A Miniaturized GC with MEMS-Enabled Selective Preconcentration for Monitoring Exposure to Transportation-Related Air Pollutants

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Contents

Abstract

The NIOSH-supported project was aimed at the development of a miniaturized gas chromatography system to identify air hazardous pollutants (HAPs) found in transportation-related and other workplaces. Exposure to HAPs has been linked to a variety of health effects, such as cancer, asthma, autism, reduced fertility, and lower intelligence. Development of effective strategies for reducing occupational exposure to HAPs requires accurate, time-resolved measurement of exposure, but doing so is restricted by the unavailability of compact, lightweight, inexpensive portable analytical instruments. The research took important steps to address the need for lower cost, compact exposure monitors by merging microelectromechanical systems (MEMS) technology, microelectronics, and analytical chemistry to develop a portable GC system. The research resulted into the development of a *Zebra GC*, a ready-to-deploy microfabricated gas chromatography (µGC) system. The Zebra GC was characterized for detecting HAPs at parts-per-billion (ppb) concentrations in complex mixtures. Microfabricated preconcentrator (µPC), a MEMS separation column with on-chip thermal conductivity detector (µSC-TCD), the flow controller unit, and all the necessary flow and thermal management as well as user interface circuitry were integrated to realize a fully functional µGC system. The research team performed extensive characterization of µPC and µSC-TCD for target analytes: benzene, toluene, tetrachloroethylene, chlorobenzene, ethylbenzene, and *p*-xylene. Limit of Detection (LOD) of ~1 ng was achieved, which corresponds to 10 min sampling time at a sampling flow rate of 1 mL/min for analyte present at 25 ppbv. The µGC system was compared against conventional Automated Thermal Desorption-Gas Chromatograph–Flame Ionization Detector (ATD GC-FID) system for real gasoline samples in simulated car refueling scenario. The µGC system detected five peaks—three of those were identified, and required ~3 orders of magnitude lower sample volume as compared to the conventional system. The other major contribution of the research has been the development of a new GC detector and its integration with a MEMS separation column. The detector is a plasma-based photo ionization detector and has been able to yield 10pg detection limit, comparable with that of FID, while consuming a few milliwatts of power. The stand-alone detector has been integrated with a separation columns on a single chip improving the overall separation efficiency of µGC. The new detector has a detection limit 2 orders of magnitude better than TCD and its output has insignificant fluctuation in the presence of temperature or pressure programming. The detector is more suitable than TCD for integration into Zebra GC and provides a better solution for near real-time detection of HAPs.

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Significant Findings

- A ready-to-deploy microfabricated gas chromatography (µGC) system has been developed and characterized for detecting hazardous air pollutants (HAPs) at parts-per-billion (ppb) concentrations in complex mixtures has been described. Microfabricated preconcentrator (µPC), a MEMS separation column with on-chip thermal conductivity detector (µSC-TCD), the flow controller unit, and all the necessary flow and thermal management as well as user interface circuitry were integrated to realize a fully functional µGC system. Limit of Detection (LOD) of ~1 ng was achieved, which corresponds to 10 min sampling time at a sampling flow rate of 1 mL/min for analyte present at 25 ppbv. An innovative method using flow-manipulation generated sharp injection plugs from µPC even in the presence of a flow-sensitive detector like µTCD. The µGC system was compared against conventional Automated Thermal Desorption-Gas Chromatograph–Flame Ionization Detector (ATD GC-FID) system for real gasoline samples in simulated car refueling scenario. The µGC system detected five peaks—three of those were identified, and required ~3 orders of magnitude lower sample volume as compared to the conventional system.
- A new microfabricated gas detector (µDPID) has been designed and fabricated. The chip-based detector is a plasma-based photo ionization detector. The electric output of the detector has insignificant dependence on pressure or temperature variations, and hence, is more suitable for gas chromatography. The detector has been designed in both silicon and glass substrates. µDPID has achieved detection limits down to 10pg. Its performance is comparable to that of commercially available flame ionization detectors. The detector has also been integrated with a microfabrication separation column. The integration chip is less than 3cm on each side and is capable of separation and identification of analytes even when the column is temperature or pressure programmed to improve separation. The next generation of the Zebra GC can include these chips instead of µSC-TCD. This will facilitate the detection of fast eluting compounds including benzene.

