic air (Sapio S.r.l., Italy).

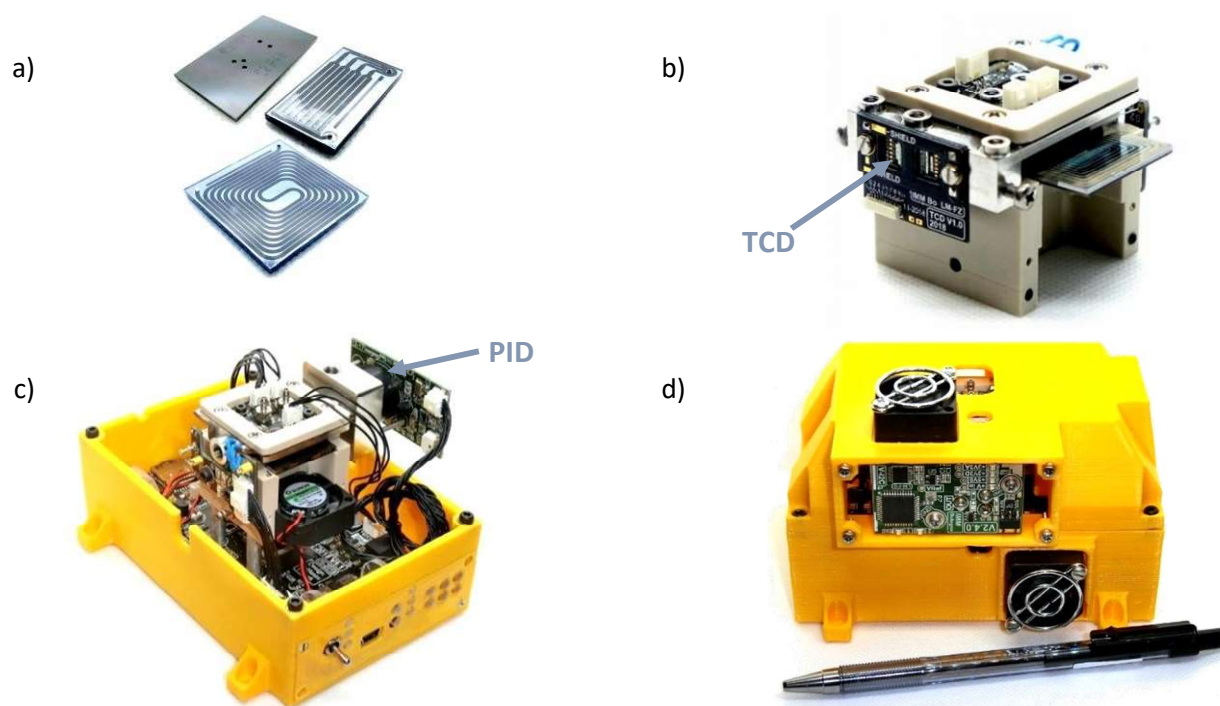


Figure 5: Photographs of the prototypes: a) three MEMS components (injector, dual-bed pre-concentrator and packed GC column); b) compact-GC/TCD core analytical module; c) packaged compact-GC/PID prototype without cover; d) completely packaged GC/PID device, sized 12.0 cm x 8.0 cm x 7.5 cm.

### 3. Results and discussion

#### 3.1. Natural gas analysis

Natural gas is a mixture of several light alkanes, methane (CH<sub>4</sub>) being the most abundant, together with some other permanent gases like nitrogen, argon, CO<sub>2</sub> and O<sub>2</sub>. While the alkanes contribute to the calorific power of the natural gas mixture with different coefficients, the other permanent gases are considered contaminants which decrease the energy density of the mixture. It is therefore becoming more and more important to monitor the exact composition of the natural gas on-line, and portable, low-power stand-alone micro-GCs are the most promising technology. A compact-GC with an integrated loop injector, a micro-packed GC column (50 cm long, rectangular cross-section 0.8 x 0.7 mm<sup>2</sup> packed with Carbograph® 2 mesh 80-100, LARA s.r.l., Formello, Italy) and a micro thermal conductivity detector was used to measure the composition of a natural gas sample. The TCD mandates for the use of a high thermal conductivity carrier gas, therefore Helium was used as pressurized carrier for this application.

