MICROFABRICATED MODULAR PHOTOIONIZATION DETECTOR FOR VOLATILE ORGANIC COMPOUNDS

PhD THESIS

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DECLARATION

November 2019,

The substance of this thesis is the original work of the author, and due reference and acknowledgement has been made, where necessary, to the work of others. No parts of this thesis has been submitted in candidature for any degree.

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Air quality has become a major concern worldwide. Volatile organic compounds (VOCs) are hazardous chemicals that can cause cancer and are commonly found in indoor air. In Europe, increasing pressure from regulations on the VOCs exposure drive the need for portable, sensitive and fast gas analyzers. The gas chromatograph (GC) is a common gas analyzer and can be equipped with a photoionization detector (PID) for VOC analysis. Miniaturization of the PID can enhance the performance and portability of a GC gas analyzer.

This work describes the design, fabrication and characterization of a micro PID (µPID) that can be integrated into a portable GC. The µPID uses a commercial UV lamp (with energy of 10.6 eV) emitting light into a microchannel, which is where the signal is measured. The device was microfabricated using micromilling and electrical discharge machining, with a final design that is modular. This enables the easy mount-dismount operation and replacement of components, while the miniaturized PIDs state of the art uses mainly fixed components. Four microchannel geometries are fabricated with varying electrode and illumination area and ionization chamber volume (1.1 µL to 6.7 µL). Low ionization chamber volume enables a reduction in sample volume, speeding up the analysis process and improving portability of gas analyzer.

The prototype was tested for the four microchannel geometries with a direct injection of toluene 100 ppm and produced a signal from 0.5 to 2.5 nA. The results showed that the main geometrical parameters influencing the signal level were illumination area and electrode area. A detection limit down to 37 ppb for toluene can be reached if a digital moving average filter is applied to the signal for noise reduction.

The µPID was also integrated with the portable GC from a French start-up company (In’Air Solutions), resulting in a GC-µPID gas analyzer. The GC-µPID results were obtained for an optimized cut-off frequency from a current preamplifier ($f_c =0.3$ Hz), which provided the best signal-to-noise ratio. The detection limit of the GC-µPID was 73, 138, 308, 262 and 254 ppb, for benzene, toluene, ethylbenzene, m,p-xylene and o-xylene, respectively. An analysis of the ionization chamber volume influence on the GC signal was evaluated and showed that, for the chamber volume and sample volumes used in this work, the variation in chamber size is not significant for a relevant GC signal change (measured by peak height and peak width change). Finally, a response of the GC-µPID when integrated with a preconcentrator (PC) in the sampling process is provided and showed that the whole system can have a detection limit lower than 5 ppb of toluene.
PUBLICATIONS

Peer-reviewed journal articles:


Conference articles and presentations:


For my parents, Wander & Marivone, for the blessing of life.
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To my wife, Izzy Szneczuk Oliveira, who patiently supported my long days of work and made it possible for me to return to a joyful home.
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NOMENCLATURE

\( a_1, \ldots, a_n \) Curve fit coefficients (depend on the coefficient)

\( A_e \) Electrode area (m²)

\( A_i \) Illumination Area (m²)

\( C_{DL} \) Concentration detection limit (ppm)

\( C_{mix} \) Concentration injected after mixture (ppm)

\( C_p \) Concentration in the gas cylinder (ppm)

\( f_c \) Cut-off frequency (Hz)

\( h \) Planck’s constant (J.s)

\( h_c \) Chromatograph peak height (A)

\( H \) Plate height (-)

\( H \) Microchannel height (m)

\( L \) Microchannel length (m)

\( n \) Number of measurements (-)

\( N \) Noise (A)

\( Q \) Flow rate (m³/s)

\( r^2 \) Coefficient of determination (-)

\( R \) Resolution (unit of measurement)

\( R_s \) Separation resolution (-)

\( S_b \) Baseline signal (A)

\( S_r \) Signal rise (A)

\( S_p \) Pollutant signal (A)

\( SNR \) Signal-to-noise ratio (-)

\( t \) Time (s)

\( t \) Student’s distribution coefficient (-)

\( t_r \) Retention time (s)

\( T \) Temperature (K)

\( u_x \) Longitudinal linear flow velocity (m/s)

\( u(X) \) Standard uncertainty of \( X \) (same units of \( X \))

\( U(X) \) Expanded uncertainty of \( X \) (same units of \( X \))

\( v \) Frequency (Hz)

\( v \) Degrees of freedom (-)

\( V \) Voltage (V)

\( V_c \) Ionization chamber volume (m³)

\( w_{1/2} \) Peak width at half max (s or mL)

\( w_{av} \) Average of peak width at half max (s or mL)

\( W \) Microchannel width (m)

\( X_Q \) Dilution ratio (-)
\[ \alpha \quad \text{Sensitivity of detector (A/ppm)} \]
\[ \sigma(X) \quad \text{Standard-deviation of } X \text{ (unit of } X) \]

**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ADC</td>
<td>Analog to digital converter</td>
</tr>
<tr>
<td>Ag-NW</td>
<td>Ag-Nano Wires</td>
</tr>
<tr>
<td>BTEX</td>
<td>Benzene, Ethylbenzene, Toluene and m,p,o-Xylenes</td>
</tr>
<tr>
<td>BV</td>
<td>Ball Valve</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>D-PID</td>
<td>Discharge photoionization detector</td>
</tr>
<tr>
<td>DRIE</td>
<td>Deep reactive ion etching</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental protection agency</td>
</tr>
<tr>
<td>ESR</td>
<td>Early stage researcher</td>
</tr>
<tr>
<td>FC</td>
<td>Faraday cage</td>
</tr>
<tr>
<td>( \mu )GC</td>
<td>Micro gas chromatograph</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>GC-PID</td>
<td>Gas chromatograph coupled with photoionization detector</td>
</tr>
<tr>
<td>ID</td>
<td>Inside diameter</td>
</tr>
<tr>
<td>L-PID</td>
<td>Lamp photoionization detector</td>
</tr>
<tr>
<td>MAF</td>
<td>Moving Average Filter</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass flow controller</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro electro mechanical systems</td>
</tr>
<tr>
<td>MFM</td>
<td>Mass flow meter</td>
</tr>
<tr>
<td>OD</td>
<td>Outside diameter</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed circuit board</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma enhanced chemical vapour deposition</td>
</tr>
<tr>
<td>( \mu )PID</td>
<td>Micro photoionization detector</td>
</tr>
<tr>
<td>PID</td>
<td>Photoionization detector</td>
</tr>
<tr>
<td>PC</td>
<td>Preconcentrator</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>PR</td>
<td>Pressure regulator</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>TVOC</td>
<td>Total volatile organic compounds</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>WHO</td>
<td>World health organization</td>
</tr>
</tbody>
</table>
Chapter 1  Introduction

1.1  Air Quality and Volatile Organic Compounds

Air quality affects directly human wellbeing, and clean air is a basic requirement for a healthy society. However, air pollution threatens global health and is caused by direct or indirect introduction of energy or substances in the air resulting deleterious effect in nature and human health. Recently, a class of chemicals named “volatile organic compounds” (VOCs) have raised the attention of international organizations due to their presence in indoor environments and their potential threat to health and wellbeing [1].

VOCs are a class of carbon-containing molecules with a high vapour pressure at ambient temperature. The WHO defines VOCs as organic compounds with a saturation vapour pressure greater than 100 kPa at 25 °C [2]. This means VOCs are volatile enough to be released in the air by solids or liquids at normal room temperature.

VOCs can be emitted by anthropogenic activity, and many of them are harmful to human health. Their outdoor main sources may come from fossil fuels as a direct product (e.g., gasoline) or by-product (e.g., automobile exhaust). Moreover, many products used in indoor environments release VOCs, such as paints, solvents, wood preservatives, aerosol sprays, cleanser and disinfectants, air fresheners, dry-cleaned clothing, pesticides, furniture, copying machines, etc. [3].

In many countries, most people spend a large part of the day indoors. In the United States, the US Environmental Protection Agency statistics study reports that a person spends on average 86.9 % of their daily time indoor, which includes time in a residence, office, factory, bar, restaurant, vehicles, etc. [4]. Within the European Union, the average indoor time spent by a person per day is 85-90 % [5].
Indoor concentration of VOCs can be high compared to outdoor, given their numerous sources. An EPA study found that VOCs can have 2 to 5 times higher concentration indoor than outdoor homes, independent of rural or industrial location [6]. In Europe, indoor environments are also more contaminated with VOCs compared to outdoor environments [7–9]. The adverse health effects caused by indoor air pollution are referred to as “sick building syndrome”.

Symptoms related to VOC exposure include headaches, loss of coordination, nausea, eye and respiratory tract irritation, and memory impairment. More severe health effects can include damage of liver, kidney, central nervous system and cancer [3,10]. Benzene, toluene, ethylbenzene, m,o,p-xylene are VOCs commonly found in indoor environments and are referred by the acronym BTEX. The most harmful of them is benzene, because its chronic exposure may cause chromosomal aberrations and cancer [11]. The World Health Organization Indoor Air Quality Guidelines suggest no safe level of exposure to benzene [12]. The European Union established a directive with effect in 2010 to limit benzene exposure at 5 μg/m³ (1.6 ppb) on average during a calendar year [13]. The French government is pushing down this benzene exposure limit to 2 μg/m³ (0.64 ppb) from January 2016 [14]. The tighter policies on VOC exposure given all the consistent science about its harmful effects raise the need for a robust, reliable, sensitive and effective method to identify and quantify the pollutants present in indoor environments in a local and real-time manner.

1.2 VOCs Analysis

Gas chromatography is a typical technique used for VOCs analysis because it can identify and quantify the compounds present in a gas sample. The equipment that performs gas chromatography is named gas chromatograph (GC). The main processes of a GC include: 1) Sampling; 2) Separation and 3) Detection. Figure 1.1 shows the main elements of a GC that enable those three processes, which includes: 1) Carrier gas cylinder; 2) Injection port; 3) Separation column; 4) Oven and 5) Detector. Some GCs might also be equipped with a preconcentrator in the sampling process. This device
takes the original sample concentration and increases it during the preconcentration process, delivering it to the separation column at a higher concentration; thus, it can improve the GC system sensitivity and consequently the detection limit.

The carrier gas cylinder provides pressurized gas to push the sample through the separation column after the injection. The carrier gas is usually a compound that does not influence the detector signal (e.g., nitrogen or helium). The separation column is a capillary tube with a stationary phase inside: a viscous liquid bonded to the inside wall or onto the surface of solid particles packed inside the column [15], depending on the type of separation column, open tubular or packed respectively. The affinity of the sample component with the stationary phase defines the adsorption strength of each compound which in turn separates them. The stronger the adsorption, the longer the solute will take to flow through the column and the oven sets temperatures to optimize the separation in the column. Thus, all compounds can get separated and leave the separation column at different times following this principle. Figure 1.2 shows a schematic drawing of the separation process inside the separation column by depicting three images of the separation column at three different times.
4 Introduction

Figure 1.2 – Schematics of the separation process inside the column when a mixture of gas with 3 elements is injected. The column and sample separation are depicted in three different moments. In this example, the element 1 has more affinity with the stationary phase; therefore, it takes longer to move throughout the column. Conversely, element 3 has less affinity with the stationary phase; thus, it moves faster and arrives sooner at the detector in the end of the separation column.

The time it takes for a component of the gas sample to flow from inlet to outlet of the separation column is the retention time ($t_r$). The typical signal obtained from a detector at the end of the separation column is the chromatograph, which shows the separated compounds as peaks with an approximately Gaussian shape. Figure 1.3 shows the chromatograph with three elements separated by a separation column and their respective retention times.

Figure 1.3 – Chromatogram representing the signal of three components after their separation in the column. $t_1$, $t_2$ and $t_3$ represent the retention time of each compound.
The efficiency of compounds separation makes important impact on GC performance. In order to distinguish two elements separated by the column, they have to present adequate difference in retention time and a sharp peak. Approximating the peaks to a Gaussian shape, it is possible to identify the main parameters of a peak, as indicated in Figure 1.4.

![Figure 1.4](image)

**Figure 1.4** – Peak parameters: Standard deviation ($\sigma$); Peak height ($h$); Peak width at half max ($w_{1/2}$) and full width ($w$).

When the sample is introduced into the separation column, all compounds are ideally within an infinitesimal pulse. However, the compounds arrive at the detector with a distributed concentration profile. Multiple factors can cause the spread of the concentration profile, including dead volumes in the GC and non-smooth connections between column and detector or injector. Each process contributing to the concentration profile spreading can be associated to a standard deviation $\sigma_i$. Therefore, the total standard deviation of the peak can be calculated as the sum of the variances created by all processes:

$$\sigma_{total}^2 = \sum \sigma_i^2$$  \hspace{1cm} (1.1)
One of the main causes of band spread is diffusion inside the separation column. The Van Deemter equation provides a relation between the sample flow rate and the column separation:

\[ H \approx A + \frac{B}{u_x} + C \cdot u_x \]  

(1.2)

Where \( H \) is the plate height, a constant of proportionality between the variance of the band (\( \sigma^2 \)) and the longitudinal distance it in the column (\( x \)). A small plate height means narrow peaks and better separation of the gas sample.

The sample linear flow rate is represented by \( u_x \), and \( A \), \( B \) and \( C \) are constants, which are specific for each column. Constant \( A \) accounts for the band broadening due to multiple paths and depends on the type of separation column, it is equal to zero for open tubular columns. The second term of Equation 1.2 accounts for the contribution of longitudinal diffusion and the constant \( B \) is proportional to the coefficient of diffusion of the pollutant gas in the carrier gas; this term tells that the longer a sample stays in the column, the broader the peaks will be due to the longitudinal diffusion. The third term accounts for a combined effect of mass transfer of the pollutant with the stationary phase and of the pollutant with the carrier gas. The constant \( C \) is dependent on the diffusion coefficient of the pollutant with the solid inside wall of the separation column and of the diffusion coefficient of the pollutant with the carrier gas.

Finding the right parameters for separation is a relevant task for the GC operation. A large peak is undesirable and represents a depletion of the detection limit of the gas chromatograph, because it is a consequence of a reduced height due to band spreading. Therefore, it diminishes the sensitivity of the GC.

GCs in the market with low detection limits (~0.05 ppb) are still heavy (6.6 – 20 kg), bulky, slow (up to 15 min total analysis time at 50 mL/min carrier gas flow rate) and lab-based [16–19]. In contrast, current regulations with strict air quality control raise the demand for efficient gas analysers with enhanced portability, reduced resource consumption, improved robustness, high analysis speed, decreased cost and low
detection limits. One possible way to achieve these improvements is through miniaturization of all the gas analyser components, including the detector itself.

Among the existing detectors used with GCs, the photoionization detector (PID) is suitable for miniaturization. In addition, it is commonly used for VOC analysis due to its selectivity, which is the capacity of a detector to distinguish a group of chemicals from the rest. The PID uses ionization of gaseous compounds by light as a working principle to quantify chemicals in the gas samples. 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 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 expressed as a chemical compound concentration.

For PID miniaturization, reducing the external size of the detector is not the main issue because some commercial PIDs are already small (external dimensions of 20 mm) and lightweight (8 g) [18,20]. The challenge is to design a sensitive micro PID (µPID) that is compatible with a portable GC and has an ionization chamber small enough to enable a reduction in the sample size and a consequent reduction in carrier gas consumption, increasing overall portability of the GC system.

Commercial PIDs either have relatively large ionization chamber volumes ranging from 40 to 200 µL [21–23] or have a membrane installed in the chamber, which is not ideal for integration with a GC [18,20]. A PID chamber without a membrane, which can be directly filled by the sample flowing into the chamber, is a flow-through ionization chamber. This chamber design is preferable for GC-PID because it allows the chamber fill time to be directly proportional to the flow rate of the sample, instead of depending on the diffusion through the membrane. The main motivation of this work is to develop a µPID with a small flow-through ionization chamber compatible to the development of a portable GC. This work describes the design, fabrication, assembly and characterization of a flow-through µPID prototype.
1.3 MIGRATE Project

This work is part of the MIGRATE project (MIniaturized Gas flow foR Applications with enhanced Thermal Effects), which is a Marie Skłodowska-Curie Innovative Training Network (ITN) funded by the European Union under the Horizon 2020 Programme (call H2020-MSCA-ITN-2014, Grant Agreement No. 643095). MIGRATE was created to address some of the current challenges to innovation that face the European industry with regard to heat and mass transfer in gas-based micro-scale processes. The MIGRATE network gathers intersectoral and multidisciplinary collaboration between 11 academic and 6 industrial participants from 10 European countries.