Translation of Findings

According to the US Department of Labor, there are 8 million workers in the transportation and material moving occupations, which fall under **NIOSH's Transportation, Warehousing, and Utilities (TWU) sector**. These occupations have been associated with increased risk of lung cancer, cardiovascular disease, and gastrointestinal disorders. These workers are exposed to chemical vapor health hazards that have well-documented associated health effects. These include aromatics, polycyclic aromatic hydrocarbons, and carbonyls. Benzene is an established leukemogen, and chlorobenzene is associated with neoplastic liver changes. Ethyl acrylate causes respiratory and gastrointestinal irritation and has the potential for sensitization. Exposure to methyl ethyl ketone is associated with central nervous system effects and peripheral neuropathy. Naphthalene exposure results in cataract formation, ocular toxicity, and blood dyscrasias. Styrene health effects include deficits in color vision and high frequency hearing loss, in addition to respiratory irritation. Tetrachloroethylene is a confirmed animal carcinogen, with unknown relevance to humans. Toluene occupational exposure has been associated with cerebellar disintegration, cardiac and hematological toxicity. Xylene is well documented as an irritant of the eye and upper respiratory tract. Current sampling and analytical methods for these compounds require collection of samples at the work site and subsequent laboratory analysis.

Thus, they do not provide real-time measurements that could alert workers to a chemical hazard in a timely manner. Additionally, the resulting data represent a time-weighted average (TWA) of exposure for the duration of sampling and cannot be used to identify specific tasks with elevated risk for exposure. A portable field instrument for rapid analysis and characterization would significantly advance the understanding of occupational health risks stemming from exposure to chemical hazards. Our project is a response to this need and provides a µGC prototype that can be used for detection and analysis of HAPs.

Outcomes/Impacts

The work has been presented in several conferences and also published in reputable journals. The work, therefore, has been widely disseminated to the scientific and technical communities. The work will continue to integrate the µDPID with the rest of the system and create the second generation of the Zebra GC. In addition, Virginia Tech's Intellectual Property (VTIP) is in contact with several companies who may be interested in this technology and is currently exploring the opportunity of licensing the technology to interested companies.

Scientific Report

Specific Aims

The National Occupational Research Agenda for the Transportation, Warehousing and Utilities (TWU) sector lists as one of four strategic goals, "Identify, evaluate, and reduce chemical, biological, and physical occupational hazards and exposures that results in a reduction of occupational injuries, illnesses, and fatalities in the TWU sector" (NIOSH, 2009). Exposure to hazardous air pollutants (HAPs), also known as air toxics, is especially challenging to measure because standard methods are only able to provide time-integrated, rather than continuous and real-time, information. Current practice typically requires collection of a sample in the field using a canister or sorbent tube, transport to the lab, and then analysis by gas chromatography (GC) with a detector to identify and quantify the species present. This limitation makes it very difficult to prioritize exposures that should be targeted for mitigation strategies, such as engineering controls, personal protective equipment improvements, communication tools, and substitution programs. The aim of this project was to address this critical need and employ microelectromechanical systems (MEMS) technology to develop a miniaturized GC (µGC) for field analysis of HAPs. The system integrates sampling and laboratory analytical functions on a portable printed circuit board platform. This project had two specific aims:

