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MICRO PHOTO IONIZATION DETECTOR FOR VOLATILE ORGANIC COMPOUNDS: STATE OF THE ART AND FUTURE STUDIES

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ABSTRACT

Volatile Organic Compounds (VOCs) are a class of carbon-containing chemicals that have a high vapor pressure at ambient temperature. Typical indoor sources of VOCs are varnishes, paints, solvents, cleaning materials, etc. In addition, outdoor sources such as automobile and industrial waste also contribute to both indoor and indoor VOC pollution [1]. Many VOCs are harmful to humans, including benzene, which is carcinogenic and has no safe recommended level of exposure [2], [3]. The European Commission established, with effect from 2010, a regulation for benzene exposure at a maximum limit of 5 µg/m³ (1.6 ppb) [4]. In addition, within the European Union, regulations and guidelines are established to maintain a healthy indoor air quality [4], [5].

Gas Chromatographs (GC), which can separate, identify and quantify different chemicals, can be used to detect airborne VOCs. However, commercial GCs are still heavy, bulky, slow, lab-based equipment. The development of a transportable, sensitive and fast GC analysis can improve gas evaluation and device miniaturization can contribute to this achievement. One of the main components of a GC is the detector, responsible for quantifying the chemicals. This work is centered on a GC detector, namely the photo ionization detector (PID). The objective is to report the state of the art in PID miniaturization with emphasis on its fabrication processes and suggest future studies and designs as solutions for further development of µPIDs.

PIDs can be classified according to the ionization source. When the ionization source is unseparated from the ionization chamber by a window, the ionization source is usually a discharge on a noble gas such as Helium, and is called discharge photo ionization detector (D-PID); or when the ionization source has no fluidic connection to the ionization chamber, which is the lamp photo ionization detector (L-PID). Fig. 1 shows the basic elements of two types of photo ionization detectors. In both devices, a gas sample containing the chemicals flows through the ionization chamber, where photons emitted by the ionization source reach the sample molecules. As a general rule, if the ionization energy of the photon is greater than the ionization potential of the molecule, ionization occurs. The electrodes establish then an electric field in the ionization chamber where the ionized molecules generate an ionization current

proportional to their concentration. Based on an external calibration, the electrical signal can be translated into a VOC concentration.

Commercial PIDs have dimensions of the order of 10 mm, which are already small compared to overall commercial GCs sizes, and the ionization chamber of commercial PIDs have volume ranging from 100 µl to 200 µl. Recently, PIDs with ionization chambers 100 times smaller (volume close to 1 µl) were developed, where the reductions in ionization chamber size were achieved with microfabrication techniques using photolithography and etching [6]–[11]. The miniaturization of PIDs is favorable to improve both PID and GC performance. Small ionization chamber size allows for faster response times at a given flow rate. Diminishing ionization chamber also reduces carrier gas consumption from the gas chromatograph, which enables greater autonomy of the GC in field use. At the detector performance level, a lower ionization chamber volume facilitates a smaller gap between the electrodes, improving ion and collection efficiency [7]. There is also the possibility of avoiding remixing of elements eluting from the separation column. Miniaturized PIDs developed recently are presented in the two paragraphs below and in Tab. 1.

For PIDs using a UV Lamp as the ionization source, the first considerable reduction of ionization chamber volume was achieved by Sun *et al.* (2013) [6], where they introduced a nozzle inside a conventional ionization chamber, yielding a 10 µl volume chamber. Another important feature of this design was placing the collection electrode close to the UV lamp window, in a region that optimizes collection of ions. Also the accelerating electrode was placed in a groove in the nozzle, which protected it against direct UV radiation. Recently, Zhu *et al.* (2014) [7] used photolithography and microfabrication to make a L-µPID on a conductive silicon wafer and glass architecture. Their device consisted in a microfluidic channel in Si etched with deep reactive ion etching (DRIE) and the electrodes were the Si walls of the channels, a commercial UV lamp with 10.6 eV was mounted on top of the channel and the final ionization chamber volume was 1.3 µl. Zhou *et al.* (2016) [8] fabricated another L-µPID using conductive silicon wafer and glass. Their design had a 2 cm long straight channel with cross section etched by DRIE, resulting in an estimated 0.5 µl ionization chamber volume.