This thesis was developed under the Early Stage Researcher position number three (ESR 3) of the MIGRATE project, whose goal is to create a miniaturized photoionization detector for VOC analysis. This goal is achieved with the partnership between 3 European academic institutions: University of Limerick, Karlsruhe Institute of Technology (Germany) and CNRS at University of Strasbourg (France); and one French start-up company, In’Air Solutions, which develops portable gas analysers for VOCs analysis. Within the MIGRATE network, two other researchers are also working with the sampling and separation column of the In’Air Solutions gas analyser.

1.4 Objectives and Outline

The main objective of this work is to develop a µPID prototype for VOC analysis. The detector should be compatible with the In’Air Solutions GC system. Moreover, it should have a low ionization chamber volume, enabling a faster chamber fill time compared to the current commercial solutions. The central objectives are:

1. Evaluate the recent developments in photoionization detectors miniaturization and increase the understanding of the main factors affecting the PID performance.
2. Propose an innovative design of flow-through µPID with small ionization chamber volume.

3. Characterize what influences the performance of the µPID prototype when the gas sample is injected directly into the device (without the GC).

4. Investigate the performance of the µPID prototype integrated with a portable GC analyser (In’Air Solutions VOC analyser) and compare it with the commercial PID.

To address those objectives, Chapter 2 shows how the PID works, how each of its main components affects the signal intensity and what design features lead to maximal performance. Chapter 2 also presents the PID miniaturization state of the art and proposes research opportunities in this field. Chapter 3 shows the design of the µPID developed during this work, including details about the device design, fabrication and assembly. Chapter 4 describes the methods and results when the µPID is tested without the GC. Chapter 5 describes the methods and results when the µPID is integrated into the GC from In’Air Solutions and compare its results with the commercial PID. Finally, Chapter 6 provides the main conclusions from this work and recommends future investigations and improvements in the current PID technology.
Introduction
Chapter 2  Photoionization Detector

This chapter presents the photoionization detector and the current state of the art [24]. Section 2.1 outlines the main types of PIDs used commercially with and without GC for VOC detection. Section 2.2 details the working principle of the PIDs and define two types of ionization source design. Section 2.3 describes the main components of the PIDs and how their design influences the performance of the detector. Section 2.4 provides a summary of miniaturized PIDs state of the art followed by a discussion (Section 2.5) and conclusion (Section 2.6) on the topic, including suggestions for future studies and improvements in such devices.

2.1 Introduction

A photoionization detector is a device that uses the ionization of gaseous compounds by light as a working principle to quantify chemicals in gas samples. Typical applications include leak detection, industrial hygiene and safety, soil contamination and air quality monitoring. PIDs can be used with or without a GC [16,17,19,25–27]. The latter, often used to detect Volatile Organic Compounds (VOCs) and some inorganic substances in ambient air, is non-specific; this means the PID gives a weighted total response for all detectable chemical species. In order to identify each individual sample component, a separation column is necessary; therefore, the PID can be used selectively with a gas chromatograph (GC-PID).

Most commonly used PIDs are nevertheless not universal because some molecules are not detected if their ionization energy is lower than that provided by the light source used, usually given in units of electron volts (eV). It may be even specific to certain
families of molecules if the energy of the light source is voluntarily lowered. Table 2.1 shows the ionization potential of common molecules found in VOC samples. Photoionization detectors used with gas chromatographs usually have low detection limit; however, the detector itself is relatively large (~200 mm) [28] and the whole gas analyser (GC-PID) is commonly a non-portable bulky lab equipment.

Table 2.2 presents characterization data of PIDs commonly used with and without GCs to detect VOCs, which are referred here as lab based PIDs or portable PIDs, respectively. Figure 2.1 shows a schematic of a lab based and a portable PID [20,21]. While lab based PIDs are designed to be coupled to gas chromatography, portable PIDs are mostly used to quantify Total Volatile Organic Compounds (TVOC) concentration in units of isobutylene equivalent. TVOC results account for the total contribution of VOCs in a gas sample without specifying which compounds are present; TVOC results are obtained from the PID signal without using a GC to separate the chemicals.

The lab based PIDs have a flow-through sample ionization chamber whereas the portable PIDs are equipped with a membrane for passive sampling where the molecules diffuse through it. With the membrane, water vapour and particulates from the gas sample are limited in the ionization chamber, improving ionization efficiency and detector life. If solid particles reach the interior of the ionization chamber they can damage the lamp window and as a consequence the light energy can change, which changes the sensitivity of the detector. The humidity can absorb light reducing the light intensity reaching the target VOCs and reducing sensitivity; moreover, vapour condensation inside the ionization chamber can cause a false positive current signal (also known as “leak” current) [29].
Table 2.1 – Ionization potential of common elements found in VOC detection.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>Ionization Potential (eV) [30]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>15.58</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>12.06</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>12.62</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>9.24</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>8.83</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>C₈H₁₀</td>
<td>8.77</td>
</tr>
<tr>
<td>o-,m-,p-Xylene</td>
<td>C₈H₁₀</td>
<td>8.56, 8.56 and 8.44</td>
</tr>
</tbody>
</table>

Table 2.2 – Typical characterization data for commercial PIDs.

<table>
<thead>
<tr>
<th>Technical data</th>
<th>Lab based PID [21–23]</th>
<th>Portable PID [18,20]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit</td>
<td>0.05 ppb a</td>
<td>0.1 – 1 ppb a</td>
</tr>
<tr>
<td>Weight</td>
<td>3 kg</td>
<td>8 g</td>
</tr>
<tr>
<td>Characteristic external dimension</td>
<td>200 mm</td>
<td>20 mm</td>
</tr>
<tr>
<td>Ionization chamber volume</td>
<td>40 - 200 µL</td>
<td>Not specified</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>30 - 50 mL/min b</td>
<td>0 - 300 mL/min</td>
</tr>
<tr>
<td>Ionization chamber fill time</td>
<td>0.1 s (for 50 µL and 30 mL/min)</td>
<td>&gt; 10 - 120 s c</td>
</tr>
<tr>
<td>Ionization chamber type</td>
<td>Flow-through d</td>
<td>Diffusion e</td>
</tr>
<tr>
<td>Common application</td>
<td>Individual chemical species measurement</td>
<td>TVOC measurements f</td>
</tr>
</tbody>
</table>

a This detection limit is given for benzene; b This value includes an additional gas flow called “make up” to reduce the residence time in the detector and refine the peaks; c Estimated value through experimental observation; d Sample flow through the ionization chamber; e Sample crosses a membrane by diffusion; f Total Volatile Organic Compounds, the concentration is usually provided in isobutylene-equivalent.
The portable PID described in Table 2.2 has external dimension ten times smaller compared to the lab based PID. However, it is not ideal for portable GC because its chamber fill time is slow (10 to 120 s) due to the nature of its ionization chamber, which uses a membrane. This membrane reduces the ionization chamber fill time (see Table 2.2) and may potentially result in low quality chromatographic peaks when applied to the GC.

Reducing the ionization chamber volume of the PID can play an important role in overall GC-PID miniaturization. A small ionization chamber can improve both gas analyser performance and portability. Ionization chamber miniaturization can yield higher surface to volume ratio, which translates into a more sensitive signal [31]. A small ionization chamber should also result in a higher signal-to-noise ratio. In addition to that, the smaller the ionization chamber volume, the smaller the gas sample volume
can be (without depleting signal intensity), and for a fixed carrier gas flow rate this means also faster analysis time and lower consumption of carrier gas. Low carrier gas consumption is important to enable reduction in carrier gas cylinder size (reducing gas analyser weight) and maintain carrier gas cylinder autonomy, both important qualities for portability of GC-PIDs.

## 2.2 Photoionization Detector

To enable the photoionization process, a high-energy light source is required. The photon energy from the light source sets the selectivity of the detector, determining the chemical species it can sense. Light wavelengths used in PIDs for VOC detection are typically below 130 nm translating into a photon energy of 9.6 eV (lower wavelengths yield higher photon energy), enabling detection of most commonly found VOCs like the BTEX. PIDs using light sources with energy higher than 16 eV can be referred as universal, since they have the potential to detect the most relevant chemical compounds in the air, including VOCs. Non-universal PID light sources have lower energy to enable detection of a smaller group of chemicals, e.g. the lamps used for BTEX detection. Non-universal detection allows optimization of the gas analysis for specific chemicals.

In most cases, when the ionization potential of the sample molecule is lower than the ionization energy of the photons, the molecule can get ionized. This means that an electron is released from the molecule, yielding an electron and an ion; therefore, a positive and negative charge whose movement inside the ionization chamber of the PID is directed by the electric field of the detection electrodes, generating a current signal. This signal is referred to as ionization (or photoionization) current, and it is proportional to the concentration of ionized species [32]. The ionization current is detected by the two electrodes inside the ionization chamber of the PID subjected to a voltage. The photoionization process is represented by

\[
AB + h\nu \rightarrow AB^+ + e^-,
\]

(2.1)
where $AB$ is the ionisable substance hit by photon energy $h \cdot v$. Figure 2.2 illustrates the photoionization detection process, noting that the sample leaves the detector with same composition as it came in. This makes the PID a non-destructive detector and allows it to be used in series with other gas detectors such as the flame ionization detector (FID).

![Diagram of Photoionization Detection Process](image)

Figure 2.2 – Photoionization detection process.

PIIDs can be classified according to the ionization source used. The first type is when the ionization source is integrated into the ionization chamber, where the sample ionization occurs. In this case, the ionization source is usually a discharge to generate plasma in a noble gas such as helium or argon. Such devices are referred to as plasma or discharge photoionization detector (D-PID). The early PIIDs were first developed using this concept [33–40]. Figure 2.3a shows the main elements of this device. The main advantage of the D-PID is that its ionization source generates energy high enough to detect even permanent gases, including nitrogen and oxygen in air samples. However, some of the main disadvantages include: 1) Instability of the photon source; 2) Instability of detector response; 3) Necessity to supply constantly very pure gas into the discharge region; 4) Mechanical and operational complexity; 5) Optimal light radiation intensity occurs at low pressures, requiring a vacuum pump [41,42].

A solution to the disadvantages associated with D-PIIDs was to separate the radiation source and ionization chamber into two distinct spaces, which led to the development of the lamp photoionization detector (L-PID). In this second type of PID, the ionization source has no fluidic connection to the ionization chamber. This simplifies the sensor operation, because the ionization chamber can be used at a different pressure than the ionization source. In addition, it improves the sensitivity of the detector [42].
Figure 2.3b shows the main components of an L-PID, including the ionization source, which is an enclosed lamp with a noble gas inside (generally Kr, Ar or Xe) that produces photons when excited. The window separates the ionization chamber from the lamp and serves as a cut-off filter for the photon energy reaching the sample molecules. The photon energy reaching the ionization chamber depends on the lamp fill gas and the window. The early PIDs using an UV lamp as ionization source were published in the 1970s [42–44] and the first commercial use was by the company HNU Systems.
2.3 PID Components

The core components of PIDs are: the ionization source, the electrodes and the ionization chamber. This section contains brief design guidelines and explanations on how the main components influence PIDs performance.

2.3.1 Ionization Source

In L-PIDs, the combination of lamp and window defines the photon energy reaching the ionization chamber. The highest photon energy of a lamp ionization source is defined as the nominal photon energy, which varies from 8.3 to 11.8 eV [45,46]. The lower the ionization energy of the photons, the more selective the PID. Conversely, in the case of VOCs, species with fixed ionization potential can have an enhanced response when a higher energy lamp is used. The 10.6 eV lamp has the highest photon flux and, therefore, provides greatest sensitivity; it uses magnesium fluoride as window (MgF$_2$) [47,48].

Common window materials are LiF, MgF$_2$ and CaF$_2$ [41], which have cut off values of 105 nm, 112 nm and 122 nm respectively [47]. Solarization of the window, which changes the material color temporarily, can be a problem for high energy UV lamps (11.7 eV or higher) [47]. The temperature can influence the photon energy output since it influences the window transmission coefficient [49]; therefore, the lamp spectrum can change substantially with window heating.

2.3.2 Signal Electrodes

The electrodes inside the ionization chamber create an electric field and collect the ionization current. The photoionization process has a maximum intensity in the immediate vicinity of the lamp window. Therefore, it is important to place the electrodes as close as possible to the lamp window (ionisation locus) [50,51]. Typically, a voltage ranging from 100 to 200 V is applied on the electrodes to push the ions to the collection electrode [45,47]. The ion collection efficiency can be increased by
increasing the electromagnetic field strength, thereby avoiding quenching and recombination of ions [51]. Reducing the distance between the electrodes also enhances the field strength and larger electrodes yields larger photoionization signal [52]. Shielding electrodes from the photon flux is also important to minimize the background noise generated by the photoelectric effect at the electrode surface [45, 47, 50, 51, 53]. The direction of gas flow relative to electrical field has also been shown to have an influence on the ion collection efficiency, but further investigations still need to be done to understand this influence [50].

2.3.3 Ionization Chamber

The ionization chamber is the cavity filled by the gas sample between the fluidic inlet and outlet, where the ionization source and signal electrodes are in contact with the sample. Within this chamber, the gas sample molecules are ionized by the photons and the corresponding ionization current is then generated. Ionization chamber materials, temperature and pressure are characteristics that influence the PID performance, independent of whether the PID is used with or without a GC separation stage.

The chamber size and the distribution of gas flow inside are key factors influencing PID performance when it is used with a GC. The ionization chamber should ensure uniform flow, otherwise the quality of the signal can decrease [54]. Stagnation regions and recirculation of the sample can result in deformation of the chromatographic peaks, causing widening and asymmetry, which depletes the gas analyser signal intensity and separation resolution. A small volume and its design can also avoid remixing of species that have been previously separated in the separation column. Additionally, it can ensure uniform ionization of the sample, contributing to better linearity and signal-to-noise ratio.

Commercial PIDs have ionization chamber volumes ranging from 40 to 200 µL [47]. Recent papers have been published on PIDs with ionization chambers up to ~100 times smaller (volume close to 1 µL) where most improvements in ionization chamber size were achieved with silicon microfabrication techniques using photolithography and etching.
2.4 Recent Micro PIDs Developments

The diagram in Figure 2.4 shows the evolution of PID miniaturization, where three main milestones can be identified: 1) Lab based PIDs, which are compatible with lab bench GC-PIDs; 2) Portable PIDs, commonly used for field TVOC analysis and 3) micro PIDs (µPIDs), compatible with microfluidic gas analysis. The lab based and portable PIDs are already very established in the market. The µPIDs are still in an early development stage, where most devices developed are prototypes.

This section describes the recent literature on PID miniaturization, including discharge and lamp PIDs. A summary of section 2.4.1 and section 2.4.2 regarding the PIDs main features, fabrication and characterization results (also when integrated with GC) are presented in Tables 2.3, 2.4 and 2.5.

![Milestones diagram of photoionization detectors miniaturization.](image-url)
2.4.1 Plasma or Discharge micro PID (D-µPID)

Akbar et al. (2015) [55,56] fabricated and evaluated a microfluidic discharge photoionization detector integrated on a chip with a micro separation column (µSC), as in Figure 2.5. The device was implemented in a silicon-glass architecture with a chip size of 1.5 cm × 3 cm. The ionization chamber was created with deep reactive ion etching and the detector electrodes were made from 700 nm/40 nm thick Ti/Au metal stack by e-beam evaporation. The auxiliary flow and the analyte flow are parallel to each other before they reach the ionization chamber. Helium is used as an auxiliary gas (plasma generation) and as a carrier gas with flow rate measured at the outlet in the range of 0.77 to 2.5 mL/min. Two samples were used, a multi-analyte gas mixture consisting of eight compounds (n-heptane, toluene, tetrachloroethylene, chlorobenzene, ethylbenzene, p-xylene, n-nonane and n-decane) and a mixture of heavier alkanes. The device uses low power (1.4 mW) and is universal, given the high ionization energy produced by the helium discharge, and non-destructive. The chromatographic separation and detection of tested compounds can be performed in less than 1 min and the minimum detection limit observed was ~10 pg. The monolithic integration of the separation column and detector alleviates the need for transfer lines, improving the performance of the individual components, reducing chromatographic peak distortion and also reducing fabrication and implementation costs.