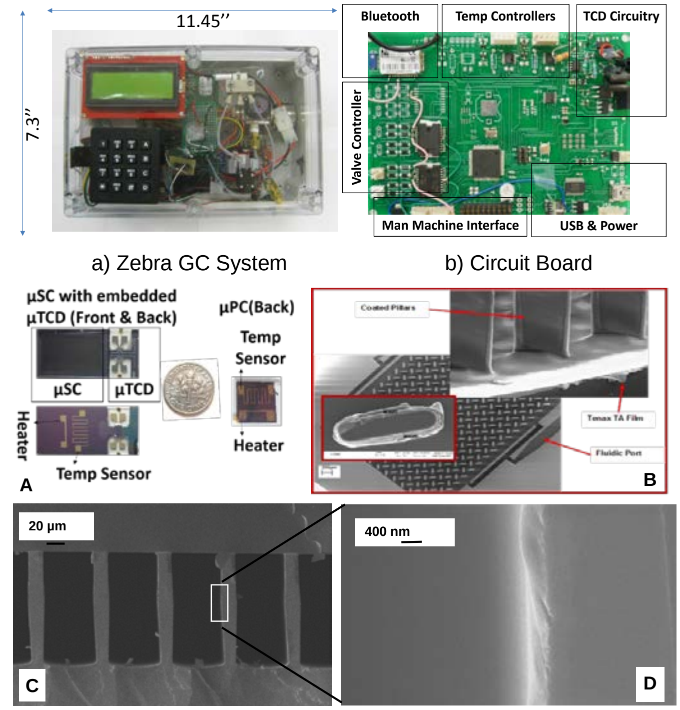
1. **Design, develop, and evaluate the µGC system for measuring exposure to HAPs.**
2. **Evaluate the system functionality for on-field HAP monitoring through comparison with conventional techniques.**

In the long term, the development of such a unique technology provides us with a powerful tool to assess on a near real-time basis the effects of workplace conditions and activities on HAP generation and subsequent exposure. This capability has three major applications: (1) to allow identification of specific activities that are associated with elevated exposures so that mitigation efforts might be applied most effectively; (2) to enable greatly improved monitoring of personal occupational exposure in health effects studies; and (3) to provide a platform for a real-time detection system that can alert workers to hazardous conditions.

Results and Discussions

1. Development of Zebra GC system:

The research team, through invention and innovation, has developed a MEMS enabled portable GC (**Figure 1**) consisting of a micropreconcentrator (µPC), a MEMS separation column (µSC) with an embedded micro thermal conductivity detector (µTCD), the flow controller unit, and all the necessary flow and thermal management units as well as the user interface circuitry. The µPC is a 240µm deep cavity in silicon with micro-posts coated with Tenax® TA thin film.[1, 2] The µSC is a 240µm deep, 80µm wide, 2m-long OV-1 coated channel in silicon. A glass substrate having patterned 40nm/100nm/25nm Cr/Ni/Au stack caps the silicon channel. The metal films on the glass serve as the on-chip µTCD. The resistor at the channel entrance acts as the reference TCD and resistor at the channel outlet acts as the detector.[3, 4] A differential measurement of the signal creates the chromatogram. Monolithic integration (on a single chip) of µSC with µTCD minimizes chip-to-chip interfaces and the band-broadening. Our µPC and µSC have their own on-chip heater and temperature sensor located on the backside. More details about the operation of our µPC and our µSC with embedded TCD can be found in our previous publications.[1-8] The Zebra GC operation consists of four major phases: loading, injection, analysis, and cleaning, as shown in **Figure 2**. During the loading phase, the environment sample is loaded in the µPC at a steady flow rate of 1mL/min using a micro-pump. Once loaded,



a) Zebra GC System

b) Circuit Board

c) Micro Devices & SEM images

Figure 1: Portable Zebra GC. (c-B) SEM images showing Tenax TA coating and micro-posts in µPC (c-C, d-D) dimethyl-polysiloxane coating on the interior wall of the column channel.