The compact-GC/TCD system was tested on a synthetic sample of natural gas transferred from a certified cylinder (Agilent technologies part X11ME69CP17C001) into a Tedlar® bag and autonomously sampled into the loop by the system's sampling pump. Figure 6 shows the chromatogram of the C<sub>2</sub>-C<sub>6</sub> alkanes (including the isomers) and their quantitative determination, while nitrogen and argon co-elute with the methane peak and cannot be quantified individually. The development of an optimized packed GC column separating the other permanent gases from the methane peak is ongoing.

The total cycle time is as low as 2 minutes, including the cooling of the MEMS column, ensuring a high measurement throughput for this type of GC analysis.

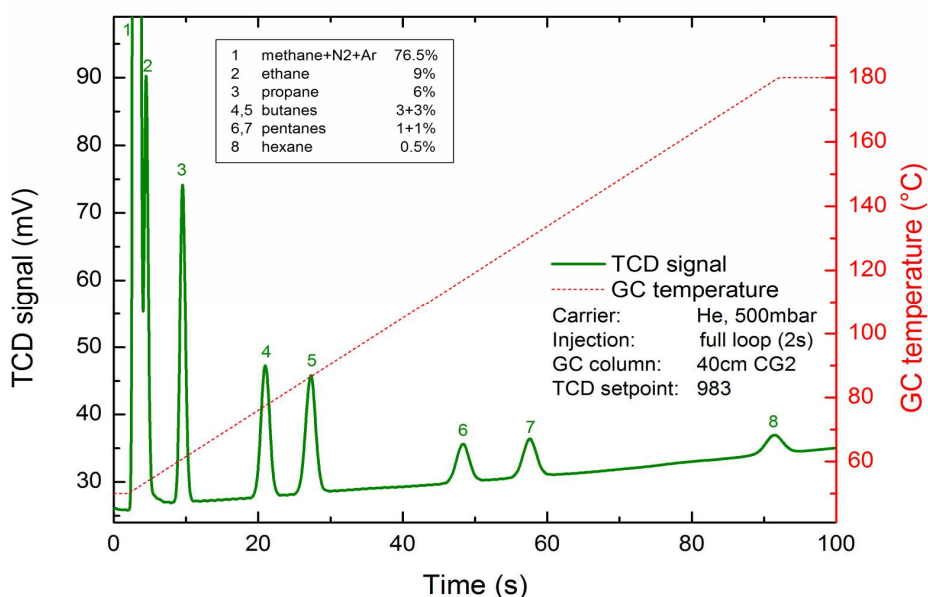


Figure 6: Chromatogram of a natural gas sample acquired with the compact-GC/TCD configuration, using helium as carrier gas. The temperature ramp on the MEMS GC column is shown on the right y-axis (red dotted plot).

#### 3.2. Volatile organics and benzene

Benzene is a particularly significant carcinogenic environmental pollutant, and devices for capillary on-line monitoring were proposed [11], particularly for urban areas. On the other hand, many volatile organics are present also in indoor environments, mainly due to the use of cosmetics, cleaning agents and cooking activities, but also permeating from outdoor pollution. Therefore, indoor air monitoring requires the capability to discriminate between harmless volatiles (like ethanol and acetone) and dangerous or carcinogenic volatiles (like benzene and trichloroethylene). Figure 7 shows a set of chromatograms of several



volatile compounds in part per billion (ppb) concentrations, acquired with a compact-GC/PID, equipped with a purge&trap pre-concentrator packed with 67mg Carbograph® 5 and a micropacked GC column, 50 cm long, rectangular cross-section 0.8 x 0.7 mm<sup>2</sup> packed with with Carbograph® 1 (both mesh 80-100, LARA s.r.l., Formello, Italy), and using filtered ambient air as carrier gas.

The samples of ethanol, acetone, isopropanol, cyclohexane and trichloroethylene were prepared by multiple dilution of saturated headspace vapors from vials filled with pure liquid standards, therefore their exact concentration is not known. In any case, the dilutions were calculated to provide samples with concentrations lower than 20 ppb for each of these samples. The benzene sample was provided by the automated gas mixing system described above. As can be disclosed from the set of chromatograms, acetone background in the laboratory air cross-contaminates all headspace measurements.

The chromatograms of Figure 7 confirm the capability of the device to clearly separate and quantify the peaks, while the lower plot of Figure 7 shows the linear calibration curve for benzene, acquired in the range between 1 and 20 ppb (the chromatograms at the different concentrations are shown in the supplementary material, Figure S4). For this set of acquisitions, the total analysis cycle time, including pre-concentration, was 15 minutes.