Another micro discharge photoionization detector was designed, fabricated and characterized by Zhu et al. (2016) [57] (see Figure 2.6). They used 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 and 500 µm thick Borofloat 33 glass wafer as main materials for fabrication. Si wafer was diced and wet etched with 49 % buffered HF to remove oxide layer and glass wafers were diced into desired shapes. The diced Si and glass were bonded with UV-curable optical glue. As a result, the device is a microchannel formed by a conductive p-type silicon wafer (sidewalls) and glass wafer (top and bottom wall). Three main channels compose the microfluidic device (see Figure 2.6): auxiliary gas channel, which flowed only Helium for the discharge; analyte channel, where carrier gas (helium) and sample flows; and outlet channel, which can be considered as the ionization chamber. The cross-section of the channel is 380 µm square. The bias and collection electrodes are the walls of the conductive silicon wafers, which form the channel and are 6 mm in length. From the channel geometry, the estimated ionization chamber volume is ~1.4 µL, with virtually zero dead volume (~6 nL, estimated from simulation). The performance of the device was tested to detect permanent gases (hydrogen, nitrogen and oxygen), BTEX and others. The authors observed an optimal voltage applied between the collection and bias electrode of 40 V to generate maximal ion collection efficiency and signal to noise ratio. In theory, considering only the theoretical residence time for 1.5 mL/min, the peak width can be as sharp as 56 ms. A linear dynamic range higher than 4 orders of magnitude and a detection limit of 3.2 pg (benzene) were obtained.

Figure 2.6 – Miniaturized helium discharge PID [57].
Narayanan et al. (2015) [58,59] developed and tested the first microfabricated PID to be coupled with a µGC (see Figure 7). The main substrate of the device consists of two borosilicate glass wafers (top and bottom) with 700 µm thickness. Channels were made with wet etching, at the bottom wafer with 250 µm maximum depth; and in the top wafer, the electrodes were fabricated by lift-off process. The top and bottom borosilicate glass wafers were bonded together with epoxy and capillary tubing were slid into the channel inlets and outlets then epoxied in place. Helium was used as a carrier and auxiliary gas for discharge across a 20 µm gap. The detector was tested regarding discharge, sample mass injection and concentration. The authors distinguished the sampling for the concentration test and multi-component detection test. A 10 µL gas-tight syringe was used to inject samples for tests. Volume/minimum amount = 1 µL or 2 µL (concentration and multi-component tests, respectively) / 50 ppm of octane in air (concentration test). The limit of detection estimated for n-octane was 50 ppm, which translated to an absolute mass of 350 pg. The authors suggested future improvements in the collector electrode design and the orientation of the plasma relative to the analytical column.

![Diagram](image)

Figure 2.7 – Glass structure microfabricated PID [58,59].

### 2.4.2 Lamp micro PID (L-µPID)

Sun et al. (2013) [51] presented the design, fabrication and characterization of a portable PID. The ionization chamber of his device had its volume reduced to 10 µL with the introduction of a nozzle as shown in Figure 2.8. In order to reduce noise, the electrodes were shielded from the photons and electromagnetic shielding was placed around the ionization chamber. The collection electrode was positioned close to the
lamp window, where most of the molecules ionization occur, in order to increase the ion collection efficiency. To further enhance ion and electron collection efficiency, a high voltage was applied between the collecting and accelerating electrodes (100 V to 300 V). The lamp energy used was 10.6 eV, the carrier gas was hydrogen and the PID was tested with and without a microfabricated GC separation column. The background noise achieved was low (noise < 0.01 pA) with small baseline drift. The response time was less than 30 ms and the signal had a linear range of $10^6$ and a detection limit lower than 5 ppb (1 ppb estimated for benzene). A similar design was published by Sun et al. (2019) [60] without the nozzle. The latter mentioned an ionization chamber also with volume of 10 µL and was made from polytetrafluoroethylene (PTFE).

![Side cut view of PID with nozzle introduced in ionization chamber according to Sun et al. (2013)](image)

Figure 2.8 – Side cut view of PID with nozzle introduced in ionization chamber according to Sun et al. (2013) [51].

In order to further miniaturize the detector, Zhu et al. (2015) [54] developed a microfluidic Lamp PID (Figure 2.9). The materials used are 500 µm thick Pyrex glass wafers and 380 µm thick p-type <100> silicon wafer with single side polishing and 0.001 to 0.005 Ω.cm resistivity. The device was microfabricated on a conductive silicon wafer using deep reactive ion etching to form a microchannel with spiral shape. The silicon was anodic bonded on top of Pyrex yielding a channel with cross section 150 µm (width) $\times$ 380 µm (depth) and length 2.3 cm. On top of the channel, a UV lamp was placed and sealed with optical glue. This design resulted in a short distance between electrodes (150 µm), large electrode area 8.74 mm², short illumination path 380 µm,
large illumination area 3.5 mm$^2$ and low ionization chamber volume 1.3 µL. The entire overall channel size was 15 mm × 15 mm and the microchannel area covered by lamp was 2.4 mm × 2.4 mm. The design was made in order to avoid dead volumes; in fact, the authors reported a virtually zero dead volume of ~2 nL, caused mainly from the connections between GC column and microfluidic PID inlet. With this design, the response time can be as fast as 78 ms for flow rate of 1 mL/min. The voltage applied on electrodes was only 6 Vdc and generated an electric field of approximately 400 V/cm. The microfluidic PID shows results of full width at half maximum for toluene at flow rates of 2.3 and 10 mL/min showed 250 ms and 85 ms respectively using helium as a carrier gas. The authors tested the linearity and detection limit for five compounds (benzene, toluene, ethylbenzene, m-xylene and hexane), which ranged from a few picograms to a few micrograms. The detection limit observed for benzene was 4.25 pg (1.4 ppt), a value almost 200 times lower than the commercial PID tested at the same conditions.

Zhou et al. (2016) [61] presented the design of a portable gas chromatography system for VOC detection in water with a µPID as the detector. The materials used were conductive p-type <100> silicon wafer and glass. The µPID consisted of two conductive silicon wafers with 380 µm thickness separated by a 380 µm gap, forming a 2 cm long microchannel. The top was covered with a krypton UV lamp and the bottom with a glass slide. The top and bottom parts were glued to the silicon wafer with optical epoxy. Two copper wires with copper tape were bonded to the wafers and connected to an amplifier. Two guard columns were inserted into the channel inlet and outlet leaving only a path of 3.5 mm from the channel exposed to the UV lamp. The ionization
chamber volume estimated from the geometry yield 0.5 µL. The GC-PID achieved detection limit lower than ppb levels (not quantified by authors) operating with a pre-concentrator/injector.

Zhou *et al.* (2018) [62] presented an L-µPID design based on optimization results obtained from simulations of gas flow and electrostatic field. The simulations aimed at improving the ionization chamber design and ion collection efficiency. The ionization chamber was constructed using two sealing layers (top and bottom) of borofloat 33®; an UV lamp (Baseline Inc., 10.6 eV); a pair of electrodes made of conductive material (not specified) and capillary tubes inserted in the inlet/outlet. Laser etching was used to cut the top (0.5 x 20 x 20 mm) and bottom sealing layers (1 x 30 x 30 mm). Laser etching made an 8 mm opening on the top sealing layer; at the bottom layer, it also was used to make the microchannel of the ionization chamber, the electrode groove, and a conduit groove. The electrodes were integrated into the etched groove using MEMS technology. Top and bottom sealing were closed with anodic bonding; UV curing bond sealed the capillary inserted into the microchannel and around the UV lamp. The device was tested at different voltages ranging from 85 to 165 V, and the best voltage was used to apply to a range of toluene concentration from 0.5 ppm to 5.1 ppm. At a flow rate of 50 ml/min and 150 V the device could reach ppb level detection limit.
Agbroko et al. (2018) [63] presented the design, fabrication and evaluation of a PID that can provide two outputs: a signal proportional to TVOC concentration and a compositional information of the sample. The sensor was designed based on a single PCB, where one part of the PCB was used to house the electrodes responsible for the compositional information and signal generation, and the other to house the electronics to process the signal. The sample path was enclosed by the PCB and an aluminium block with a machined chamber. A 6.1 mm bore was opened at the top of the ionization chamber to fit the UV lamp and an O-ring was placed between the aluminium block and PCB making the flow chamber leak free. The overall size of the device is $7 \times 5 \times 4$ cm with a mass of $\sim 200$ g. Figure 2.12 illustrates the operation of the sensor. After sample introduction into the inlet, it is ionized in the ionization region. Then, the ions pass through a region of the detector where an electric field is applied perpendicular to the ion flow direction, resulting in a deflection of the ions. Thus, by changing the electric field intensity it is possible to determine which species reach the detection electrodes, providing some selectivity. Two electrodes arrays were used for deflection of the ions: 1) one array provides a constant output, for TVOC detection; 2) the second array the electric field can be varied from $-10$ kV/m to $+10$ kV/m and provides some composition information of the sample. It was observed that an electric field of 1 kV/m in the composition electrode resulted in a 0.67 V separation between the signal of isobutylene and 2-pentanone and that the device can reach detection limit in the ppb level.

![Figure 2.12 – Schematics of sensor operation [63].](image-url)
Pyo et al. (2019) [31] presented a PID sensor with 1D nanostructures implemented in the detection electrodes. The sensor electrodes were interdigitated structures and the device was tested with toluene at different concentrations. The performance of the electrodes with and without the nanostructures was also compared. Two types of nanostructures were used: Ag-nanowires (Ag-NW) and carbon nanotubes (CNT). The electrodes were fabricated using traditional MEMS fabrication methods, including photolithography, sputtering, wet and dry etching (DRIE). The electrodes substrate was fabricated using doped Si and then coated by nanostructures with drop casting. The device was inserted into a gas chamber with a toluene and air mixture flowing; therefore, this is not a closed chamber microfluidic PID but can evolve into one. It was observed that the coating increased the device sensitivity, and that CNT yielded the highest sensitivity compared to Ag-NW. The superior response of CNT was explained by two reasons: 1) the CNT ability to provide better surface area and 2) its material is not oxidized, which depletes the signal. The detector has linear response for low toluene concentrations (0.1 – 1 ppm) with response time ~ 600 s at sample flow of 500 mL/min. Estimated detection limit is below 100 ppb for toluene with very low applied voltage (0.2 V).
2.5 Discussion

The main characteristics of the micro detectors reported in this work are shown in Tables 2.3, 2.4 and 2.5. The ionization chamber volume of the µPIDs are ~100 times smaller compared to the commercial PIDs. In addition, while commercial PIDs can have flow through and membrane ionization chambers, most µPIDs developed so far have flow through chambers, with the exception of Pyo et al. (2019) [31]. For flow through µPIDs, the ionization chamber volume relates directly to the fill time. Therefore, the fill time of the µPIDs can be up to ~100 times faster than the commercial PIDs. To reach low ionization chamber volumes, some devices were fabricated using MEMS fabrication techniques, which are costly for prototyping.

Table 2.3 shows information about the µPIDs ionization source, ionization chamber and electrodes. All lamp µPIDs used a 10.6 eV UV lamp as light source, which has energy enough to detect most VOCs [51,54,61,62,64,65]. In contrast to that, the discharge µPIDs used helium as auxiliary gas for the plasma, which can generate photons with energy high enough to ionize chemicals such as O₂ and N₂ [55–59]. The flow of auxiliary gas in the works presented could be parallel or perpendicular to the sample flow [55–59]. A relevant feature of most µPIDs presented is that the ionization chamber has become a microchannel, which makes such devices compatible with microfluidic gas chromatography. In cases where the microchannel had vertical walls close enough, made either of conductive silicon or metal, these walls were the electrodes for ionization current measurement with distances of 150 µm or 380 µm [54,57,61,64,65]. Two discharge µPID devices presented electrodes made of Ti/Au [55,56,58,59] and one of them with a distance of 1.5 mm between the signal electrodes [55,56]. As an option to enhance sensor sensitivity, coating of electrodes with nanostructures was presented with Ag-NW and CNT [31], which increase the electrode area and local electric field density.

Table 2.4 summarizes the information regarding the fabrication of the µPIDs. Silicon and glass are the main materials used in their fabrication [54–59,61,62,64,65]. The device reported by Sun et al. (2013) did not mention the materials used for fabrication.
and Narayanan et al. (2014, 2015) used only glass as main substrate. With the exception of the works of Sun et al. (2013) and Agbroko et al. (2018), all other microfabricated devices ionization chamber are microchannels. The fabrication techniques used include deep reactive ion etching (DRIE), wet etching, laser etching, drop casting, e-beam evaporation, plasma enhanced chemical vapour deposition, lithography evaporation and lift off, anodic bonding, gluing and dicing.