the valves are switched to flow helium which serves as carrier gas from an on-board mini-cylinder to register µTCD's baselines. **For improved chromatographic resolution, we generate a sharp injection plug by heating the µPC first (ramp rate 30°C/s) and then flushing it with helium. This reduces the peak width at half height (PWHH) from 2s to about 350ms. The flow switching is made transparent to the µTCD by providing an alternate flow path as shown in the schematic.** After injection, the analytes separate in the column and are subsequently detected at the outlet by interfacing µTCD equipped with an ultra-low noise on-board 24-bit ADC. Once the analysis phase is completed, the µPC is heated to an elevated temperature with helium flowing through it to remove any residual analytes. The average running time and power consumption for one complete measurement cycle, assuming 5 minutes loading and 2 minutes separation time, are 7 minutes and 1.1 Watts, respectively. Each battery charge (capacity – 2200mAh) and helium refill (95 mL, 2700 psi) will last more than 150 and 5000 complete measurement cycles, respectively. **It should be mentioned that our NIOSH-funded Zebra GC compared to other previous efforts in µGC is novel in that** 1) it does not use any commercial traps while providing high sample capacity with the unique micro-pillar based preconcentrator developed in the PI's lab, 2) it does not utilize any valve between the µPC and the µSC, hence suppressing the dead volume, 3) it uses an on-chip detector, hence alleviating the need for any transfer lines between the column and detector, a source for chromatographic degradation, and 4) it uses a bypass line and two Y-connectors along with a temperature ramping scheme to generate a very sharp injection plug width while having continuous gas flow through the column/detector. We have characterized the µPC in terms of sample capacity, breakthrough volume, desorption peak width, and desorption

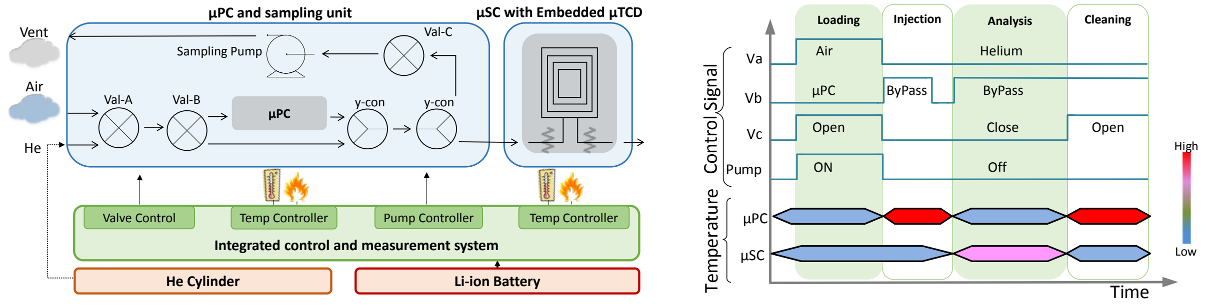


Figure 2: (left) System block diagram, and (right) operation cycles and timing diagram

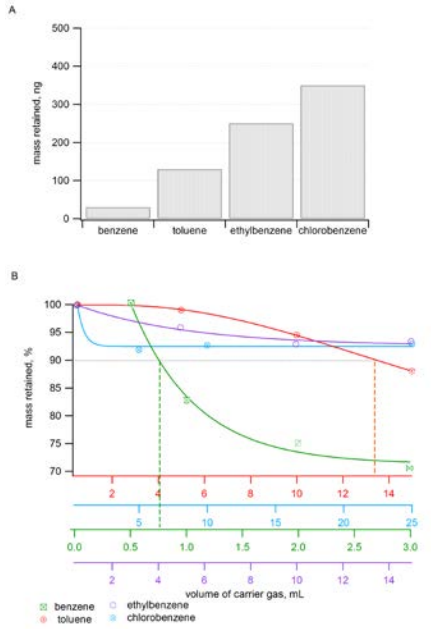


Figure 3: (A) µPC sample capacity. (B) Breakthrough curves for benzene, toluene, chlorobenzene, and ethylbenzene.