Microfabrication techniques are also used to make discharge PIDs. [9] Akbar et al. (2015) used silicon-glass to fabricate a D-µPID where the channels and chambers of the detector were etched with DRIE. His device was also integrated with a separation column on a single chip. The detector electrodes were made with e-beam evaporation of 700 nm/40 nm thick Ti/Au metal stack. Also using silicon-glass architecture Zhu *et al.* (2016) [10] designed a D-µPID on a straight channel where the Si wafer was diced and wet etched. The glass wafers were also diced and the Si/glass parts were bonded together to form the three microchannels of the device with estimated ionization chamber volume of 1.4 µl. In a slightly different approach, Narayanan *et al.* (2016) [11] developed a D-µPID using two 700 µm thickness Borosilicate glass wafers. After wet etching the main fluidic parts and creating the electrodes, the two parts were diced and bonded with epoxy.
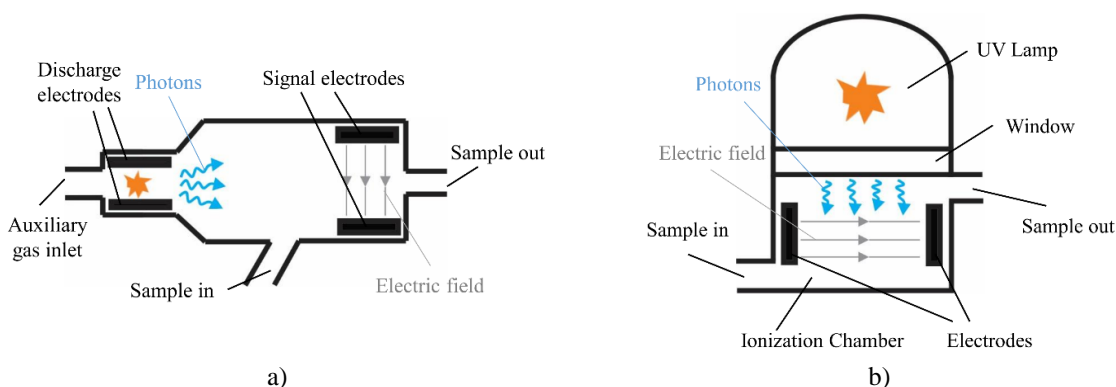

Figure 1: Photo ionization detectors. a) D-PID. b) L-PID.

Table 1: Microfabricated PIDs manufacturing and design properties.

Reference	Ionization source	Manufacturing Main Materials	Design main features and dimensions	Ionization chamber
Sun *et al.* (2013)	UV Lamp, 10.6 eV	-	Introduced nozzle inside a conventional ionization chamber.	10 µl
Zhu *et al.* (2015)	UV Lamp, 10.6 eV	Highly doped p-type <100> single-sided polished conductive Si wafers with resistivity 0.001 - 0.005 Ω.cm and 380 µm thickness; 500 µm thick Pyrex glass wafers.	Ionization chamber is a microchannel with cross-section 150 µm (width), 380 µm (depth) and length 2.3 cm. Entire overall channel size is 15 mm × 15 mm. Microchannel area covered by lamp is 2.4 mm x 2.4 mm.	1.3 µl
Zhou *et al.* (2016)	UV Lamp, 10.6 eV	conductive p-type <100> silicon wafer and glass.	Conductive silicon wafer and glass architecture. Channel etched 380 µm (width) × 380 µm (depth) x 2 cm (length).	0.5 µl
Akbar *et al.* (2015)	Helium discharge	Silicon and glass architecture.	Micro separation column fabricated on the same chip. Overall size (1.5 cm x 3 cm)	Not mentioned
Zhu *et al.* (2016)	Helium discharge	500 µm thick p-type <100> double side polished Si wafer with 500 nm thick thermal oxide layers; 100 µm thick Borofloat 33 glass wafer; 500 µm thick Borofloat 33 glass wafer.	Microchannels formed by Si and glass. Three main channels: 1) Auxiliary helium; 2) Analytes; 3) Outlet channel. Cross-section 380 µm (width) and 500 µm (depth);	1.4 µl
Narayanan *et al.* (2014)	Helium discharge	Two (bottom and top) Borosilicate glass wafers 700 µm thickness and 100 mm diameter used as substrate.	Channel etched 250 µm (depth).	Not mentioned

Most of the recently published literature on PIDs mentioned here show important features in the miniaturization of the devices, such as low ionization chamber volume, a shortened distance between electrodes and low energy consumption. These characteristic are relevant to improve the PID and GC performance. Despite that, the field of miniaturized PIDs have multiple aspects to improve in terms of knowledge and design. For example, D-PIDs still suffer from high noise and L-PIDs are still using commercial PIDs lamps. Also, the direct incidence of photons on the electrodes of microfabricated PIDs are still a problem, since it causes photoelectric effect, which depletes minimum detectable limit. Most miniaturized PIDs are fabricated using etching and lithography, which are expensive manufacturing techniques. Future designs should be able to have cheap prototypes for testing how µPIDs parameters influence their performance, such as flow, pressure, temperature, rarefaction, carrier gas, construction materials, etc. Our team is working to develop a design to address those needs.

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