Table 2.5 summarizes the information regarding the experiments with µPIDs when they were integrated with a GC, with the exception of Zhou et al. (2018), Agbroko et al. (2018) and Pyo et al. (2019) which did not use a GC and injected the sample directly into the detector. The L-µPIDs samples were mostly VOCs (e.g. benzene and toluene); on the other hand, D-µPIDs included VOCs and gases with high ionization potentials such as H₂, O₂ and N₂. Various sampling techniques were employed such as gas-tight syringe, 6 port sample injector with micro pump, and Tedlar-bags. The carrier gas used were mostly helium and nitrogen, with exception of the work of Sun et al. (2013) which used hydrogen. The separation columns were microfabricated [51,55,56,58,59] or commercial columns [54,57,64,65]. The response time of microfabricated PIDs could be as fast as 78 ms at 1 mL/min carrier gas flow rate and the detection limit could reach 1.4 ppt for benzene. However, a true comparison of the detection limit in parts per units between all the presented detectors is not possible, since some were reported in mass units without information about the sample volume. Moreover, Zhou et al. [61,64,65] used a preconcentrator, but the concentration factor was not mentioned, therefore comparison of its detection limit with other works is not possible.
### Table 2.3 – Micro PIDs main components data.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Ionization source</th>
<th>Ionization Chamber</th>
<th>Distance / Area</th>
<th>Electrodes</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>[55,56]</td>
<td>Helium discharge</td>
<td>-</td>
<td>D = 1.5 mm</td>
<td>Tested voltages 0 – 60 V. Optimum value = 30 V. Power consumption 1.4 mW</td>
<td>Ti/Au</td>
</tr>
<tr>
<td>[57]</td>
<td>Helium discharge</td>
<td>~1.4 µL (estimated from geometry)</td>
<td>D = 380 µm; A ~ 4.56 mm² (estimated from geometry)</td>
<td>Variable bias voltage of 40 Vdc</td>
<td>P-Silicon</td>
</tr>
<tr>
<td>[58,59]</td>
<td>Helium discharge</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Ti/Au</td>
</tr>
<tr>
<td>[51]</td>
<td>UV Lamp, 10.6 eV</td>
<td>10 µL</td>
<td>Nozzle placed inside the chamber to reduce its volume</td>
<td>100 – 300 V</td>
<td>-</td>
</tr>
<tr>
<td>[54]</td>
<td>Baseline MOCON UV lamp (P/N 043 – 257), 10.6 eV, Krypton fill gas, MgF₂ window</td>
<td>1.3 µL</td>
<td>Spiral microchannel w = 150 µm, d = 380 µm and l = 2.3 cm</td>
<td>6 Vdc (400 V.m⁻¹)</td>
<td>P-Silicon</td>
</tr>
<tr>
<td>[61,64,65]</td>
<td>Baseline MOCON UV lamp, 10.6 eV, Krypton fill gas, MgF₂ window</td>
<td>~0.5 µL (estimated from geometry)</td>
<td>Straight microchannel w = 380 µm, d = 380 µm and l= 2 cm</td>
<td>-</td>
<td>P-Silicon</td>
</tr>
<tr>
<td>[62]</td>
<td>Baseline MOCON UV lamp, 10.6 eV, Krypton fill gas, MgF₂ window</td>
<td>-</td>
<td>Straight microchannel, length ~ 8 mm</td>
<td>Tested voltages 85 - 165 V</td>
<td>-</td>
</tr>
<tr>
<td>[63]</td>
<td>Alphasense Ltd. UV lamp, 10.6 eV, Krypton fill gas</td>
<td>-</td>
<td>Inside aluminium block of 46 x 18 x 10 mm; Contains electrodes for field deflection of ionized species</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[31]</td>
<td>UV Lamp, 117 nm wavelength</td>
<td>-</td>
<td>Interdigitated geometry with coating of 1D nanostructures (Ag NW or CNT)</td>
<td>D = 10 – 30 µm</td>
<td>0.2 – 0.5 V</td>
</tr>
</tbody>
</table>
# Table 2.4 – Micro PIDs fabrication.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Materials</th>
<th>Features and Dimensions</th>
<th>Device Fabrication</th>
</tr>
</thead>
<tbody>
<tr>
<td>[55,56]</td>
<td>Silicon and glass</td>
<td>Ionization chamber is a microchannel. Micro separation column fabricated on the same chip. Overall detector and column size is 1.5 cm × 3 cm</td>
<td>Deep reactive ion etching (DRIE) on Si wafer; E-beam evaporation of 700 nm/40 nm thick Ti/Au metal stack; Anodic bonding of Si and glass</td>
</tr>
<tr>
<td>[57]</td>
<td>P-type silicon wafer (500 µm thick); Borofloat 33 glass wafers (100 µm and 500 µm thick)</td>
<td>Ionization chamber is a microchannel. Cross-section 380 µm (width) and 500 µm (depth); Three main channels: 1) Auxiliary helium; 2) Analytes; 3) Outlet channel. Electrodes are the vertical walls of the microchannel</td>
<td>Dicing Si and Borofloat 33; Wet etching to remove oxide layer; Wafers bonded with UV-curable optical glue</td>
</tr>
<tr>
<td>[58,59]</td>
<td>Borosilicate glass wafers (700 µm thick)</td>
<td>Ionization chamber is a microchannel</td>
<td>Wet etching; e-beam deposition and lift-off of 1 µm/30 nm thick Ti/Au; Epoxy bonding</td>
</tr>
<tr>
<td>[51]</td>
<td>-</td>
<td>Nozzle inside ionization chamber; Accelerating and collecting electrode shielded from UV light; Electromagnetic shield to avoid noise</td>
<td>-</td>
</tr>
<tr>
<td>[54]</td>
<td>P-type silicon wafer (380 µm thick); Pyrex glass wafer (500 µm thick)</td>
<td>Ionization chamber is a microchannel (width = 150 µm; depth = 380 µm; length = 2.3 cm). Overall channel size is 15 mm × 15 mm. Electrodes are the vertical walls of the microchannel</td>
<td>Deep reactive ion etching (DRIE) on Si wafer; Plasma enhanced vapour deposition for SiO₂ on Si; Lithography evaporation and lift-off for Aluminium layer; Anodic bonding of Si and Pyrex</td>
</tr>
<tr>
<td>[61,64,65]</td>
<td>P-type silicon wafer; Glass wafer</td>
<td>Ionization chamber is a microchannel; Electrodes are the vertical walls of the microchannel</td>
<td>Microchannel is not etched. Anodic bonding of Si to Pyrex</td>
</tr>
<tr>
<td>[62]</td>
<td>Borofloat 33®</td>
<td>Ionization chamber is a microchannel; Electrodes are vertical walls of the microchannel</td>
<td>Laser etching on Borofloat 33®; Anodic bonding of glass; UV curing adhesive of lamp and capillary column</td>
</tr>
<tr>
<td>[63]</td>
<td>PCB and aluminium</td>
<td>Weight ~ 200 g; Overall size = 7 x 5 x 4 cm; Two 1/8” tube fittings (inlet/outlet); Sample path machined on aluminium block; 6.1 mm bore machined over the ionization chamber to fit the lamp; O-ring between aluminium and PCB</td>
<td>-</td>
</tr>
<tr>
<td>[31]</td>
<td>Si wafer with three layers: 1) 50 µm thick arsenic doped n-type Si (0.005 Ω.m resistivity); 2) 2 µm thick oxide; 3) 400 µm thick Si substrate</td>
<td>Rectangular interdigitated electrodes with nanostructure coating. Overall size of electrodes structure is ~ 6 x 6 mm; Depth of electrodes = 50 µm</td>
<td>Aluminium sputtering to be used as mask; Photolithography; wet and dry etching (DRIE); Nanostructures applied by drop casting</td>
</tr>
</tbody>
</table>
Table 2.5 – Micro PIDs experimental and performance data.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Analytes</th>
<th>Sampling</th>
<th>Carrier Gas</th>
<th>Separation Column</th>
<th>Response Time and Flow Rate</th>
<th>Detection Limit (original units of publication)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[55,56]</td>
<td>N-heptane, toluene, tetrachloroethylene, chlorobenzene, ethylbenzene, p-xylene, n-nonane and n-decane, n-nonane, n-decane, n-undecane and n-dodecane</td>
<td>Autosampler module (7359A) on a 7890 series Agilent GC system</td>
<td>Helium</td>
<td>Microfabricated GC using silicon and glass</td>
<td>~1 s at 0.9 – 2.5 mL/min</td>
<td>~10 pg (n-octane)</td>
</tr>
<tr>
<td>[57]</td>
<td>Benzene, toluene, ethylbenzene, p-xylene, and others, including permanent gases (H₂, N₂ and O₂)</td>
<td>1177 injector on a Varian 3800 GC system</td>
<td>Helium</td>
<td>Mol Sieve 5A PLOT column; RTX-VMS and RTX-1 from Restek Corp.</td>
<td>56 ms at 1.5 mL/min (theoretical result)</td>
<td>3.2 pg (benzene)</td>
</tr>
<tr>
<td>[58,59]</td>
<td>Benzene, heptane, toluene and octane</td>
<td>Gas-tight syringe injected into the separation column</td>
<td>Helium</td>
<td>Microfabricated GC using silicon and glass</td>
<td>5 min run for a mixture of benzene, heptane, toluene and octane</td>
<td>~100 ms</td>
</tr>
<tr>
<td>[51]</td>
<td>Benzene, toluene and styrene</td>
<td>6 port sample injector and micro pump</td>
<td>Hydrogen</td>
<td>Microfabricated GC using silicon and glass</td>
<td>30 ms at 30 sccm flow rate</td>
<td>&lt;1 ppb (benzene)</td>
</tr>
<tr>
<td>[54]</td>
<td>Benzene, toluene, ethylbenzene, m-xylene and hexane</td>
<td>Gas-tight syringe injected into injection port of Varian 3800 GC</td>
<td>Helium</td>
<td>HP-5 column</td>
<td>78 ms at 1 mL/min (theoretical result); 250 ms at 2.3 mL/min (experimental result)</td>
<td>1.4 ppt (benzene)</td>
</tr>
<tr>
<td>[61,64,65]</td>
<td>Benzene, toluene, ethylbenzene, p-xylene and others</td>
<td>Tedlar-bag; Micro preconcentrator/injector; Microthermal injectors</td>
<td>Helium</td>
<td>RTX-5 and RTX-200</td>
<td>~100 ms</td>
<td>0.28 ppb (benzene)</td>
</tr>
<tr>
<td>[62]</td>
<td>Toluene</td>
<td>Direct injection</td>
<td>Nitrogen</td>
<td>Not used</td>
<td>-</td>
<td>0.5 ppm (toluene)</td>
</tr>
<tr>
<td>[63]</td>
<td>2-hexanone, isobutylene, propanol, 2-pentanone, 2-octanone, 2-heptanone</td>
<td>Direct injection</td>
<td>-</td>
<td>Not used</td>
<td>2x; 7 – 9 mL/min</td>
<td>~ 1 ppm</td>
</tr>
<tr>
<td>[31]</td>
<td>Toluene</td>
<td>Electrodes and lamp placed inside gas chamber</td>
<td>-</td>
<td>Not used</td>
<td>~ 600 s at 500 mL/min*</td>
<td>&lt; 100 ppb (toluene)</td>
</tr>
</tbody>
</table>

* The authors attribute the high response time to the fact that the sensor was used inside a large gas chamber 15 x 15 x 25 cm instead of having its own chamber.
2.6 Conclusion

Recent developments in the literature relating to µPIDs were reported in this chapter. Notable achievements include devices with ionization chamber volume reduced about 100 times compared with commercial PIDs. The reduced volumes can improve overall GC-PID properties, such as: portability, resource consumption, analysis speed, cost and detection limit. The lowest reported detection limit was 1 ppt for an L-µPID. Such value was achieved in a response time of 56 ms for 1.5 mL/min carrier gas flow rate.

Most of reported reduction in PID size were achieved using microfabrication techniques such as etching and photolithography on silicon and glass wafers. These techniques have good miniaturization potential for high volume production; however, they become expensive for scientific research and prototyping.

Some of the µPIDs are microchannels with well-defined cross-section compatible with microfluidic studies. This presents advantages that enables future investigation of different channel shapes, materials, temperature, pressure (including rarefied pressures) and its influence on the detector performance. A detailed study about influence of parameters in the µPID performance such as electrode materials, electrode area, distance between electrodes, illumination area, and dimensions of the channels would add to the µPID scientific knowledge.

In the L-µPIDs, a commercially available lamp was used as ionization source. Such lamps present limiting factors for miniaturization. The sealing between the lamp and channel can be challenging and the channel has to adapt its shape to the lamp geometry. Developing ionization sources for L-µPIDs that solve those two problems is a future opportunity. For the D-µPIDs, a good opportunity is also to study the different auxiliary gas in microfluidic detectors and the parameters of discharge like the distance between the plasma discharge and the sample inlet, the materials and shape of the discharge electrodes.
For this thesis, the L-PID configuration is more suitable compared to the D-PID. The L-PID provides energy high enough to detect the VOCs targeted by the In’Air Solutions gas analyser and has a simpler operation. On the other hand, the D-PIDs require an additional flux of auxiliary gas for the discharge, which is not ideal for a portable gas analyser that aims to reduce resource consumption. The use of an auxiliary gas would require a larger gas cylinder needed to operate the portable gas analyser.

As an alternative to the lithography based fabrication techniques used in the state of the art, this work presents a simpler µPID design that can be fabricated using PMMA, copper and PVC as main materials; and uses micromilling and electrical discharge machining as main fabrication techniques. Those materials and fabrication techniques are more flexible and cheaper compared to lithography based techniques because they don’t need a photomask or specialized clean rooms, which are costly.

The µPID ionization chamber developed in this thesis is also a microchannel with small ionization chamber volume (1.1 to 6.7 µL), as required for the miniaturization of the whole GC analyser. Four different channel designs are proposed to investigate the consequences in PID performance caused by a change in the geometrical parameters such as electrode area, illumination area and ionization chamber volume. Another feature of the µPID design proposed in this thesis is its modular construction, which enables an exchange of the channel and lamp for maintenance or cleansing. As an attempt to improve sensitivity and avoid the photoelectric effect, two electrode coatings materials are proposed in the next chapter.
Photoionization Detector
Chapter 3  Design

This section describes the design of a µPID fabricated using micromilling and electrical discharge machining. The goal is to produce a device with low ionization chamber volume which is modular and can be integrated into a portable GC. It should have a simple design to be produced by accessible fabrication techniques compared the µPIDs state of the art, which use mainly clean room based fabrication methods. The components are assembled together, dispensing any chemical or physical bonding process and use O-rings for sealing. Section 3.1 presents the µPID design main components, including microchannel, core and shell. It also describes the materials, fabrication and assembly. Section 3.2 evaluates the microchannels dimensions and assembly. Section 3.3 describes the importance of protecting the electrodes from the UV light and proposes two solutions based on coating of the electrodes top surface (shielding).

3.1 µPID Design

The detector has a microchannel as a flow-through ionization chamber. Two main structures are framed around the microchannel: the core, which contains the sensing element; and the shell, whose main functions are to clamp together all parts to ensure structural stability and enable the world-to-chip connections (electronic and fluidic) [66].
3.1.1 Microchannel

The microchannel is the ionization chamber of this design where the gas sample flows and the detection of the sample occurs. The µPID design proposed can produce an ionization chamber with volume up to 100 times smaller compared to some commercial PIDs [16,17]. Figure 3.1 shows four microchannel designs proposed for this work: Channel A, B, C and D. The four shapes displayed have the objective to change gradually the electrodes area, the illumination area and the ionization chamber volume to verify how those parameters can influence the signal of the detector.

The shape of the microchannel is designed to maximize the use of the illumination diameter of a commercial UV lamp (~6 mm) and Figure 3.1 shows a dashed circle indicating the area above the channel that is illuminated by the lamp. Figure 3.2 shows the UV lamp used for the µPID featuring its main dimensions and components. Notice that the lamp window diameter (8 mm) is larger than the bulb diameter (6 mm). However, it is within the bulb diameter where light intensity is higher. The channel vertical walls are made of copper, which are the signal electrodes. The channel height is the same as the copper plate thickness, 0.5 mm. The size of the copper plates were chosen to ensure structural stability so the plate would not bend and they also had an overall size large enough to enable easy manipulation with free hands. The top wall of the channel is the UV lamp window and the bottom is made of PMMA, which will be described in detail in Section 3.1.2.

Important channel geometrical properties are represented in Figure 3.3, considering a simple straight channel as an example. The properties are 1) Width ($W$): representing the distance between the copper electrodes. Therefore, it is inversely proportional to the sensitivity; 2) Height ($H$): shallow channels yield more uniform sample ionization, but less electrode area; 3) Electrode area ($A_e$): depends on the shape and the height of the microchannel. It is directly proportional to sensitivity; 4) Lamp illumination area ($A_i$): top surface of the channel illuminated by the UV lamp. Higher illumination area means more ionized molecules; and 5) Volume of the chamber ($V_c$): volume of the microchannel from inlet to outlet. Large volumes can deplete the signal of GC-PIDs.
From channel A to B, the main objective of the geometry change is to evaluate the effect of width, which causes a change in illumination area and ionization chamber volume as a consequence, but keeps constant the electrode area. Channels C and D are designed to investigate the influence of an increased illumination and electrode area. From channel B to C the width is kept constant (500 µm); however, channel D has reduced width (400 µm) which was necessary to include all the microchannel inside the lamp illumination area with a symmetric design. As a consequence of this reduction in $W$, the electric field will be higher for channel D, and according to PID design guidelines described in Section 2.2, smaller width gives better sensitivity. The $W$ of channel D is not reduced even further to fit more curves because it can make the copper structures too thin and cause their failure either during fabrication or when assembling the channel on the bottom PMMA.

The changes in microchannel design also have influence in the flow pattern, and a uniform flow is desirable to have a good GC-PID performance, according to the design guidelines mentioned in the Section 2.3.3. Channel A and B are straight, which makes them more likely to maintain a uniform flow. Channel C has 90° bend with sharp internal edges and channel D has 180° bend with internal radius of 0.2 mm. The sharp internal edges are more likely to result in recirculation in the channel flow pattern, which can cause distortion in chromatogram peaks. Moreover, sharp edges can cause local intensified electric field, which influences the ion and electron collection efficiency, and consequently affects the sensitivity of the detector.

Table 3.1 presents the dimensions of the four microchannel designs. Notice that channel D has electrode area at least 4 times higher than channels A and B. In addition, the illumination area of channel D is around 6 and 4 times higher than those values for channels A and B, respectively. Channel D has the highest ionization chamber volume, almost 7 times higher than the chamber volume of channel A.
Figure 3.1 – Four microchannel designs used in the µPID: Channel A, B, C and D. A dashed-line circle indicates the UV lamp illumination diameter (~6 mm) above the channel.