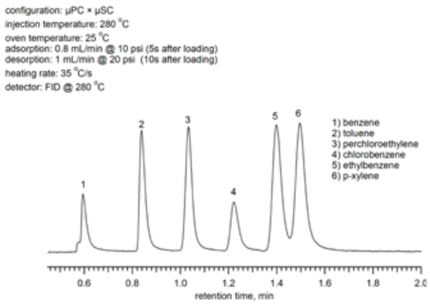


Figure 4: Separation of test compounds on an integrated µPC/µSC.

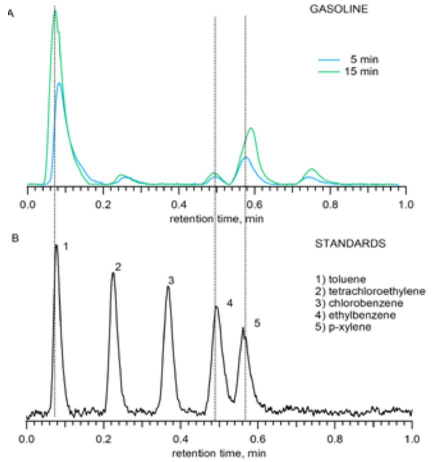


Figure 5: Chromatogram of (top) a gasoline vapor and (bottom) a standard mixture using the Zebra GC.

efficiency. **Figure 3A** illustrates that the µPC can adsorb compounds ranging from ~30-400ng. These results indicate that µPC can retain sufficient amount of compound well above the detection limit of our µTCD (~1ng). It is evident from the graph that the Tenax® TA retains compounds with high boiling points more effectively as compared to low boilers such as benzene. However, the amount of benzene retained by the µPC is still enough to be detected by the µGC. **Figure 3B** illustrates that for four of the compounds tested only benzene has a breakthrough volume less than 1mL. While toluene, chlorobenzene and ethylbenzene have breakthrough volumes above the typical volume sampled in our experiments. Additionally, we achieved 99% desorption efficiency by heating the µPC to 250°C for these compounds. We also characterized the performance of the µSC and were able to successfully separate the compounds in a standard test mixture containing benzene, toluene, perchloroethylene, chlorobenzene, ethylbenzene, and p-xylene when the sample was injected through the µPC and detected by a commercial FID (**Figure 4**). We also tested the fully-assembled µGC system. We used **gasoline** to mimic occupational exposure to BTEX. We placed 50mL of gasoline in a 100mL beaker and placed it inside a large glass chamber. We circulated air inside the chamber but outside the beaker that contains gasoline at 500mL/min to simulate a car refueling scenario. We sampled vapor at ambient temperature and pressure with the chamber open to the atmosphere. We allowed the chamber to be filled with vapor for 5min. After that, we analyzed the VOC emitted using the µGC for 5 and 15 minutes sampling times and room temperature separation. As seen in **Figure 5**, the Zebra GC detected four peaks in the gasoline vapor among which three were present in the standard test mixture: toluene, ethylbenzene, and p-xylene. It should be noted that the column separates benzene from these compounds, however, since it elutes very early, the negative and positive peaks generated by the TCD at the onset of sample injection and flow switching between the µPC and the bypass line, masks the detection of benzene and any compound eluting in the first 12 seconds in the chromatogram. **As seen later, using our micromachined PID, this issue is resolved as PID response is insensitive to this flow switching.** To compare results with a conventional system,

