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# Miniature 3D gas chromatography columns with integrated fluidic connectors using high-resolution stereolithography fabrication

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**Abstract**

In this manuscript we report on design, fabrication, and characterization of miniature gas chromatography columns with arbitrary 3D geometry and integrated connectors as separation elements for a mobile ethylene sensor system. In contrast to planar microfabrication, these columns have been realized in a single step additive manufacturing process using high-resolution stereolithography printing. This maskless technology enables the combination of freeform 3D microstructures with packaging aspects in one bulk element. For applications in food monitoring, the columns were packed with Carbosieve®-SII particles as adsorbents. With the printed columns a minimal gas concentration of 35 ppb (3σ) ethylene can be detected. Retention times of 400 s for ethylene and 1035 s for water and no signal peak overlap show an improved separation capability.


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*Keywords:* gas chromatography; ethylene; miniature separation column; additive manufacturing; high-resolution stereolithography;

## 1. Introduction

Ethylene detection is an important task in fruit monitoring. This gaseous organic compound is a product during the ripening process of climacteric fruit. Precise measurement of ethylene concentration in fruit containers can be used as an important parameter for calculating remaining shelf life during transport and storage [1]. Classic ethylene measurement systems are laboratory setups and bulky tools [2]. Miniature sensor systems can overcome these limitations in the whole supply chain to optimize storage conditions such as temperature and ventilation [3].

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Gas chromatography (GC) is an analytical separation technique to distinguish different molecular compounds based on differing adsorption and desorption at a stationary phase, the characteristic retention time. This process is also suitable for miniaturization of its bulky components. A gas chromatography system primarily consists of an injection unit, a separation column with a stationary phase for retention, and a non-selective gas sensor.

The design of the GC column is a critical aspect for a successful separation of different gas species over time. Additive manufacturing introduces additional degrees of freedom for the design of miniature separation columns compared to devices realized with standard planar microfabrication [4, 5]. With high-resolution stereolithography printing [6] arbitrary 3D geometries can be realized on the microscale and combined with aspects of packaging. This allows not only the realization of freeform spiral designs for a higher column length per footprint, but also the integration of other, previously separate components such as gas-tight fluidic connectors in the same bulk element.

## 2. Design and fabrication

Our sensor system consist of an injection unit for the addition of ethylene, a preconcentrator, a heated, packed separation column, and a $SnO_2$ metal-oxide (MOX) gas sensor (Fig. 1). Synthetic air was used as carrier gas and Carbosieve®-SII particles were packed into the columns as stationary phase for ethylene retention. For characterization of the separation performance, ethylene can be injected directly into the carrier gas flow. For higher sensitivity of the overall system, we also employ a miniature preconcentrator element using planar microtechnology developed in earlier work [7].

We developed multiple GC columns using both single and stacked spiral designs to validate freeform geometries (Fig. 2). These designs include columns with 1 mm diameter fully encased in a solid block and integrated M3 threaded connectors for pressure-tight combination with our measurement setup. In similar work we validated the material and fluidic connections up to a pressure of 5 bar and observed air-tight behavior at even higher pressures.

The columns were fabricated with a high-resolution stereolithograpy printer (*Perfactory Micro HiRes*, EnvisionTEC Inc., USA). We utilized a high-temperature acrylic polymer (*HTM140 M*, EnvisionTEC Inc.). There was no detectable outgassing from this plastic evident in our measurement results.

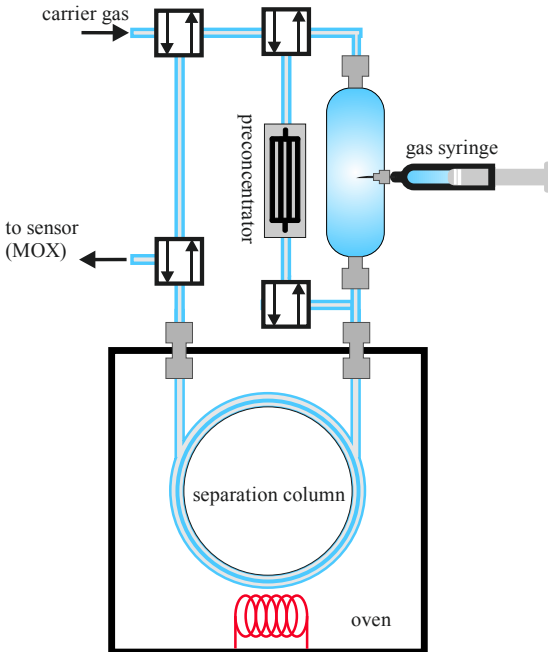


Fig. 1. Ethylene sensor system consisting of injection unit, preconcentrator, heated GC column, and MOX gas sensor.

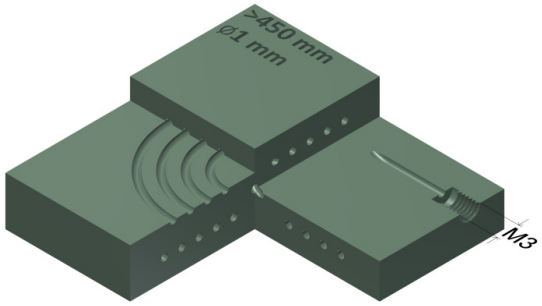


Fig. 2. Stacked spiral of 36x36x18 mm$^3$ dimensions, 1 mm channel diameter, 45 cm total column length, and integrated M3 threaded connectors.