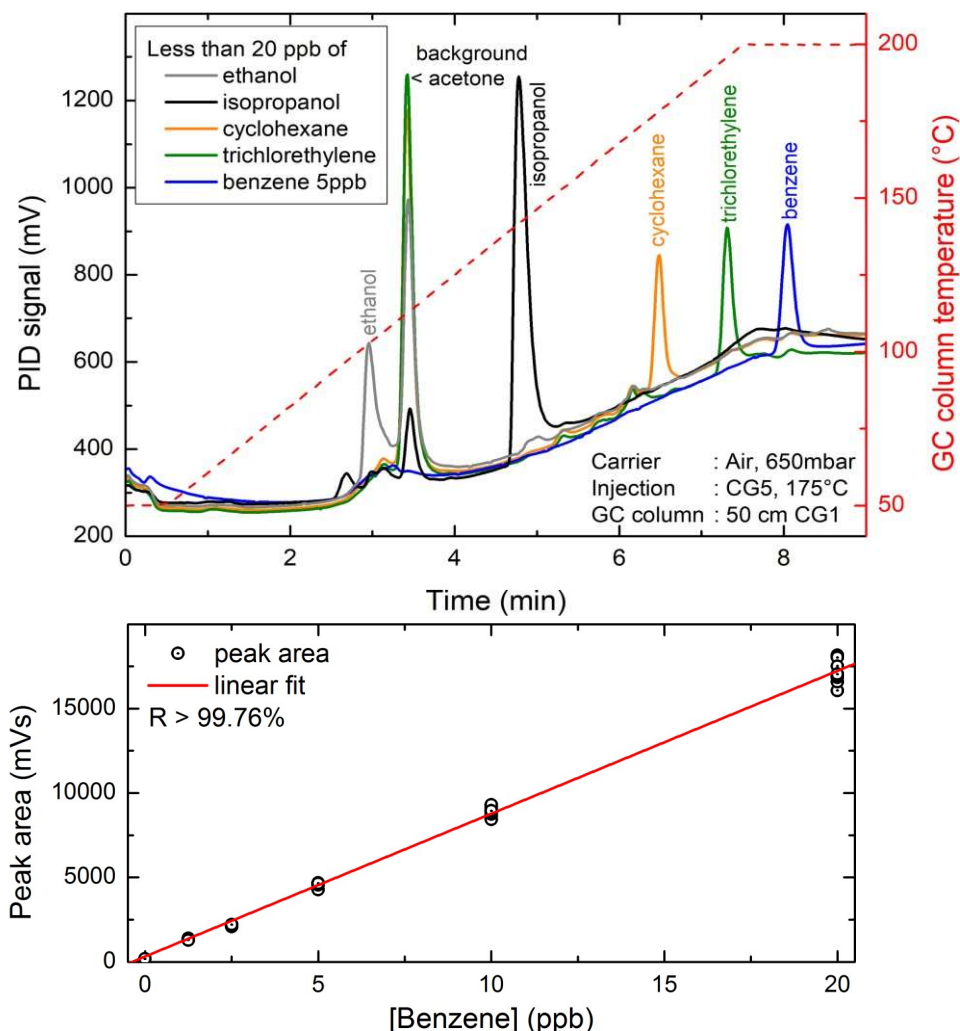


Figure 7: Chromatograms of several organic volatiles in ambient air, using filtered air as carrier gas (top) and calibration curve of benzene peak area in the range [1-20] ppb.

To further assess the capability of the compact-GC/PID system to separate and detect benzene in a very complex mixture, a test with a cigarette smoke sample was performed. As shown in the left part of Figure 8, the sample inlet was connected to a lighted cigarette and the system sampled the cigarette smoke using its sampling pump for only 1 second. The resulting chromatogram shows several peaks, some of which are not completely separated while others saturate the PID detector despite the very short sampling time. But most

notably, the peak of benzene inside the cigarette smoke can be easily disclosed at a retention time of 8.05 minutes, although not completely separated from the preceding peak tail. The rather low separation capability of the 50cm short packed GC column is the main reason for the peak broadening in Figure 8, meaning that the analysis of cigarette smoke with such column is challenging. Nevertheless, a rough estimation of the benzene concentration in the cigarette smoke is possible and is reported in table 2.

