



Characterization of a micro-helium discharge detector for gas chromatography



Shree Narayanan^a, Gary Rice^b, Masoud Agah^{a,*}

^a VTMEMS Lab, Bradley Department of Electrical and Computer Engineering, Virginia Tech, Blacksburg, VA, USA

^b Department of Chemistry, College of William and Mary, Williamsburg, VA, USA

ARTICLE INFO

Article history:

Received 2 April 2014

Received in revised form 20 July 2014

Accepted 6 September 2014

Available online 16 September 2014

Keywords:

Micro gas chromatography

Gas detector

Photoionization

Helium discharge

ABSTRACT

The characterization of a miniaturized helium discharge ionization detector (μ HDID) for micro gas chromatography through a number of parameterized experimental measurements is presented. The response of the detector is directly related to the He discharge voltage, bias electrode-to-discharge distance, and collector-to-bias distance by a simple mathematical expression. The effect of the bias voltage and the bias and collector electrode spacings relative to the He discharge were found to improve the detector response as much as 12-fold depending on the design and various operational parameters. The detection of octane from a headspace injection was performed over 24 h of continuous operation with no noticeable degradation. Finally, a sensitivity test for octane in air was conducted using the design and parameters with the best response to obtain an absolute limit of detection of 60 pg for octane in air at 3.3 mW.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Micro gas chromatography (μ GC) is based on developing miniaturized, portable systems capable of identifying the composition of a gas mixture by separation into its individual components. Such analyses are highly applicable for homeland security, space exploration, on-site or distributed environmental monitoring mechanisms, food assessment, etc. [1–13]. In a typical μ GC system, the sample mixture is first collected on an adsorbent bed referred to as the pre-concentrator. When thermally spiked, this device releases the adsorbed species in a sharp vaporized plug. This narrow plug enters a microfluidic channel, called the separation column, which is coated with a stationary phase film to chemically interact and retard the various analytes of the plug to different extents. The analytes are then separated in time and, ideally, elute out of the column one-by-one into a detector. The movement of the analytes through the entire system is facilitated by an inert carrier gas (mobile phase) such as helium or nitrogen.

Miniaturization offers unique advantages such as light-weight, low power consumption, less reagent usage and innovative architectures apart from lower cost when batch fabricated [14–27]. Stereotypical miniaturization utilizes components fabricated in silicon/glass. Common implementations involve etching a narrow bore microfluidic channel in silicon/glass wafers, with capillary

dimensions similar to conventional GC columns, or fabricating posts within the silicon cavity and coating with an adsorbent material. The primary incentive is the ability to conveniently pack a 1–2 m length tubing (cavity) into a 2 cm \times 4 cm \times 500 μ m silicon die without having to wind equivalent length capillary tubing into a large coil. In addition, heating a silicon die with on-chip heaters is energetically far less taxing compared to heating capillary tubing with a convection oven.

The choices for detectors in the micro-world are numerous. While traditional GC systems are dominated by flame ionization detectors (FID), electron capture detectors (ECD) and flame photometric detectors (FPD), μ GC offers the possibility of obtaining signals via other forms of reactive processes using sorptive sensors that transduce into electrical, acoustic or optical domains [28–34]. In general, any concentration-sensitive detector, such as the thermal conductivity detector (TCD), is more pliable to be reduced in size [35,36]. It should be noted that while ionization detectors such as the FID provide robust performance and sensitivity, efforts to miniaturize them do not yield comparable detection levels since the hydrogen flame loses its ionizing potential when reduced in size [37,38]. On the other hand, sorptive and thermal sensing detectors have inherent limitations since they are more temperature sensitive and hence their implementation and application has been inadequate as well. Mass spectrometry (MS), considered the gold standard in conventional analytical techniques, has also been subject to miniaturization. A majority of these efforts has focused on reducing the size of a MS using techniques that are not found in silicon micromachining. This has resulted in dimensions slightly

* Corresponding author. Tel.: +1 5402312653.

E-mail address: agah@vt.edu (M. Agah).

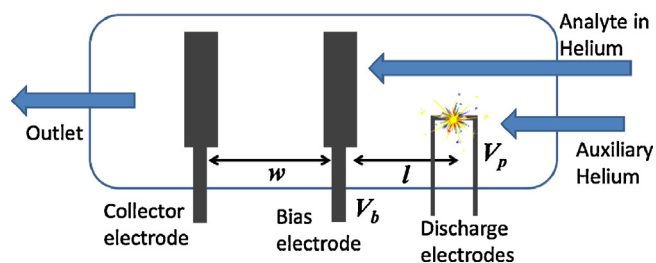


Fig. 1. A schematic diagram showing the dual-inlet, single-outlet μ HDID. The analytes from a micromachined separation column are introduced at the top of the bias electrode, bypassing the auxiliary channel fed helium microdischarge. Ionization of analytes in the region between the collector and bias electrodes results in the detector response at the collector electrode. The parameters of interest, namely l , w , V_p , and V_b are denoted.

larger than that found in microGC and a power dissipation on the order of tens of watts [39].