Figure 3.2 – Commercial UV lamp (Baseline MOCON Inc.) main components and dimensions.
3.1.2 Core

The components of the core, when assembled, yield the microchannel. The main parts of the core are numbered in Figure 3.4. The top and bottom PMMA are made using micromilling and the electrodes are fabricated with electrical discharge machining (both processes with tolerances ±0.02 mm). Micromilling and electrical discharge machining are cheap compared to the lithography based fabrication techniques and can be used for prototyping. Electrical discharge machining was chosen for the electrodes.
due to availability and for its capacity of producing very thin profiles, which is important for the microchannel design on the copper electrodes. Micromilling would not be compatible for the electrodes because the thickness of the copper plate is too small. In this case, the stress caused in the plate from the end mill could cause deformation of the thin structures formed in the channel D, for example.

PMMA was chosen due to its transparency (to facilitate visual inspection of the assembly), structural stability, chemical inertness to the VOC gas samples used and low porosity (minimal sorption-desorption of the gasses passing through the ionization chamber). Copper was chosen for the electrodes owing to its high electrical conductivity, ready availability and relative low cost compared to other high conductivity metals, such as silver. The O-rings are made of Viton (ERIKS) and its softness is required to avoid breaking the UV window which is made of magnesium fluoride (MgF₂), a fragile material. In addition, a commercial UV lamp was used (Baseline MOCON Inc., USA), with nominal output energy of 10.6 eV (117 nm wavelength).

The design of the top and bottom PMMA were chosen as a function of the copper electrodes shapes. The bottom PMMA is a square block with dimensions 20 x 20 x 3.5 mm and constitutes the bottom wall of the microchannel. It contains the inlet/outlet pores, which have two diameters, 0.5 mm (inside face) and 1 mm (outside face). The smaller inside diameter was chosen to get closer to the microchannel width dimension and the outside diameter size facilitates fabrication.

Also on the bottom PMMA, two holes of 3.10 mm diameter were designed to fit the electronic connection to the copper electrodes. In addition to that, two elevation structures were designed on the top face of the bottom PMMA with 0.5 mm height, same value of electrodes thickness. These structures serve to fit the electrodes in the right position, resulting in the microchannel vertical walls, and to isolate electrically the positive and negative electrode. On top of the electrodes, it is possible to have a shield layer of deposited material to protect the copper from direct incidence of high energy radiation from the lamp.
To enclose the microchannel, the UV lamp is placed on top of the copper electrodes. Two O-rings with 1 mm cross section, 8 and 6 mm inside diameter, fit in the pockets designed on the top PMMA, which closes the channel and ensures that the lamp is fitted to the right position in the centre of the fluidic path between the inlet/outlet pores. The top PMMA has external dimensions 26 x 26 x 5 mm and is designed to fit tightly to the bottom PMMA, make the alignment of the components and reduce the probability of leaks. For this purpose, a recess with 2 mm depth was designed with the silhouette of the bottom PMMA.

Figure 3.4 – Assembled and exploded view of the detector core. (1) Top poly(methyl methacrylate) (PMMA), (2) O-ring 1, (3) UV Lamp, (4) O-ring 2, (5) shield, (6) copper electrodes, (7) bottom PMMA, (8) electrode connection holes, (9) elevation structure, (10) micro-pores.

3.1.3 Shell

The shell mechanically presses all the components together to minimize leakage, and makes the world-to-chip connectivity (fluidic and electronic). The electronic
Design connections are to power the UV lamp, apply voltage on the electrodes and acquire the photoionization current. The fluidic connections connect the sample inlet/outlet to the microchannel.

Figure 3.5 shows two isometric views of the assembled shell (top and bottom) and the main components that can be seen from its outside. The main structures are the top and bottom shell, which were made of PVC and fabricated by micromilling. PVC was chosen due to its stable mechanical properties, ready availability, low price and its good compatibility with the micromilling fabrication process. Top and bottom shell have four passing holes for M3 screws and nuts that press all the parts at appropriate pressure for fluidic sealing and structural stability, meaning, no part would move unnecessarily during operation of the device. On the top shell, two M3 female threads were machined to fit two M3 screws. They were used to fix the lateral pin slide at the right position when the UV lamp electronic pin touches (Feinmetall, F670) the lamp pads. The lateral pins also ensure complete enclosing of the UV lamp for safety reasons, to avoid high energy light from reaching the detector operator. The lower surface of the bottom shell had M3 threads machined to assemble the FESTO connector type QSM-M3-2, which is a fast plug-in connector to 2 mm OD tubing. It also contains two holes to pass the copper electrodes electronic pins (Feinmetall, F670).

Figure 3.5 – Top and bottom isometric view of the shell. (1) Top shell, (2) bottom shell, (3) M3 screws, (4) M3 pin fix screws, (5) lateral slide pin, (6) UV lamp electronic pin, (7) copper electrodes electronic pin, (8) fluidic connectors for 2 mm OD tubing, (9) nuts.
Figure 3.6 provides section view in two directions of the fully assembled device, illustrating how the fluidic and electronic connections reach the ionization chamber, copper electrodes and the lamp. Also, it provides an amplified detailed view on the microchannel in longitudinal (Figure 3.6b) and cross-sectional (Figure 3.6d) directions, illustrating the simple geometry of the microchannel and how it is formed by the lamp window, PMMA and electrodes. The bottom shell has two O-ring pockets on its top surface to fit O-rings with 3 mm outside diameter and 1 mm cross section. They are also made of Viton (ERIKS) and connect the inlet/outlet gas sample to the ionization chamber. The top shell fits the top PMMA and positions the core so that it is aligned with the fluidic and electronic connections. Two square holes on the top shell fit the lateral pins, which has an electronic spring pin that reaches the lateral contact pads of the UV lamp. The spring allows freedom of the electronic pin tip movement after touching the lamp, which is important to avoid any excessive load transferred to the fragile lamp, which might break it.
In comparison with the current state of the art [54,56–59,61], the proposed design has the following features: 1) Easy prototyping, since the manufacturing do not require multiple fabrication techniques; 2) Lower fabrication cost, this device does not require clean-room complex and high-cost facilities and processes. In addition, the materials used are cheaper compared to silicon wafers; 3) Modular and easy mount-dismount,
which provides the advantage of easy replacement of parts such as copper electrodes and UV lamp.

After some operation time, the electrodes might get oxidized which could reduce significantly the sensitivity of the device. In addition to that, lamps suffer from window solarisation, and have limited lifetime; illustrating the importance of easy replacement of those components. Another advantage of exchanging components is that lamps with different energy could be easily exchanged, changing the selectivity of the device according to the application need. Avoiding to use bonding technique for sealing, might however cause leakage when high pressure is applied, which can be undesirable, especially if the device is used with small volume samples coupled with gas chromatography. Technical drawings of the µPID prototype components can be found on Appendix E.

### 3.2 Evaluation of the Microchannel

Since the fabrication processes are not perfect, they generate variations in the parts dimensions, which can translate in assembly problems for the device. For example, Figure 3.7 shows an undesirable gap created by improper fitting of the copper electrode on the bottom PMMA elevation. The gaps have approximated sizes varying from 15 to 70 µm. This improper fitting can create deviations in channel width from the nominal values, and the gaps might also increase leakage from the microchannel. Leakage values for all microchannels can vary between 8 and 28 % depending on the flow rate and channel design used. Details about leakage measurement are presented in the Appendix B.

The width of all the channels were measured with a digital optical microscope (KEYENCE, VHX-600 digital microscope), and the measurements are displayed on Table 3.2. The values are an average of n measures taken. The table also presents the relative standard deviation of the measurements and how much it deviates from the nominal value. Channel D has greatest deviation from the nominal value and channel B has the lowest, ~13 and ~1 %, respectively. Channel C runs in two directions (x and
y), which should have the same width. However, the measurements were found different, with $W_x$ and $W_y$ presenting $\sim 10\%$ lower and $\sim 10\%$ higher values than the nominal width, respectively. This variation is visible in the microscope image on Figure 3.8.

Deviations in the channel dimensions are caused mainly by imperfections in the fabrication, which as a consequence yield deviation in the shapes of the pieces, and results in imperfect fitting between the copper electrodes and the bottom PMMA. As mentioned before, the fabrication tolerances of the machines used to fabricate the prototypes are $\pm 0.02$ mm, which is already $8\%$ of the width of the channel A, for example. This tolerance combined with other imperfections in the fabrication process such as: improper positioning of the piece inside the machine and worn out tools like the end mill (in the case of micromilling) can result in relatively large deviations. Nevertheless, for the development of a working prototype those values are still acceptable. Future improvement should be done by checking systematically the calibration of the fabrication tools and state of the end mill. Also, when the optimal design is achieved, injection moulding technique can be used for batch-fabrication which allows for easier standardized and high precision reproduction of the design.

Figure 3.7 – Elevation structure and copper electrodes fitting. Gap existing between PMMA and copper due to misfit.
Figure 3.8 – Zoom on channel C to show difference in horizontal and vertical widths.

Table 3.2 – Average channel width ($\bar{W}$), relative standard deviation ($\sigma(\bar{W})/\bar{W}$), percent deviation of the measured value from the nominal value (Deviation) and number of measurements for all channels ($n$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Channel A</th>
<th>Channel B</th>
<th>Channel C x</th>
<th>Channel C y</th>
<th>Channel D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{W}$ [µm]</td>
<td>278.3</td>
<td>504.3</td>
<td>454.0</td>
<td>547.7</td>
<td>347.8</td>
</tr>
<tr>
<td>$\sigma(\bar{W})/\bar{W}$</td>
<td>1.8 %</td>
<td>2.2 %</td>
<td>5.3 %</td>
<td>1.3 %</td>
<td>3.4 %</td>
</tr>
<tr>
<td>Deviation</td>
<td>11.3 %</td>
<td>0.9 %</td>
<td>-9.2 %</td>
<td>9.5 %</td>
<td>-13.1 %</td>
</tr>
<tr>
<td>$n$</td>
<td>11</td>
<td>7</td>
<td>7</td>
<td>6</td>
<td>30</td>
</tr>
</tbody>
</table>

3.3 Shielding

When the copper electrodes are exposed to radiation at a frequency that has photon energy higher than the copper work function, the photon energy can cause the electrons on the copper surface to be ejected, resulting in signal noise. Therefore, it is desirable to protect the electrodes from the high-energy radiation coming from the UV lamp. A possible solution is to create an UV light shield on the copper surface reached by the radiation. Ideally, a good shield will filter out all the radiation with an energy greater than the work function of the metal used as electrodes (in the case of copper the work function is 4.48 to 4.94 eV [30]). In addition, it should be thin, to ensure that the thickness of the coating does not increase the volume of the ionization chamber. It also must not cover the area of the electrode used for ion and electron collection. Other
Design

important characteristics are: chemical compatibility with the electrode materials and gas samples, resistance to temperature oscillation, humidity and mechanical stress and strain. Two materials were considered for use as an electrode shield: diamond-like carbon (DLC) and polymethyl methacrylate (PMMA). In summary, the main design requirements of the shield are: to avoid transmission of light energy higher than copper work function and to have low thickness.

Diamond-like carbon is a metastable form of amorphous carbon that can be used as a protective coating. It can be applied as thin film with dimensions ranging from a few nm to µm [67]. Even very thin films (nm thickness) can block unwanted radiation, which renders it potentially suitable as an electrode coating in this application. A 0.1 µm thickness layer of DLC can have 5 – 18 % UV transparency at 350 – 450 nm wavelength range (3.54 – 2.75 eV) and 0.2 µm DLC thickness yields 2 – 8 % UV transparency [67]. Also, DLC preferentially blocks short wavelengths, which are the high energy radiation that can cause photoelectric effect on copper [68,69].

A first sample of DLC coating was produced on one side of a 1 mm thick copper plate. Before the coating was applied, the surfaces were polished and etched, to remove impurities and for better adhesion of the DLC layer. The coating was made using plasma enhanced chemical vapour deposition (PECVD) and had 1 µm thickness. Figure 3.9a and 3.9b show the difference between the coated and uncoated side, where the DLC coating yields a grey surface on top of the copper. This sample started to peel off after a few weeks, likely due to exposure to sunlight and summer ambient temperatures/humidity (~30 °C and ~70 %). Figure 3.9c shows the state of the peeled off sample.

The scanning electron microscope (SEM) images on Figure 3.10 show that the DLC coating detached from copper like a peeled off thin foil, suggesting poor adhesion between the coating and substrate. In order to create a stable coating, a second sample was produced on the same type of substrate, this time, incorporating a titanium layer between the DLC and copper to increase adhesion. The new sample had considerably better stability and did not fail (crack or break) during the test period (1 month).
Another electrode coating considered to produce a thin layer, avoiding unnecessary ionization chamber volume increase, on the copper electrodes to block photons with energy higher than the copper work function is the PMMA coating. This material does not transmit wavelengths below 360 nm (or energy higher than 3.44 eV) [70], which should be sufficient to avoid photoelectric effects in the copper electrodes. PMMA is a relatively cheap material compared to DLC and can be deposited as a top layer on the electrodes by spin coating, an inexpensive process. Besides that, spin coating does not require complex machinery. Disadvantages to be considered are: 1) difficulty to produce perfectly flat surfaces to avoid leakage; 2) difficulty to produce very thin layers (< 0.1 µm) and 3) During fabrication, the PMMA might run inside the channel wall, isolating the electrodes from the ions, then reducing the active current area inducing a lower signal.
3.4 Conclusions

This chapter presented the design of the µPID developed for this thesis. It was possible to develop a design that uses simpler fabrication methods and materials compared to the lithography based techniques and silicon/glass materials presented in most state of the art miniaturized PIDs. The ionization chamber of the µPID presented in Chapter 3 is a microchannel formed between the commercial UV lamp (10.6 eV energy), copper electrodes fabricated by electrical discharge machining and the micromilled PMMA structures. The world-to-chip connections to power the lamp, inject the gas sample and measure the current signal were designed in a micromilled PVC shell.

The miniaturized PID prototypes developed in the last decade use mostly lithography based fabrication techniques, which can be good for batch producing devices with a well-defined design. However, those techniques require specialized clean room installations and the machines used can cost up to a hundred thousand euros. Moreover, recent PID miniaturization devices report detectors that have their ionization chamber bonded to the UV lamp. This can pose a problem to the operation of the PID because the UV lamp is a sensitive part and needs periodical cleansing of its window to maintain full light intensity, which affects PID sensitivity. Besides, lithography based techniques require a photomask, which has an approximate cost of one thousand euros.

Chapter 2 mentioned the importance of having a small ionization chamber as a design requirement for PID miniaturization with the ultimate goal to enhance the GC system portability. The chamber volumes of the µPID presented in Chapter 3, with values ranging from 1.1 µL and 6.7 µL, are up to 100 times smaller than the volumes of the commercial PIDs [21–23], these values are aligned with the whole GC miniaturization strategy. The size of the ionization chamber was decided as a function of the microchannel design, which depended on lamp illumination area, the accuracy of the fabrication techniques (± 0.02 mm) and the structural stability of the copper plate.

The four microchannel designs (channels A, B, C and D) have variations in their geometry so that further investigation can be done on how the geometrical parameters of a microchannel-shaped ionization chamber influence the µPID performance. The
main differences between the channels that can impact the GC-µPID sensitivity are channel width ($W$), electrode area ($A_e$), illumination area ($A_l$) and ionization chamber volume ($V_c$). Channel A and B main difference is the change in width and illumination area. Channel B, C and D main difference is the increasing electrode area and illumination area. The different ionization chamber volumes presented between the microchannels can impact the sensitivity of the overall GC system if the peaks leaving the column are sharp enough.

Another microchannel geometry aspect to take into consideration in the µPID sensitivity is the influence on the flow pattern and the electric field intensity caused by the shape of the curves of channels C and D. Channel C has 90° bend with sharp internal edges and channel D has 180° bend with an internal radius of 0.2 mm. Those two characteristics can influence the flow pattern and electrical field local intensity inside the ionization chamber. Sharp edges can create less uniform flow profile, which can distort chromatogram peaks, leading to a lower GC system performance; they can also cause local intensified electric field, which affects the ion and electron collection efficiency.