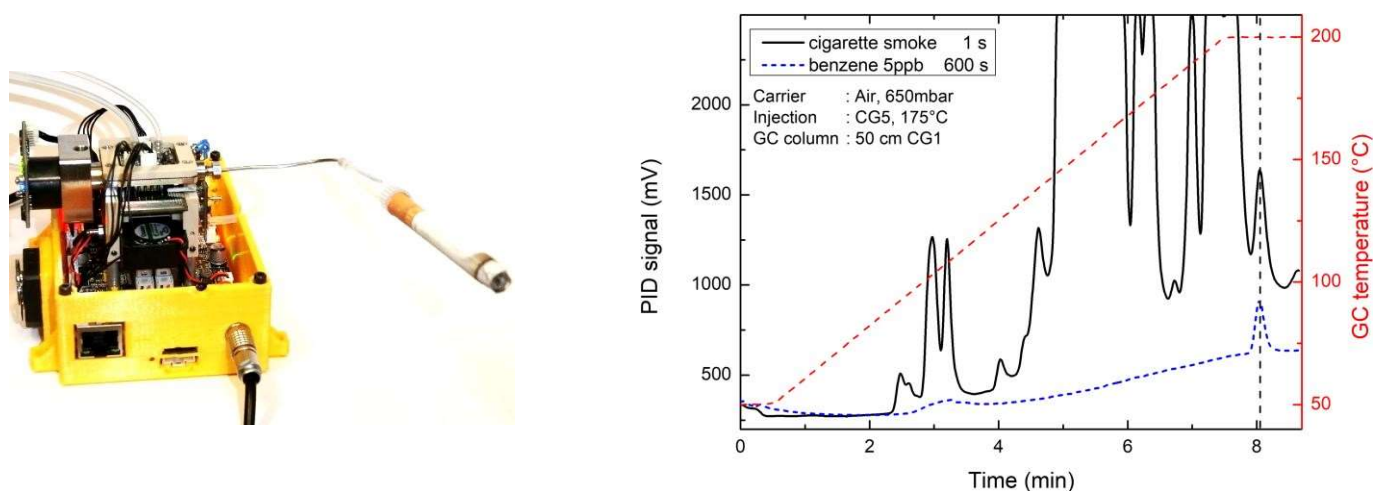


Figure 8: Compact-GC/PID system acquiring cigarette smoke (left) for 1 second, and resulting chromatogram (right, black plot) compared to a 10 minutes 5 ppb sample of benzene (right, blue plot).

TABLE II. ESTIMATION OF BENZENE CONCENTRATION IN CIGARETTE SMOKE

<b>Chromatogram</b>	<b>Sampling time (s)</b>	<b>Peak area (mVs) at 8.05 min</b>	<b>Benzene concentration</b>
Benzene calibration (Figure 8 blue dashed plot)	$600 \pm 0.2$	$4600 \pm 100$	$(5 \pm 1)$ ppb
Cigarette smoke (Figure 8 black continuous plot)	$1 \pm 0.2$	$8400 \pm 200$	<b><math>(5.5 \pm 1.6)</math> ppm</b>

### 3.3. Ethylene quantification for fruit ripening monitoring

Ethylene is released by climacteric fruit during the ripening process, and acts as hormone promoting the ripening process for other non-climacteric fruit types. Monitoring the evolution of the ethylene concentration during fruit storage, transport and logistics with small and stand-alone devices would be of primary importance to control fruit ripening. We have demonstrated the ability of a compact-GC/PID with a pre-concentrator using a carbon-based molecular sieve as sorbent (52 mg Carbosieve® S-III, Supelco) and a micro-packed GC column (50 cm long, rectangular cross-section 0.8 x 0.7 mm<sup>2</sup> packed with Carbograph® 5 mesh 80-100, LARA s.r.l., Formello, Italy) to acquire ethylene peaks in the sub-ppm range, as shown in Figure 9 together with the linear calibration in the range between 70 and 950 ppb.

It is worthwhile to notice that ethylene is a very volatile gas (the boiling point is at -103.7°C), which makes the purge&trap pre-concentration difficult and results in rather low break-through volumes. For this reason, together with the low sensitivity of ethylene detection by a PID at 10.6eV, the sensitivity of the compact-GC/PID device on ethylene is 2 orders of magnitude lower than for benzene and VOCs, though still sufficient for the concentration range of most fruit ripening monitoring applications.