Commercially available μ GC systems have adopted a hybrid approach wherein the detector is similar in style to conventional ultraviolet photoionization detectors (UV-PID). These systems offer excellent detection sensitivity, but are somewhat restricted by the photoionization energies available (<11.7 eV with argon lamps) as well as incorporation into a μ GC system. Micro-discharges or plasmas have also been utilized in gas detectors since 1991. Eijkel et al. reported on a detector for μ GC that fragmented the analytes in a DC microplasma to produce diatomic fragments from which emission was detected spectrophotometrically [40]. Improvements on this technique included an innovative electrode structure to generate a pulsed plasma with drastically reduced power consumption [41,42]. Spectrophotometric detection is an intensive operation that can consume power on the order of watts. An alternative is to monitor the current through the discharge itself as reported by Fu et al. [43]. However, a common concern with these designs is the fouling of the electrodes due to fragmentation of the analytes. Fragmentation also does not allow for the analytes to be subjected to further analysis.

We previously reported on a proof-of-concept micro-helium discharge detector [44] to address the need for a sensitive, low-power, easy-to-fabricate universal detector. This microdischarge utilizes high-energy photons and excited state helium metastable species to ionize the analytes and the resultant current monitored on a remote collector electrode. Their lack of sensitivity to temperature makes them suitable for robust gas detection systems [45]. A limit of detection (LOD) of 350 pg for octane was demonstrated. Additional design parameters for our μ HDID are considered here. Specifically, the effect of the He discharge voltage, distance of the bias electrode from the He discharge, collector electrode from bias electrode, and the bias voltage are parametrically studied. The results were used to choose the best design to enhance the LOD.

2. Theory

The micro-helium discharge ionization detector (μ HDID) is an ionization style detector that operates by measuring the resultant current from ionization of the analytes without molecular fragmentation (Fig. 1). It utilizes a high voltage DC discharge in helium across a 20 μ m gap as the source of high energy photons and metastable excited helium atoms, which are thought to be the dominant species responsible for the ionization of analyte species. This is partly inspired by a pulsed discharge helium ionization detector that utilizes a pulsing technique to arc across an electrode pair to generate the excitation source [46,47]. Fig. 1 is a schematic showing the concept and design parameters of the detector. Apart from the discharge electrode pair to produce the He micro-discharge, the

device also consists of a bias electrode and a remote collector electrode downstream from the microplasma. Analytes contained in a helium carrier from the separation column are introduced into the detector at the bias electrode. The space between the bias and collector electrode defines the “volume of the collector” and dictates to some extent the level of signal response generated.

When suitably excited, the He discharge results in the generation of a complex mix of positive and negatively charged ions, metastable He atoms, electrons, and photons. These omnidirectional energetic particles constitute what is called the ionizing flux. Some of these particles, such as metastable helium atoms and ions, flow downstream due to pressure-driven flow. Thus, the ionizing flux at the bias electrode is a mix of positive and negatively charged particles as well as high energy photons and metastable He atoms. The high energy components of this ionizing flux (normally considered to be photons with energies >10 eV and metastable He atoms with energies of 19.8 eV) are responsible for ionization of analyte species eluting from the GC column. The transmission of this flux through the detector volume decays exponentially due to absorption, and is given by

$$I_b = I_0 e^{-\alpha l} \quad (1)$$

I_b , the flux observed at the bias electrode is related to the initial discharge emission I_0 by Beer–Lambert’s law for photon flux transmission. α is the absorption coefficient of helium over the length of the detector (l) from the He discharge to the bias electrode. One can rationalize that l should be minimized to increase the flux density available at the bias electrode. On a similar note, the gap width w should be maximized to increase the total flux available for the analyte species within the collector volume where the photon flux needs to be absorbed to the maximum extent. However, recombination processes with electrons within this volume can cause a portion of the generated carriers to be neutralized and hence not detected. The net effect of these factors determines the distance from the collector electrode in which a generated charge carrier will result in a favorable current. In the presence of a bias voltage, the effect of an electric field between closely spaced bias and collector electrodes can be advantageous in isolating the generated carriers within the collector volume more efficiently. The lifetime of metastable He species available for collisional energy transfer to analyte species will be a factor as well. A number of these factors are considered in the following discussions.

3. Experimental

3.1. Materials and sample preparation

Borosilicate glass wafers (Borofloat 33, Schott, NY) of 700 μ m thickness and 100 mm diameter were used as substrate wafers for fabrication of the microplasma devices. The separation columns were prepared from 100 mm <100> silicon wafers (Test grade, University Wafers, MA) of 500 μ m thickness.

For the design characterization experiments, the headspace of a 1.8 mL autosampler vial filled with about 120 μ L of reagent grade n-octane served as the source for constant vapor phase concentrations for gas-phase injections. For the limit-of-detection (LOD) experiments, 25–200 μ L of analytical grade n-octane were pipetted into a custom-made 1 L volumetric flask. The mouth of the flask was sealed with a 24/40 septa and left overnight for the octane to volatilize. To prepare a different dilution, the octane in the flask was cleared by removing the septa seal and running the flask through a cycle of nitrogen purging, oven heating at 80 $^{\circ}$ C, and repurging with nitrogen. After letting the flask cool down to room temperature, the volume of octane corresponding to the desired concentration

Download English Version:

<https://daneshyari.com/en/article/744359>

Download Persian Version:

<https://daneshyari.com/article/744359>

[Daneshyari.com](https://daneshyari.com)