The main advantages of the design presented in this chapter include: 1) Simpler fabrication techniques and materials; 2) Modular construction; 3) Use of multiple channel designs with the same UV lamp; 4) Coating on electrodes with DLC or PMMA. The design met the initial objective to deliver a prototype with simpler fabrication compared to the state of the art of miniaturized PIDs. Future improvements should be applied in the precision of the fabrication and assembly, which generated undesirable deviations in channel size and possible leakage paths. A possible solution to leakage is to modify the µPID parts to include extra O-rings.
54  Design
Chapter 4  Experimental Results for Direct Injection of the Gas Sample into the µPID

This chapter presents the experimental setup and results to characterize the µPID prototype when the gas sample is injected directly into the device. Section 4.1 describes the experimental setup used to perform the tests, including details about the gas delivery system and signal acquisition. Sections 4.2 to 4.5 evaluate several aspects of the µPID, including the influence of channel design, UV lamp degradation, PMMA coating on electrodes, applied voltage on signal electrodes, sample flow rate. The uncertainty calculation of the measured signal is also presented in Section 4.2.1. Moreover, Section 4.6 shows two response curves of the µPID using the most sensitive channel and the detection limits obtained according to a range of signal filtering options. Section 4.7 investigates the influence of other aspects such as position sensitivity of the device and the impact on the signal caused by high humidity level in the sample.

4.1 µPID Experimental Setup

Figure 4.1 shows an experimental setup built to evaluate the µPID prototype. Two gas sample supplies are used, one containing a VOC pollutant and another with nitrogen. Both are isolated by ball valves (BV1 and BV2) and connected to a mass flow controller (MFC). The MFC regulates the flow rate of gas sample into the µPID and the flow rate leaving the device is read by a mass flow meter (MFM).

The MFCs and MFMs used in this work were all from the same manufacturer (Bronkhorst) and multiple devices with a range of flow rates were used. Table 4.1
indicates the abbreviation used in this work to indicate a MFC with a specific flow rate range, the product model code and the full scale of the flow rate of the MFCs and MFM used for the experiments. All tubing connecting the gas flow are made of PTFE. For safety reasons, the experimental setup is installed inside a fume hood to avoid spreading of the pollutant gases into the test room. The sample outlet is left to atmospheric pressure.

The µPID 10.6 eV lamp is powered by the UV lamp drive circuit from a commercial PID (piD-TECH® eVx™, 045-010), which is supplied with 4 V and 35 mA from the power supply 1. To measure the current inside the ionization chamber, the power supply 2 applies a voltage between the copper electrodes, and the current generated by the PID detection process passes through the current preamplifier (Low-Noise Current Preamplifier, Stanford Research Systems, SR570), which can filter and amplify low current signals. After amplifying the current signal to voltage signal, the voltage magnitude is measured by an analog to digital converter (ADC) from National Instruments (NI-USB-6001). A MATLAB algorithm reads and stores the digital signal in a computer. The MATLAB code creates a virtual session to communicate with the National Instruments ADC where measurement channels are added with 200 Hz acquisition rate. The original MATLAB code used for data acquisition is presented in the Appendix C.

Figure 4.1 – Experimental setup used for experiments with the µPID prototype.
Table 4.1 – List of the Bronkhorst mass flow controllers (MFC) and mass flow meter (MFM) used in the experiments. All MFCs and MFMs are expressed in volumetric units, since they use the same normalized condition (0°C and 1.013 bar).

<table>
<thead>
<tr>
<th>Name</th>
<th>Model</th>
<th>Full Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC1</td>
<td>FG-201CV-RAD-22-V</td>
<td>1000 mL/min</td>
</tr>
<tr>
<td>MFC2</td>
<td>F-201DV-AAD-33-V</td>
<td>21 mL/min</td>
</tr>
<tr>
<td>MFC3</td>
<td>F-201DV-AAD-11-V</td>
<td>50 mL/min</td>
</tr>
<tr>
<td>MFC4</td>
<td>F-200DV-AAD-33-V</td>
<td>10 mL/min</td>
</tr>
<tr>
<td>MFC5</td>
<td>F-201DV-AAD-22-V</td>
<td>500 mL/min</td>
</tr>
<tr>
<td>MFM</td>
<td>F-100D-AAD-33-V</td>
<td>20 mL/min</td>
</tr>
</tbody>
</table>

Figure 4.2 shows the electronics diagram to power the lamp and obtain the signal. In addition, it displays a real image of the µPID wiring and fluidic connections. The labels indicate the visible elements and electronic connections. Table 4.2 provides a description of the elements indicated in Figure 4.2. In order to reduce signal noise, a Faraday cage (FC), as displayed in Figure 4.3, is also used.

Figure 4.2 – a) Schematics of electronics connections and circuit; b) µPID image with electronic and fluidic connections.
Experimental Results for Direct Injection of the Gas Sample into the µPID

Table 4.2 – Electronic items from Figure 4.2.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Power supply 1 (4 V)</td>
</tr>
<tr>
<td>II</td>
<td>UV Lamp drive circuit</td>
</tr>
<tr>
<td>III</td>
<td>UV Lamp</td>
</tr>
<tr>
<td>IV</td>
<td>Ionization chamber and electrodes</td>
</tr>
<tr>
<td>V</td>
<td>Current preamplifier</td>
</tr>
<tr>
<td>VI</td>
<td>Power supply 2 (0.1 to 30V)</td>
</tr>
</tbody>
</table>

Figure 4.3 – Faraday cage made of aluminium foil using cardboard for structural stability. The Faraday cage was used to reduce noise in the measured signal. (a) Faraday cage open to illustrate how the µPID was positioned inside; (b) Faraday cage closed with the µPID inside.
4.2 Sample Direct Injection: Influence of Channel Design

In order to verify the influence of different microchannel designs on the detector signal, the response using channels A, B, C and D (channel geometries referenced in Section 3.1) were obtained with direct injection of nitrogen and 100 ppm of toluene (nitrogen balance gas) at 50 mL/min (using MFC1). Figure 4.1 shows the experimental setup used to obtain the signal.

Before each data acquisition, the channel was purged with nitrogen during 5 min. Figure 4.4 illustrates the changes in the signal and operation of the experimental setup valves during the signal measurement. After starting the data acquisition (t = 0 s), the following procedure was applied: i) Continue the purge with nitrogen for 1 minute; ii) Close nitrogen supply valve and wait for the MFC to measure 0 mL/min (which lasts about 1 minute); iii) at 2 min of test, open the toluene 100 ppm connection valve for pollutant signal acquisition during 3 min; iv) close the toluene 100 ppm valve and wait for MFC display 0 mL/min; v) open the nitrogen valve to purge the channel so the signal level returns to the baseline. Figure 4.4b shows the state of the valves for the supply of nitrogen and toluene during the experiment procedures from (i) to (v) described above.

Figure 4.5 shows the signal (current measurement) as a function of time for all channels. For each channel, three datasets measured in a sequence are shown to demonstrate the repeatability of the results (dataset 1, 2 and 3 mentioned in the legend of the plots in Figure 4.4). The signal was obtained by applying 30 V on the copper electrodes and the current preamplifier was set for a low-pass first order RC filter with cut-off frequency ($f_c$) of 10 Hz, 12 dB attenuation and 1 nA/V amplification. The amplification and attenuation values used in the preamplifier will remain constant for all results obtained in this work.
Figure 4.4 – Representation of the experimental procedure used to obtain the sample direct injection signals. a) Typical signal obtained with indicated procedure stages from (i) to (v); b) Operation of the valves (open/closed) to perform the experiment and the respective procedure stage from (i) to (v).
Figure 4.5 – Signal measurement (n = 3) using four different microchannel designs with sample of nitrogen and toluene 100 ppm at 50 mL/min. 30 V applied on the electrodes and a first order RC filter at 12 dB, $f_c = 10$ Hz and 1 nA/V applied. a) Channel A; b) Channel B; c) Channel C; d) Channel D (also including representation of $S_r$, $S_p$ and $S_b$).

For each dataset, the signal representing the stable value for the baseline ($S_b$) and the pollutant ($S_p$) are obtained at 35 s and 270 s of experiment, respectively. The signal at 35 and 270 s is considered stable with less than 0.2 % variation in a 5 s interval. The difference between the pollutant and the baseline signal is the signal rise:

$$S_r = S_p - S_b.$$  \hspace{1cm} (4.1)

The $S_r$ (represented in Figure 4.5d) is what ultimately permits to estimate the sensitivity level of the detector. The average value of the signal at the baseline, pollutant and rise
Experimental Results for Direct Injection of the Gas Sample into the µPID

level for all channels are displayed in Figure 4.6. The highest variation for $S_p$ and $S_r$ is found between channel A and D, where the channel D can have values up to 3 times higher. Regarding $S_p$, the largest difference is found between channel B and D, and reaches more than two times. The error bars displayed in Figure 4.6 are 3.5 % of the measured value. This error value stems from the maximum error observed in the experiments for direct injection of sample and is calculated in detail in Section 4.2.1. The response time, which is the time it takes for the signal to go from baseline level to pollutant level, is less than 1 s for all channels.

![Figure 4.6](image-url)

*Figure 4.6 – Average signal level for all channels; a) Baseline signal ($S_b$); b) Pollutant signal ($S_p$); c) Signal rise ($S_r$).*
Table 3.1 can be used as a reference to investigate the influence on the measured signal caused by the geometry changes of each channel. From channel A to channel B, the signal level doubles and the main geometrical change between those two designs is the width of the channel \( W \), which changes the illumination area \( A_i \) as a consequence. The changes in the two parameters, \( W \) and \( A_i \), observed from channel A to channel B have opposite effects on the signal level. Channel A has smaller \( W \) which means it has a stronger electric field compared to channel B, this increases the ion and electron collection efficiency and contributes positively for the sensitivity of the detector. On the other hand, channel B, despite the larger \( W \), has a larger illumination area \( A_i \), which also contributes positively to the sensitivity of the \( \mu \)PID. The increase in pollutant signal \( (S_p) \) and signal rise \( (S_r) \) for channel B shows that, for the applied channel dimensions, illumination area is more important than width for signal level.

Figure 4.6a shows that the baseline signal \( (S_b) \) for channel A is higher than channel B, which is likely caused by a larger portion of the electrodes getting hit by photons on channel A. For channels A, B, C and D, the portion of the electrodes top surface illuminated by the lamp diminishes with increasing ionization chamber volume; however, for channels B, C and D, baseline signal increases with less electrode surface area illuminated by the lamp and channel A has an inverse effect. An explanation for this phenomenon can be that channels B, C and D generate higher current for the residual ionisable components that can be inside the ionization chamber even when nitrogen is used, since those channel designs have higher sensitivity due to the larger electrode area and illumination area compared to channel A.

From channel B to D, it is possible to attribute the increase in signal rise \( (S_r) \) to the simultaneous increase in illumination area and electrode area. From channel B to C, the signal rise \( (S_r) \) increase is small, despite the fact that the \( A_i \) and \( A_e \) of channel C are approximately double compared to channel B. This suggests that the influence of the curves added to the design of channel C can impact the sensitivity negatively. Channel D has \( A_i \) and \( A_e \) approximately 2 and 3 times higher compared to channel C, respectively; however, its signal rise \( (S_r) \) more than doubles, which makes channel D the most sensitive of the microchannel designs. Another change in channel D compared
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to channels B and C is the width, which is 100 µm lower compared to channels B and C. This has also a positive impact in its sensitivity and has contributed to establish channel D as the most sensitive one.

As a consequence of the changes in the channel shapes, ionization chamber volume increases as illumination area and electrode area increases. However, $V_c$ magnitude is still in the same order of greatness (~1 µL), therefore the increase should not have a significant impact on the signal, including when it is integrated to a GC that uses a large sample volume. This will be investigates with higher detail in Chapter 5.

4.2.1 Error of Signal Rise

The error in $S_r$ measurements is calculated by its expanded uncertainty, which is

$$U(S_r) = t \cdot u(S_r).$$

(4.2)

Where $t$ comes from the Student’s distribution for $v_{eff}$ degrees of freedom, and $u(S_r)$ is the standard uncertainty of $S_r$. Because the signal rise is measured by equation (4.1), $u(S_r)$ results from the combination of $u(S_p)$ and $u(S_b)$; thus,

$$u^2(S_r) = u^2(S_p) + u^2(S_b).$$

(4.3)

Both $S_p$ and $S_b$ are direct measurements with uncertainty from the combination of two main sources: repeatability ($u_{re}$) and measurement resolution ($u_{dr}$) from the instrument used. Therefore:

$$u^2(S_p) = u_{re}^2(S_p) + u_{dr}^2$$

(4.4)

and

$$u^2(S_b) = u_{re}^2(S_b) + u_{dr}^2$$

(4.5)

The resolution is the same for $S_p$ and $S_b$ and stems from the analog to digital converter (ADC), which has 20 V measurement range and 14-bit resolution, yielding 1.22 mV of voltage resolution. Considering the 1 nA/V amplification, the resolution ($R$) of the
measurement in electrical current units was 1.22 pA. The standard uncertainty of the resolution can be approximated assuming a rectangular distribution, yielding:

$$u_{dr} = \frac{R}{2}/\sqrt{3}.$$  \hspace{1cm} (4.6)

The repeatability for $S_p$ and $S_b$ were obtained from a series of 8 consecutive measurements (Figure 4.7) following the same procedure described to obtain the plots presented in Figure 4.5. The repeatability is calculated as the standard deviation for the average values as:

$$u_{re} = \sigma(S) = \frac{\sigma(S)}{\sqrt{n}},$$ \hspace{1cm} (4.7)

where $n$ is the number of consecutive measurements.

![Figure 4.7 – Repeatability measurements of the µPID with direct gas injection (8 runs).](image)

The effective degrees of freedom used to compute $t$ is obtained from the Welch-Satterthwaite equation, which accounts for the degrees of freedom of other associated uncertainties:

$$\frac{u^4(S_r)}{v_{ef}} = \frac{u_{re}^4(S_b)}{v_b} + \frac{u_{re}^4(S_p)}{v_p} + \frac{u_{dr}^4(S_b)}{v_{dr}} + \frac{u_{dr}^4(S_p)}{v_{dr}}$$ \hspace{1cm} (4.8)
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Where, $v_b$, $v_p$ and $v_{dr}$ are the degrees of freedom from the baseline signal repeatability, pollutant signal repeatability and digital resolution, which are 7, 7 and $\infty$, respectively.

The resulting effective degrees of freedom yields a $t$ coefficient value of 2.43, considering 95.45% confidence interval. The resulting expanded uncertainty yields ~3.5% of the signal rise intensity. This value is considered to calculate the error bars of signals measured from direct injection. For a reference, Table 4.3 presents the average, standard deviation and measurement error for $S_b$, $S_p$ and $S_r$ during the repeatability test.

Table 4.3 – Averages ($\bar{X}$), standard deviations ($\sigma(\bar{X})$) and percent errors ($U/\bar{X}$) of $S_b$, $S_p$ and $S_r$.

<table>
<thead>
<tr>
<th>Signal</th>
<th>$\bar{X}$</th>
<th>$\sigma(\bar{X})$</th>
<th>$U/\bar{X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_b$</td>
<td>0.217</td>
<td>0.0009</td>
<td>1.1%</td>
</tr>
<tr>
<td>$S_p$</td>
<td>1.049</td>
<td>0.0119</td>
<td>2.8%</td>
</tr>
<tr>
<td>$S_r$</td>
<td>0.831</td>
<td>0.0124</td>
<td>3.5%</td>
</tr>
</tbody>
</table>

4.3 Influence of UV Lamp and Electrode Deterioration

The lamp and copper electrodes can deteriorate with use. The latter is subjected to humidity and can oxidize, while the lamp has a lifetime estimated as ~4000 hours of operation and its intensity decreases with time. The lamp lifetime can be reduced depending on the gas sample injected in the detector, for example, samples that contain solid particles or droplets that damage the lamp window.