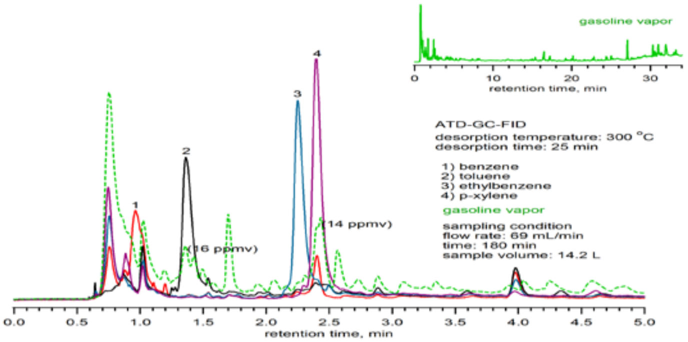


Figure 6: Chromatogram of gasoline vapor (green) sampled using sorbent tubes containing ~200mg of Tenax TA®. The conventional column contains (5% phenyl-, 95% dimethyl-polysiloxane). Toluene peak at ~1.4min (16*ppmv*) and *p*-xylene (14 *ppmv*) peak at ~2.4min. Benzene and ethylbenzene not detected. Temperature programming: 35˚C, hold for 10min, 5˚C/min to 150˚C, final hold time: 1min. Full chromatogram of gasoline vapor (*inset*). Red, black, blue, and purple chromatograms are for benzene, toluene, ethylbenzene, and *p*-xylene standards, respectively.

we sampled the gasoline vapor using sorbent tubes packed with Tenax® TA at a sampling flow rate of 69mL/min for 3hrs. We collected ~12.4L of gasoline vapor in air. We desorbed the sorbent tubes using a thermal desorption system that is coupled to a GC-FID using a conventional column. We were only able to identify toluene and *p*-xylene with concentration of 16 and 14 *ppmv*, respectively (**Figure 6**). In both systems including the µGC coupled to an FID, we were not able to clearly identify benzene because it co-elutes with the other low-boiling point components in gasoline. **Nevertheless, the sample volume we collected and analyzed in the *µ*GC was ~3 orders of magnitude lower than those collected on sorbent tubes.**

2. Micro Discharge Photo Ionization Detector: We have also developed the first micro-machined non-destructive photoionization gas detector, referred to as the micro-discharge photoionization detector (µDPID) [9]. <u>The detector is easy to fabricate, inherits the properties of being universal, non-destructive, low power (<5mW), and sensitive (LOD of ~50pg), and can be integrated with a MEMS column.</u> Our stand-alone µDPID is 20mm × 10mm and is made on a glass substrate. **Figure 7** shows the optical image of the detector. The detector has a pair of excitation electrode with a 20µm gap between them to produce a DC discharge in helium. The device also has a bias electrode and a remote collector electrode downstream from the microplasma. The discharge is excited at 500V with a helium flow of 1sccm. Helium discharge results in the generation of a complex mix of positive and negatively charged ions, metastable He atoms, electrons, and photons **(ionizing flux)**. The high energy components of this ionizing flux flow downstream towards the bias electrode and are responsible for ionization of analyte species eluting from the GC column. The ionized species thus induce a current at the collector which is measured with a picoammeter. We have tested the detector for at least 24 hours of continuous operation and observed no deterioration of the excitation electrodes. Additionally, we have demonstrated that reducing the *l* from 5mm to 1.5mm and *w* from 2.5mm to 1mm could improve the LOD from ~350pg to ~50pg. This is due to the fact that as the distance between the helium discharge and the bias electrode is decreased, the flux observed at the bias electrode increases. However, the extent to which *l* can be minimized is limited by the possibility of fragmentation of the analyte upon their introduction at the bias electrode and subsequent back-diffusion. In a similar manner, signals were observed to increase as the distance between the collector and bias

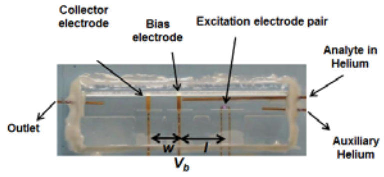


Figure 7: Our developed µDPID.

electrodes decreased owing to insufficient time for recombination in the collector volume. *These optimization results have been published in Sensors and Actuators B.*[10]