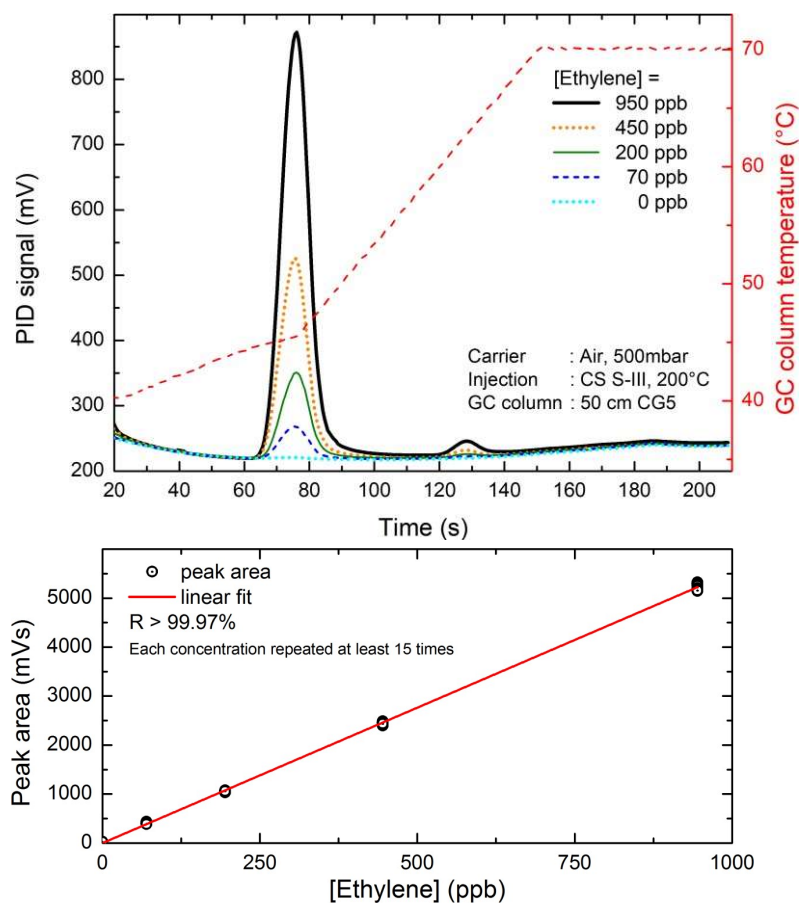


Figure 9: Chromatograms of different ethylene concentrations, using filtered air as carrier gas (top) and calibration curve of ethylene peak area in the range [70-950] ppb.

## 4. Conclusions

We have reported a miniaturized, flexible and simple all-on-MEMS platform for micro-gas-chromatography coupled to the purge&trap pre-concentration, which can be set-up with different injection configurations, different detectors and different types of MEMS GC columns and pre-concentrators. To the best of our knowledge, this is the first portable GC system where all three analytical components of the analytical chain (pre-concentrator, injector and GC separation column) are fabricated in MEMS technology and directly interconnected at assembly level, without the use of tubes or fluidic manifolds. This enables an extreme reduction of dead volumes together with a reduction of sample volume and carrier gas consumption, while maximising analytical performance and portability.

The fluidic circuit, the fabrication technology of the fluidic motherboard injector and the system integration strategy were described in detail, and the system was demonstrated in different configurations on specific and very different applications, confirming the flexibility of the proposed technology.

The detector is not part of the reported compact-GC platform, which is suitable to be coupled to any commercial or innovative gas detection technology. Besides the two detectors reported in this paper (TCD and PID), work on different MEMS-based detectors like e.g. pulsed barrier discharge detectors is ongoing.

While the reported applications all rely on short micro-packed GC columns, which have a limited separation capability, wall-coated open tubular (WCOT) MEMS columns [13] compatible with the compact-GC platform, are currently under development, targeting a much higher column plate count and enabling the fast detection of low volatility compounds which is generally not feasible with packed columns. Future work will be focused on the optimization of the GC separation column to enhance separation performance and reduce peak broadening. The capability to operate the entire analytical chain at high temperatures, as enabled by the all-on-MEMS implementation of the compact-GC platform, will be beneficial for the analysis of low volatility compounds, as generally required in safety and security applications.