In order to verify the influence of lamp and electrode deterioration, the µPID signal was measured for three different conditions, following the same procedure described in Section 4.2. The materials used for this analysis were: i) used lamp (estimated operation time ~700 h); ii) used channel D electrode (estimated operation time ~7 months) (channel D); iii) new lamp; iv) new channel D electrode. The three measurement conditions were: a) used lamp and used electrode; b) new lamp and used electrode; c) new lamp and new electrode.
Figure 4.8 shows the signal for each case and a comparison between the $S_r$ for the three conditions. By replacing the old lamp for the new one, the $S_r$ gets approximately three times higher. Changing the old electrode for the new one, yielded no perceivable impact in the signal because the change is smaller than the reported signal error. This highlights the importance of the lamp maintenance, supporting the relevance of the easy mount-dismount feature of the µPID design.

Despite being used only $\sim700$ h (less than half the lamp life), the signal obtained with the old lamp is very low. A reason for that can be the direct contact of the lamp on the copper electrode surface, which might scratch its surface damaging the light transmission. A solution to this is to have some treatment of the copper electrode top surface either by performing a better polishing to reduce roughness or adding a soft polymeric material as coating. A solution to the large reduction in sensitivity of the µPID due to lamp deterioration is to perform constant calibration of the detector and periodical cleansing of the UV lamp window. However, with loss in sensitivity, increase in detection limit will still occur.
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Figure 4.8 – Results from experiments to verify the influence of lamp and electrodes deterioration on signal level. Data obtained for channel D using nitrogen and toluene 100 ppm at 50 mL/min with 30 V on the electrodes. (a) Used lamp and used electrode; (b) new lamp and used electrode; (c) new lamp and new electrode; (d) Signal rise for the three cases (a, b and c).

4.4 Influence of the PMMA Coating on the Electrodes

In order to verify the influence of a 5 \( \mu \)m thick PMMA coating on the top surface of the electrodes, the signal of channel B was measured with and without the coating. The expected changes to occur would be a reduction in noise and baseline signal [45,47,51,53]. Figures 4.9a and 4.9b show the signal acquisition following the method described in Section 4.2 without and with the PMMA coating (\( n = 3 \)), respectively. Figures 4.9c and 4.9d show the noise level at the baseline when no filter was applied at the current preamplifier. The noise is measured by the amplitude of the oscillation in the signals presented in Figures 4.9c and 4.9d, which yield values of approximately 1.1 nA for both cases (without and with PMMA).

Figures 4.9e and 4.9f show a basic spectral analysis of the noise signal without and with PMMA, respectively. For both cases, the 50 Hz frequency has the greater contribution in the noise signal, which is the frequency of the power grid used in the laboratory. This means that noise, when no filter is applied, is caused mostly by electromagnetic field interference from other electronic equipment used close to the \( \mu \)PID. Figure 4.9e shows minor contribution to the signal at frequency \( \sim 20 \) Hz and Figure 4.9f has the minor
contributions at \( \sim 10 \) Hz. This can explain why Figures 4.9c and 4.9d have their oscillations showing distinct patterns, despite having the same noise level. Those small differences can be caused by oscillations in the power grid that can occur when other equipment are turned on/off, e.g. the exhaust fan from the fume hood where the experiment was performed or even by people moving in the lab.

The two signal acquisition experiments (without and with PMMA) were run consecutively and, as Figure 4.9 shows, the PMMA coating made no impact on the noise level, baseline signal and signal rise. This can mean that the 5 \( \mu \)m PMMA coating is not effective in blocking the photons coming from the lamp or that other factors have higher impact in the noise level \( (N) \), baseline signal \( (S_b) \) and signal rise \( (S_r) \).
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Figure 4.9 – Signal measurement with and without PMMA coating for direct injection on channel B using nitrogen and toluene 100 ppm at 50 mL/min with 30 V on the electrodes. (a) Signal without PMMA coating, $f_c = 10$ Hz ($n = 3$); (b) Signal with 5 µm PMMA coating, $f_c = 10$ Hz ($n = 3$); (c) Noise at baseline without PMMA coating, no filter applied to signal; (d) Noise at baseline with PMMA coating, no filter applied to signal. (e) Spectral analysis of signal presented in Figure 4.9c; (f) Spectral analysis of signal presented in Figure 4.9d.
4.5 Influence of Voltage and Flow Rate

Channel D yielded the highest signal compared to the other channels; therefore, it has the highest sensitivity resulting in lower detection limit and better signal stability. In this section, the influence of voltage and flow rate on the µPID signal using channel D is evaluated. A direct injection of toluene 100 ppm was performed using flow rates of 0.5, 2, 5, 10 and 20 mL/min with the MFC2. After signal stabilization, the \( S_p \) was measured at voltages ranging from 0.1 to 30 V. Those measurements are shown in Figure 4.10a. The baseline signal \( (S_b) \) as a function of voltage (Figure 4.10b) was obtained from the stable signal from a direct injection of nitrogen at 20 mL/min. Using Equation 4.1, the curve of \( S_r \) as a function of voltage for various flow rates was obtained (Figure 4.10c).

Figure 4.10c shows that \( S_r \) is more sensitive to voltage in the 0.1 – 5 V range compared to the 5 – 30 V range. To verify if this behaviour is also valid for channels A, B and C, Figure 4.11 shows the dependence of signal on voltage for all channels, using dimensionless signal for direct comparison of the shape of the curves. The signal used to make the signal dimensionless \( (S_{\text{max}}) \) is obtained from the maximum signal measured during the voltage variation experiment for each channel, which is at 30 V for each channel. Therefore, most efficient signal increase occurs from 0.1 to 5 V for all microchannel designs. However, the higher the applied voltage, the more stable the signal is, rejecting noise from small perturbations in the system. Moreover, higher voltage yields higher electric field which can avoid recombination of molecules already ionized in the ionization chamber of the PID and recombination reduces the sensitivity of the detector. Considering that, 30 V is a suitable voltage value for experimental evaluation of the µPID.

The change in signal level with flow rate as indicated in Figure 4.10a and Figure 4.10c is an unexpected result, because the µPID is a concentration-sensitive detector, rather than a mass-sensitive detector. Following this principle of concentration-sensitivity, it would have a signal level independent of the flow rate applied, unless the change in flow rate modifies the concentration inside the ionization chamber. This is a possibility
since higher flow rates result in higher pressure drop along the microchannel establishing a higher pressure at the entrance. Although the higher pressure will not modify the molar concentration, which should be the main factor of influence in sensitivity, it will increase the density of ionisable sample that can produce a photoionization current. Figures 4.10a and 4.10c show higher signal for higher flow rates. The estimated sensitivity to flow rate ranges from 0.042 nA/(mL/min) at 30 V to 0.001 nA/(mL/min) at 0.1 V. Those sensitivity values were obtained by a linear fit of the curve of signal as function of flow rate for each voltage.

Figure 4.10 – Signal at voltages 0.1 – 30 V for a) \( S_p \) measurements of channel D for toluene 100 ppm and flow rates 0.5, 2, 5, 10 and 20 mL/min. b) \( S_p \) measurements of channel D for nitrogen at 20 mL/min. c) \( S_r \) measurement of channel D and flow rates 0.5, 2, 5, 10 and 20 mL/min.
Chapter 4

4.6 μPID Response Curve

A range of toluene concentrations were injected into the μPID to obtain the response curve. The detector (using channel D) was subjected to a series of gas purge with nitrogen followed by injection of toluene (at various concentrations). A flow rate of 20 mL/min and a potential of 30 V were applied on the electrodes to yield fast stabilization and a stable signal, respectively. The gas sample was injected into the μPID using the setup of Figure 4.12. The flow rates set at $Q_1$ and $Q_2$ sum up to 20 mL/min for 11 concentration points (using MFC2 and MFC3) and are chosen to yield a dilution of the toluene concentration in the gas cylinder ($C_p$) from 100 % to 1 %. $Q_1$ and $Q_2$ are the flow rates of 100 ppm toluene and nitrogen, respectively. Two response curve tests were performed, and the signal obtained as a function of time is displayed in Figures 4.13a and 4.13b. The toluene concentration applied for both tests were the same; however, their stabilization time for the toluene injection were different, 28 s for response test 1 and 38 s for response test 2. Also, response test 2 was performed after two months and a half from the first response test; therefore, for the second test the UV lamp has its performance decreased from usage (approximately 220 h more of UV lamp use).
The toluene concentration injected into the µPID ($C_{mix}$) is estimated from the dilution of the toluene concentration ($C_p$) present in the gas cylinder. The dilution is obtained from a dilution ratio ($X_Q$):

$$C_{mix} \approx X_Q \cdot C_p,$$

where the dilution ratio is obtained from the flow rates

$$X_Q = \frac{Q_1}{(Q_1 + Q_2)}.$$

Table 4.4 provides the flow rates applied to the mass flow controllers and the dilution ratio they yield.

Table 4.4 – Mass flow controller flow rates $Q_1$ and $Q_2$ (mL/min) and dilution ratio $X_Q$ (dimensionless). $Q_1$ and $Q_2$ are the flow rates of toluene 100 ppm and nitrogen, respectively.

<table>
<thead>
<tr>
<th>$Q_1$</th>
<th>20</th>
<th>18</th>
<th>16</th>
<th>14</th>
<th>12</th>
<th>10</th>
<th>8</th>
<th>6</th>
<th>4</th>
<th>2</th>
<th>0.5</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_2$</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>12</td>
<td>14</td>
<td>16</td>
<td>18</td>
<td>19.5</td>
<td>50</td>
</tr>
<tr>
<td>$X_Q$</td>
<td>1</td>
<td>0.9</td>
<td>0.8</td>
<td>0.7</td>
<td>0.6</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.025</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The 12 dilution ratios detailed above yield concentrations from 100 to 1 ppm, which cause the diminishing signal levels with time observed in Figure 4.13. For each plateau created by the dilution of toluene, an average of the stable value was obtained ($\overline{S_p}$),
represented in Figure 4.14a for both response tests as a function of $C_{mix}$. The same was done for the baseline values before each toluene injection ($S_b$) and are displayed as a function of $C_{mix}$ in Figure 4.14b. Therefore, the signal rise is

$$S_r = \overline{S_p} - \overline{S_b}$$  \hspace{1cm} (4.11)

for each $C_{mix}$, and the corresponding response curve is shown in Figure 4.15 for each dataset.

![Figure 4.13](image)

Figure 4.13 – Signal generated during the experiment to obtain the µPID response curve for channel D at dilution varying from 100 to 1 % of the toluene 100 ppm gas cylinder. Voltage applied at 30 V and 20 mL/min flow rate. a) Response test 1; b) Response test 2 (performed 2.5 months after response test 1, with estimated UV lamp use of ~220 h).
Experimental Results for Direct Injection of the Gas Sample into the μPID

Figure 4.1 – Averaged toluene and nitrogen signal (\(S_p\) and \(S_b\)) for each concentration of response test 1 and response test 2. μPID using channel D with 30V at the electrodes and 20 mL/min sample flow rate.

The μPID signal rise (\(S_r\)) as a function of toluene concentration (\(C_{mix}\)) at the range 1 to 100 ppm follows a linear growth for both response tests, which is estimated from a linear fit function with forced zero intercept. The linear fit function angular coefficient (\(a\)) and the coefficient of determination (\(r^2\)) are presented in Table 4.5 for both response tests. Despite using the same voltage, flow rate and gas for both tests, the slope of response test 2 is about 30% lower than that obtained in response test 1, indicating that sensitivity decreases with time. This difference can be caused by lamp degradation, as mentioned before. Consequence of this decrease in sensitivity, as mentioned in Section 4.3 are: need for periodical detector calibration, lamp cleansing and increase in detection limit.
Figure 4.15 – Channel D response curve for 1 to 100 ppm toluene concentration range (response test 1 and 2) at 30 V and 20 mL/min. Vertical error bar of 3.5 % and horizontal error bar varies from 5 % to 12 % where the highest relative error is obtained for lowest concentration.

Table 4.5 – Linear fit parameters for response test 1 and 2, considering forced zero intercept. Therefore, $y = a \cdot x$.

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response test 1</td>
<td>0.02467</td>
<td>0.997</td>
</tr>
<tr>
<td>Response test 2</td>
<td>0.01659</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

In Figure 4.15, the vertical error bar is the same value obtained in Section 4.2.1. Moreover, the error bar relative to $C_{mix}$ is obtained from the expanded uncertainty of the pollutant concentration after the mixture:

$$U(C_{mix}) = t \cdot u(C_{mix}).$$

(4.12)

Since $C_{mix}$ is an indirect measurement calculated from equation 4.9, its standard-uncertainty is obtained from:
Experimental Results for Direct Injection of the Gas Sample into the µPID

\[
\left( \frac{u(C_{mix})}{C_{mix}} \right)^2 = \left( \frac{u(X_Q)}{X_Q} \right)^2 + \left( \frac{u(C_p)}{C_p} \right)^2.
\] (4.13)

Where \( u(C_p) \) is obtained from the 100 ppm toluene gas cylinder concentration accuracy, which is 2 % and \( u(X_Q) \) is calculated from

\[
\left( \frac{u(X_Q)}{X_Q} \right)^2 = \left( \frac{u(Q_1)}{Q_1} \right)^2 + \left( \frac{u(Q_1 + Q_2)}{Q_1 + Q_2} \right)^2.
\] (4.14)

The resulting error for concentration varies from 5 % to 12.5 % as shown in Figure 4.16.

![Figure 4.16 – Error of \( C_{mix} \) for the range of concentrations used in the µPID response tests.](image)

4.7 Noise and Detection Limit

The detection limit, in concentration units, of the µPID (\( C_{DL} \)) is defined as the concentration that yields a signal rise three times higher than the noise measurement at the baseline (\( N \)). The noise is measured as the maximum signal variation during 1 s at the baseline, as indicated in Figure 4.17. Considering the linear nature of the signal for the concentration range measured, \( C_{DL} \) can be estimated from the linear fit of the response curve with forced zero intercept, therefore:
\[ C_{DL} = \frac{(3N)\alpha}{a} \] (4.15)

The sensitivity \((a)\), which is also the slope of the linear fit, depends essentially on the design of the device, while the noise can be treated with filters and signal post-processing.

The low current nature of the signal makes it sensitive to noise and external perturbations. For some measurements, even walking beside the device caused noise in the signal; therefore, it is important to improve the stability of the signal using the Faraday cage and filters. In order to evaluate signal and noise, the channel D was subject to a test using 30 V on the electrodes and a stabilized signal obtained from 50 mL/min flow of nitrogen. The signal was measured for 2 minutes at different operational conditions, including: lamp off, lamp on and applying a first order low pass RC filter with varying \(f_c\) values from 1 MHz to 0.03 Hz as detailed in Table 4.6.

Two noise tests were performed and the resulting signals are shown in Figure 4.18, one without and another with a Faraday cage (FC), noise test 1 and test 2, respectively. The average signal of noise test 2 is displayed as dashed line on Figure 4.18a. Figure 4.18b presents the noise level at each operational condition for both datasets, making it clearer the influence of the FC and RC filter on the noise level. Table 4.6 presents the changes
implemented at each operational condition (from operational condition 1 to 7) with specified $f_c$ values and noise levels for the noise test 1 and 2.

For the first two minutes of data measurement, the lamp is turned off for noise test 1 and 2; therefore, the signal measured should be zero. However, noise is already present and a small offset signal can be measured (~8 pA). When turning the lamp on for both tests, the noise increases and the average offset also increases (~310 pA). This offset can be mainly caused from either residual ionisable compounds inside the ionization chamber or the photoelectric effect. For the rest of the experiment, the average offset measured suffers small variations but stays on average close to 300 pA.