## 3. Results and discussion

Fabricated columns (Fig. 3) have a total length of 36 cm (single spiral) and 45 cm (stacked spiral). The 36 cm columns were filled with 186 mg Carbosieve®-SII particles for retention and separation of ethylene gas. All measurements were performed at a constant flow rate of the carrier gas of 10 sccm. Samples of 1 ml, 3 ml, and 5 ml of 100 ppm ethylene gas were injected into the system heated to 55°C, resulting in a strong ethylene response. At a column length of 36 cm ethylene had a retention time of 631 s (Fig. 4 left).

An important aspect is the separation of the ethylene response especially to water vapor. In a second measurement a pre-concentrator was used to inject the gas sample into the column, where water is also enriched. The measurement was executed at 400 ppb and 100 ppm initial ethylene concentrations at a temperature of 65°C (Fig. 4 right). Here, the retention time was about 400 s due to the elevated temperature. Compared to 400 ppb ethylene, a retention time for water of 1035 s and a complete separation of the two sensor response peaks validates improved separation in the printed GC column. From these results we calculate an ethylene detection limit of 35 ppb (3σ) for the whole system.

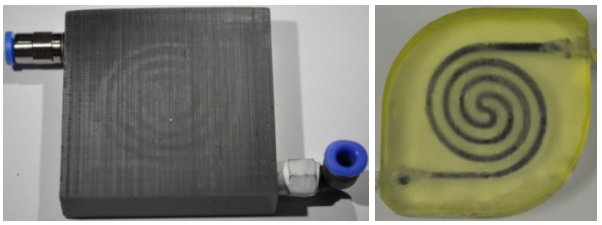

Fig. 3. Fabricated separation columns in HTM140 M plastic (left) and transparent polymer showing filling with Carbosieve®-SII particles (right).

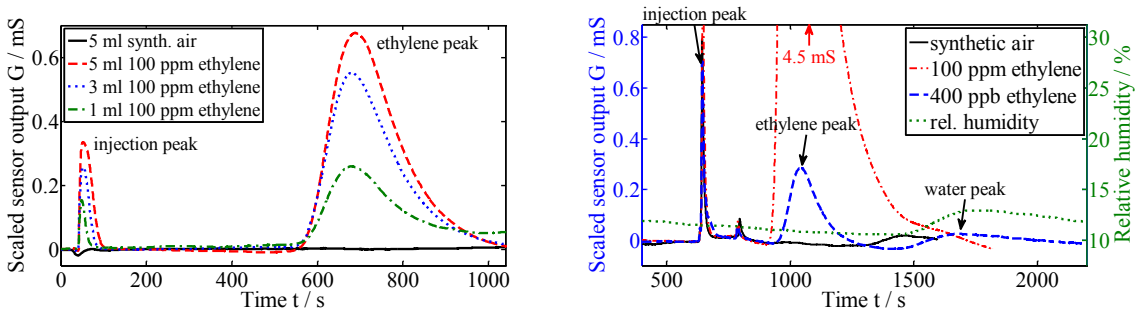


Fig. 4. Sensor response using a 36 cm single spiral column. For comparison, 5 ml synthetic air (black line) was also injected into the system.
Left: Strong output signal of the MOX sensor for 1 ml, 3 ml and 5 ml gas samples with an ethylene concentration of 100 ppm at 55°C.
Right: Output signal of the MOX sensor for 400 ppb and 100 ppm ethylene using a preconcentrator, showing a detection limit of 35 ppb (3σ) and improved separation of ethylene and water in a 36 cm column at a very low relative humidity and 65°C during the measurements.

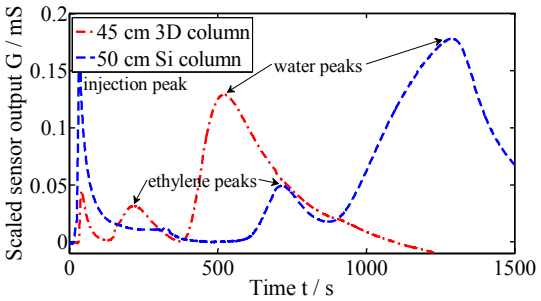


Fig. 5. Comparison of a 45 cm stacked spiral column (red) and a previously fabricated 50 cm planar silicon column with rectangular geometry (blue, see [4]), validating similar sensitivity of the 3D column at reduced retention times (faster measurements) and complete separation of a stronger water/humidity signal.

Using the stacked column design of 45 cm total length shows even better detection and separation behavior. In Fig. 5 we compare 3D column performance to a 50 cm long planar column with rectangular geometry fabricated in silicon. Measurements were executed at the same ethylene concentration but temperatures and carrier gas flow rates were optimized for the respective geometry. This along with the different lengths results in different retention times. But even at a shorter retention time, the 3D column shows similar ethylene sensitivity and much better separation to water vapor with the sensor response reduced back to baseline and thus no peak overlap. This indicates that improved packing density of the stationary phase in the round cross-section and the material of the GC column have a positive impact on separation capability.

## 4. Conclusions

We have demonstrated the feasibility of using additive manufacturing techniques to fabricate miniature separation columns for a compact, mobile gas chromatography system. The additional design freedom allows for optimization of GC column geometry with fully round cross-sections for an improved packing density of the stationary phase and vertical stacking of the column path for a higher column length per footprint. Additional, packaging aspects such as air-tight fluidic connectors can be directly integrated into the same bulk element, reducing difficulties in attaching connectors and improving reliability compared to planar chip designs. For validation we measured the ethylene response and separation, calculating a detection limit of 35 ppb and showing no signal peak overlap with humidity. Possible negative effects by using a heated plastic column such as outgassing or a negative influence on the separation could not be observed during the measurements. On the contrary, with the used material the column showed improved separation capabilities.

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