## Author contributions

**Stefano Zampolli:** conceptualization; supervision; investigation; validation; writing – original draft.

**Ivan Elmi:** clean-room process development, processes and supervision; investigation; conceptualization; validation.

**Gian Carlo Cardinali:** investigation; mask layout design; formal analysis; validation; writing – review & editing.

**Luca Masini:** electronic hardware design; mechanical design; validation.

**Filippo Bonafé:** clean-room process development and processes.

**Federico Zardi:** firmware development; mechanical design; electronic hardware design; validation.

## Acknowledgements

Fabrizio Tamarri, Michele Sanmartin, Michele Bellettato and Giulio Pizzochero are thankfully acknowledged for their contribution to this work with clean-room related activities.

## Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

The authors declare no competing interests.

## References

- [1] S.C. Terry, J.H. Jerman, J.B. Angell, Gas chromatographic air analyzer fabricated on a silicon wafer, *IEEE Trans. Electron. Devices* 26 (1979) 1880–1886
- [2] J.A. Dziuban, J. Mróz, M. Szczygielska, M. Małachowski, A. Górecka-Drzazga, R. Walczak et al., Portable gas chromatograph with integrated components, *Sens. Actuator A-Phys* 115 (2004) 318-330
- [3] P.R. Lewis, R.P. Manginell, D.R. Adkins, R.J. Kottenstette, D.R. Wheeler, S.S. Sokolowski, D.E. Trudell, J.E. Byrnes et al., Recent advancements in the gas-phase MicroChemLab, *IEEE Sens. J.* 6 (2006) 784-895
- [4] J. Wang, N. Nuñovero, R. Nidetz, S. J. Peterson, B. M. Brookover, W. H. Steinecker, E. T. Zellers, “Belt-Mounted Micro-Gas-Chromatograph Prototype for Determining Personal Exposures to Volatile-Organic-Compound Mixture Components”, *Anal. Chem.* 91 (2019), 4747-4754
- [5] M. Akbar, H. Shakeel and M. Agah, GC-on-chip: integrated column and photoionization detector, *Lab Chip* 15 (2015) 1748-1758
- [6] R. Chan, M. Agah, “Semi-Packed Gas Chromatography Columns with Density Modulated Pillars”, *J. Microelectromech. Syst.* 28 (2019), 114-124
- [7] Z. Lin, N. Nuñovero, J. Wang, R. Nidetz, S. Buggaveeti, K. Kurabayashi, Edward T. Zellers, “A zone-heated gas chromatographic microcolumn: Energy efficiency” ,*Sens. Actuators B* 254 (2018) 561–572
- [8] J.H. Seo S. K. Kim, E. T. Zellers, K. Kurabayashi, “Microfabricated passive vapor preconcentrator/injector designed for microscale gas chromatography”, *Lab Chip* 12 (2012) 717-724
- [9] E. Lussac, R., P. Cardinael and V. Agasse, Review on micro-gas analyzer systems: feasibility, separations and applications, *Crit. Rev. Anal. Chem.* 46 (2016) 455-468
- [10] B. P. Regmi and M. Agah, “Micro Gas Chromatography: An Overview of Critical Components and Their Integration”, *Anal. Chem.* 22 (2018), 13133-13150
- [11] S. Zampolli, I. Elmi, F. Mancarella, P. Betti, E. Dalcanale, G.C. Cardinali, M. Severi, Real-time monitoring of sub-ppb concentrations of aromatic volatiles with a MEMS-enabled miniaturized gas-chromatograph, *Sens. Actuator B-Chem.* 141 (2009) 322-328
- [12] A. Nubile, A. Poggi, E. Cozzani, I. Elmi, S. Zampolli, M. Messina, G.C. Cardinali, F. Mancarella, M. Belluce, A novel pneumatically driven SU-8 microvalve for high speed gas chromatographic applications, *Proceedings NSTI-Nanotech* (2012) 172-175
- [13] C. Cagliero, S. Galli, M. Galli, I. Elmi, M. Belluce, S. Zampolli, B. Sgorbini, P. Rubiolo, C. Bicchi, Conventional and enantioselective GC with microfabricated planar columns for analysis of real-world samples of plant volatile fraction, *J. Chromatogr. A* 1429 (2016), 329-339
- [14] F. Rastrello, P. Placidi, A. Scorzoni, E. Cozzani, M. Messina, I. Elmi, S. Zampolli, G.C. Cardinali, Thermal Conductivity Detector for Gas Chromatography: Very Wide Gain Range Acquisition System and Experimental Measurements, *IEEE T Instrum Meas* 62 (2013) 974-981