3. GC-on-Chip: While being universal and simple to operate, μTCD could not provide very sensitive detection and was sensitive to flow and temperature variations. This restricted the integrated module to operate under flow and temperature programming conditions, and therefore rapid screening of complex mixtures spanning over a wide range of boiling points was not possible. We have recently developed a unique GC-on-chip module (**Figure 8**) comprising a monolithically integrated semi-packed micro separation column (μSC) and a highly sensitive micro helium discharge photoionization detector (μDPID). While semi-packed μSC with atomic layer deposited (ALD) alumina as a stationary phase provides high separation performance, the μDPID implemented for the first time in a silicon–glass architecture inherits the desirable features of being universal, non-destructive, low power consumption (1.4 mW), and responsive. The integrated chip is 1.5 cm × 3 cm in size and requires a two-mask fabrication process. Monolithic integration alleviates the need for transfer lines between the column and thedetector which improves the performance of the individual components with overall reduced fabrication and implementation costs. The chip is capable of operating under the isothermal as well as temperature and flow programming conditions to achieve rapid chromatographic analysis. The chip performance was investigated with two samples: 1) a multi-analyte gas mixture consisting of eight compounds ranging from 98 °C to 174 °C in boiling point (**Figure 9a)** and 2) a mixture containing higher alkanes (C9–C12) as shown in **Figure 9b**. Our experiments indicate that the chip is capable of providing rapid chromatographic separation and detection of these compounds (<1 min) through the optimization of flow and temperature programming conditions. The GC-on-chip demonstrated a minimum detection limit of ~10 pg which is on a par with the widely used destructive flame ionization detector (FID). *These results have been published in Lab on a Chip.*[11]

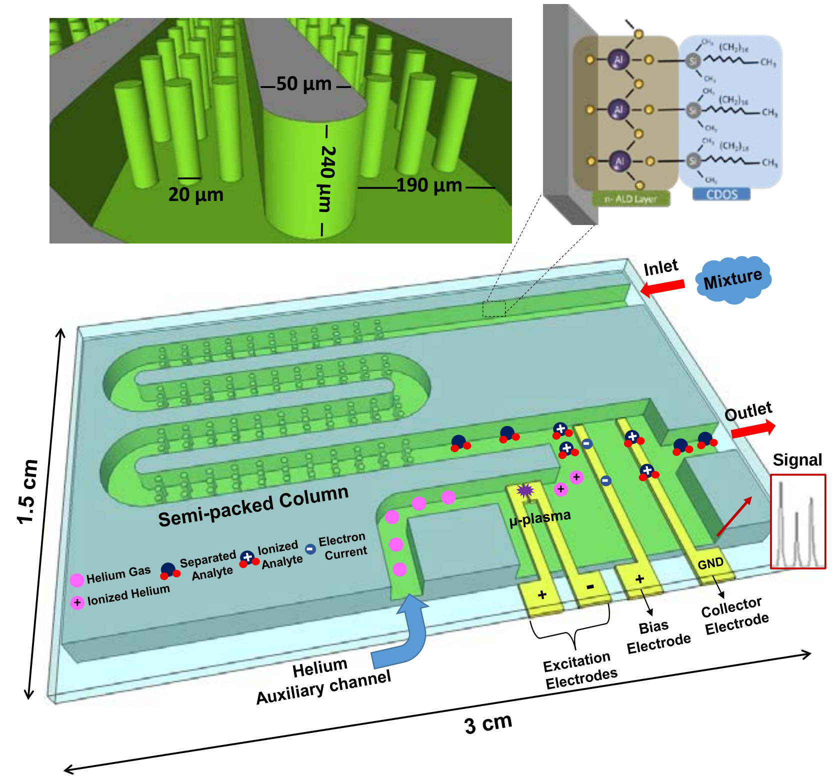


Figure 8: Conceptual image showing the operation of the monolithic integrated chip (GC-on-Chip). The top right image shows the stationary phase coating procedure while the top left image shows the channel dimensions of the micro separation column.

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