After two minutes with the lamp on, the FC was included for noise test 2 but not for noise test 1. The presence of the FC halves the noise magnitude; thus, stressing the importance of its use in this µPID. In the next steps of the experiment various $f_c$ are applied and it is possible to see that the FC still makes an impact in noise reduction even when a very low cut-off frequency is applied ($f_c \leq 0.3$ Hz). Notice that for $f_c = 0.03$ Hz, the noise with FC can be four times lower compared to the case without the FC. The relevance of the FC demonstrated in those experiments support the fabrication of a compact FC that can shield the µPID from electromagnetic interferences. In order to do that, a specialized electronic design of the signal acquisition system has to be done and some additional fabrication steps might be necessary to include the FC into the shell of the µPID.
Figure 4.18 – Signal (a) and noise (b) measurement for channel D at 30 V and 50 mL/min using nitrogen continuous flow. A series of different µPID operational conditions were applied (described in Table 4.6).

<table>
<thead>
<tr>
<th>Operational condition</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV lamp state</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
</tr>
<tr>
<td>Cut-off frequency</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1 MHz</td>
<td>10 kHz</td>
<td>10 Hz</td>
<td>0.03 Hz</td>
</tr>
<tr>
<td>Faraday Cage</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
<td>OFF</td>
</tr>
<tr>
<td>Noise value [nA]</td>
<td>1.282</td>
<td>2.226</td>
<td>2.226</td>
<td>2.219</td>
<td>1.327</td>
<td>0.071</td>
<td>0.016</td>
</tr>
<tr>
<td>UV lamp state</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
</tr>
<tr>
<td>Cut-off frequency</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1 MHz</td>
<td>10 kHz</td>
<td>10 Hz</td>
<td>0.03 Hz</td>
</tr>
<tr>
<td>Faraday Cage</td>
<td>OFF</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
</tr>
<tr>
<td>Noise value [nA]</td>
<td>1.473</td>
<td>2.386</td>
<td>1.071</td>
<td>1.061</td>
<td>0.200</td>
<td>0.013</td>
<td>0.004</td>
</tr>
</tbody>
</table>

In long duration direct injection tests, e.g. the results presented in Figure 4.4, low $f_c$ values are useful for noise reduction. However, when the detector is integrated with a GC, the chromatograph peaks can be depleted if $f_c$ is set too low. Therefore, for practical purposes the best filter for GC-µPID operation are evaluated in Section 5.2. Despite this point, it is still possible to evaluate the detection limit for direct injection considering the response curves from Figure 4.15.
Figure 4.19 shows the concentration detection limits ($C_{DL}$) obtained from Equation 4.15 for the two calibration curves (response curve 1 and 2), considering a range of noise values. The noise values derived from the noise test with FC on (noise test 2) at various cut-off frequencies. Moreover, Figure 4.19 also presents the detection limit when the signal from the lowest frequency applied ($f_c = 0.03$ Hz) is combined with a digital moving average filter (MAF) on MATLAB. The MAF can reduce even further the signal noise level.

When $f_c = 1$ MHz the detection limit is approximately the same as without any filter, and reach values of 130 and 190 ppm for response test 1 and 2, respectively. The lowest noise was obtained after the digital moving average filter (0.3 pA), which yields a detection limit of 37 ppb and 54 ppb of toluene for the sensitivity obtained in the response test 1 and 2 respectively.

![Figure 4.19 – Detection limits ($C_{DL}$) for response test 1 and 2 (considering the noise when using the Faraday cage). Results consider: no filter; only low pass first order RC filter with various $f_c$ (1 MHz to 0.03 Hz); and the digital moving average filter (MAF) combined with the analog filter at $f_c = 0.03$ Hz. Error of detection limit is 3.5 %.

Error of detection limit is 3.5 %.
4.8 Influence of Other Parameters: Position and Humidity

The influence of position sensitivity of the \( \mu \)PID was investigated. After signal stabilization from 100 ppm of toluene, the \( \mu \)PID was turned on its side (position B), as illustrated in Figure 4.20, and then returned to the original position (position A). Figure 4.21 shows the pollutant signal for the \( \mu \)PID at three moments, when it was: 1) at position A; 2) changed to position B; 3) and returned to position A. A small change of 3 % in signal value was observed after the first change (position A to B); however, this change is still smaller than the measurement error (3.5 %). When moving the device to the original position, the signal returned to the same value. The small variation in signal may be caused by the movement of the cabling and electronic connections.

![Figure 4.20 – Schematics of the \( \mu \)PID positions used to observe the change in signal level due to position change.](image)

![Figure 4.21 – Signal of \( \mu \)PID (channel D) for toluene 100 ppm using 20 mL/min and 30 V on electrodes. Measurement during the three moments: 1) at position A; 2) when moved to position B; 3) After return to position A.](image)
The influence of humidity on μPID signal was also investigated. The μPID was purged with nitrogen and then connected to the setup described in Figure 4.22. The MFC5 sets a nitrogen flow of 200 mL/min into a water bottle, this flow rate was necessary to generate large flux of bubbles. The nitrogen comes out of the bottle through the bubbles and enters the μPID with a humidity content higher than pure nitrogen sample. The signal level for the μPID with this experiment reached a signal up to 325 nA, which is ~100 times higher compared to the highest $S_r$ obtained for toluene 100 ppm. This demonstrates the importance to use methods to reduce sample humidity before injection into the μPID.

![Experimental setup used to evaluate the influence of sample humidity in the μPID signal.](image)

**4.9 Conclusion**

This chapter presented the characterization of the μPID when the pollutant gas sample was injected directly into the device. The four channel geometries were tested and channel D, which has the highest illumination area and electrode area, yielded the best sensitivity. High illumination area and electrode area are two geometrical parameters with a major contribution to the sensitivity. While other parameters such as channel width and shape of the curves (squared or rounded) are more likely to be secondary in the contribution to the design sensitivity.

The UV lamp deterioration is an important factor to the prototype sensitivity being able to reduce the signal up to 3 times. A real-world implication of this effect is the need for periodical calibration of the μPID. Although the calibration compensates for the effect of a depleting lamp, the decreasing sensitivity will increase the detection limit, which
is undesirable. The modular design of the µPID enables the maintenance of the lamp, which is important to maintain its full potential.

Voltage and flow rate also influences the µPID response. The response curve from 0.1 to 30 V showed that from 0.1 V to 5 V the improvement in signal is higher compared to the voltages from 5 V to 30 V. Despite that, 30 V was chosen for the experiments because it can produce a more stable signal. Higher flow rates yielded a higher signal, which can come from the increase in pressure at the inlet of the microchannel necessary to increase the flow rate through the µPID.

The sensitivity of the device when it was moved from one position to another showed minimal influence. Nevertheless, more stable wiring should be provided at a more developed stage of the prototype to avoid the unnecessary influence of position. A 5 µm coating on top of the copper electrodes did not cause any influence in the signal, baseline or noise. Spectral analysis of the noise showed that electromagnetic interferences from the power grid added the strongest contribution for the noise. High humidity in the sample can cause “leak current” in the signal hiding the current obtained from the photoionization of the VOCs.

The response of the channel D was evaluated for a direct injection of toluene concentrations ranging from 1 to 100 ppm. The response curve was linear and produced a sensitivity up to 0.02467 nA/ppm. The noise was evaluated for various conditions including a first order low-pass RC filter, a digital filter and a Faraday cage. The presence of an FC proved relevant for noise reduction and signal stability; therefore, it can be constructed in the future in an improved and more compact version. The lowest noise obtained was 0.3 pA which translated into a detection limit of 37 ppb for the test where the channel D had the highest sensitivity (before lamp deterioration).
Experimental Results for Direct Injection of the Gas Sample into the µPID
Chapter 5  Experimental Results for µPID Integrated with a Portable Gas Chromatograph

This chapter shows results that characterize the performance of the µPID when it is integrated with the portable GC from In’Air Solutions. Section 5.1 describes the main apparatus of the portable GC showing how the sampling works and where the µPID is integrated into the gas analyser. Section 5.2 shows the signal measurement for a range of 1st order RC filter with low pass cut-off frequencies and evaluates the chromatograph parameters for the variations in filter condition. Section 5.3 shows the calibration curve for BTEX samples with concentration ranging from 1 to 10 ppm followed by the detection limit for each BTEX compound. A comparison of the different channel designs and the commercial PID is presented in Section 5.4. Following that, Section 5.5 investigates the influence of the ionization chamber volume on the chromatograph. Finally, Section 5.6 shows results obtained after a preconcentrator was integrated into the GC sampling loop.

5.1  Experimental Setup for Tests with µPID and Portable Gas Chromatograph

The µPID is also tested with the In’Air Solutions BTEX gas analyser by substituting the commercial PID (Baseline MOCON, piD-TECH Blue, part number 045-014) for the µPID; therefore, it yields a GC-µPID system. Technical specifications of the commercial PID can be found on Appendix D. The analyser works in three steps: sampling, separation and detection. A BTEX gas mixture is connected to the inlet of
the gas analyser which uses a mini diaphragm air pump (270 EC, Schwarzer) and a solenoid 6-ports valve (MTV-6LL-N32UF-1, Takasago) equipped with a PEEK 200 μL sampling loop which is filled with the sample and then injected into the column for analysis as described in Figure 5.1b and 5.1c. At the sampling stage, the sample is directed to a waste, so that the 200 μL sampling loop is filled with the sample, which occurs in less than 10 seconds. After filling the sampling loop with a pollutant mixture, the injection stage can start. The injection is initiated by the BTEX analyser controller panel, and makes the valve switch position to reach the configuration displayed in Figure 5.1c, so that the carrier gas pushes the sample downstream. The optimal time for the injection stage was verified in previous studies and is 20 seconds [19].

The 6-port valve is connected directly to the separation column to minimize dead volume. The separation column is a 20 m long capillary from Restek with RXi-624 stationary phase and 1 μm film thickness. Internal and external diameters are 0.18 mm and 0.74 mm, respectively. The separation column is coiled in a 7.5 cm diameter inside a 10 cm × 10 cm × 1 cm aluminium plate which serves as an oven. It is heated by an electric resistor that controls the temperature with a commercial controller (CAL 3300). To improve the oven performance the column is covered by a 2 cm thick cork insulation layer. The temperature set at the column for all the experiments is 65 °C and is constant for the analysis duration (isocratic mode).

The μPID is located in the outlet of the separation column. The electronic connections for the μPID operation are the same as demonstrated in Figure 4.1 and 4.2, and a MFM can be placed after the separation column and the μPID to verify the absence of leakage. The flow rate through the system is ensured by the pressure regulator (PR), also from Bronkhorst, set at 4 bar, which yield a flow rate measured at the end of the separation column of 2.39 mL/min.
5.2 GC-µPID Signal: Influence of Signal Filtering

As already mentioned in the previous chapter (Section 4.7), filtering processes have the potential to significantly deplete the chromatographic signal because it can reduce the peak height and increase the width. An evaluation of the influence caused by a range of cut-off frequencies applied in the current preamplifier was conducted. The $f_c$ values used were: 10 Hz, 3 Hz, 1 Hz, 0.3 Hz, 0.1 Hz and 0.03 Hz. The chromatographs
obtained from those filters are presented in Figure 5.2. The red data is obtained by 200 samples/s acquisition rate using the 1st order RC filter. The black data uses a digital moving average filter (0.2 s window) on MATLAB to further smoothen the signal and visualize the data trend when the noise is high.

A sample of 10 ppm BTEX was injected into the gas analyser coupled with the µPID (channel D). The peaks, in the order that they leave the separation column are: 1st) benzene; 2nd) toluene; 3rd) ethylbenzene; 4th) m-xylene and p-xylene (coelluted in the same peak); 5th) o-xylene. The approximate retention time for each compound is presented in Table 5.1. The chromatographs in Figure 5.2 show that for $f_c = 10$ Hz the signal is buried in noise (red data), and when $f_c \leq 3$ Hz, the peaks become more visible. Also, for $f_c = 0.03$ Hz, the benzene and toluene peaks are visibly depleted, with reduced height and increased broadening.
Figure 5.2 – Chromatograms showing the influence of $f_c$ applied in µPID (channel D) signal acquisition when used with GC and 10 ppm BTEX sample. 30 V applied on electrodes. The $f_c$ values are: (a) 10 Hz; (b) 3 Hz; (c) 1 Hz; (d) 0.3 Hz; (e) 0.1 Hz; (f) 0.03 Hz.
To quantify the influence of $f_c$ on the GC-$\mu$PID signal, a series of chromatogram parameters were determined, including: baseline noise ($N$), peak height ($h$), peak width at half max ($w_{1/2}$), separation resolution between the peaks ($R_s$) and signal-to-noise ratio ($SNR$). The noise is calculated as the difference between the maximum and minimum values of the baseline signal within a 1 s interval, as illustrated in Figure 4.16. The retention time ($t_r$), peak height ($h$) and peak width at half height ($w_{1/2}$) are obtained from the chromatograph signal through a MATLAB algorithm presented in Appendix C.2.

All parameters, except the noise, are calculated from the smoothened data (black line) because noisy data results in unwanted variation of the peak parameters due to the nature of the algorithm that calculates $t_r$, $h$ and $w_{1/2}$. The separation resolution is calculated from

$$R_s = 0.589\Delta t_r/w_{av}, \quad (5.1)$$

where $\Delta t_r$ is the difference between consecutive retention times of two peaks and $w_{av}$ is the average between the two peaks $w_{1/2}$. The error for the peak height is 6.5 % and derives from the standard deviation of the repeatability test. The error for $w_{1/2}$ is also calculated from the repeatability only and yields 3.5 %. The repeatability measurement of the chromatographs (7 measurements) is presented in Figure 5.3.
Figure 5.4 shows the noise measured at baseline for each $f_c$ applied. When $f_c = 10$ Hz, noise is close to 30 times higher than the smallest noise measured (3.9 pA), which was obtained for $f_c \leq 0.3$ Hz. The parameters $h$, $w_{1/2}$, $R_s$ and $SNR$ are displayed in Figures 5.5, 5.6, 5.7 and 5.8 respectively (for all the five peaks) as bar charts. Notice that the y-axis of the bar charts used to evaluate the chromatogram do not have the same scale and have lower end in zero so that the changes obtained for each $f_c$ in each peak can be better noticed.

Figure 5.5 shows that, when $f_c \geq 1$ Hz, $h$ remains approximately constant (variation smaller than the error) for all peaks, and there is an evident peak height drop when $f_c < 0.3$ Hz. As expected, a low cut-off frequency depletes mainly the sharp peaks (benzene and toluene peaks) because they have the highest response frequencies. At $f_c = 0.03$ Hz, the signal reaches the lowest value for all species. However, some peaks suffer higher drops in peak height ($h$). The $h$ drop from $f_c = 10$ Hz compared to $f_c = 0.03$ Hz is of 66, 54, 33, 24, 20 % for benzene, toluene, ethylbenzene, m,p-xylene and o-xylene, respectively. This means that o-xylene peak height is not strongly influenced by a low frequency filter and the most influenced peak is the benzene peak.

The peak width at half height ($w_{1/2}$) for all peaks increase with lower $f_c$, except the ethylbenzene as shown in Figure 5.6. The different behaviour for ethylbenzene is caused by the shape of the last three peaks, which are partially merged. For all other peaks, significant $w_{1/2}$ increase occurs only when $f_c \leq 0.1$ Hz. From Figure 5.7 it is possible to see that the resolution depletion for all peaks is more relevant when $f_c \leq 0.1$ Hz and $R_s$ between benzene and toluene suffer the largest drop.

The $SNR$ of all peaks are optimal when $f_c = 0.3$ Hz, as shown in Figure 5.8. Therefore, taking into account all the parameters, the $f_c = 0.3$ Hz is chosen to perform the next experiments of the $\mu$PID integrated with the gas chromatograph to evaluate the analytical performances obtained.
Figure 5.3 – Chromatogram of the repeatability experiment (n = 7) for the GC-µPID (channel D) at 30 V using 10 ppm BTEX sample and $f_c = 0.3$ Hz.

Figure 5.4 – $f_c$ influence on chromatographic baseline noise ($N$) of the µPID (channel D) for 10 ppm BTEX sample. Error is estimated as 3.5 % of the measured value, and derives from the same calculation for the $S_r$ error (Section 4.2.1).
Figure 5.5 – $f_c$ influence on chromatographic peak height ($h$) of μPID (channel D) data acquisition for 10 ppm BTEX sample. Error bars are 6.5% of the measured value. a) Benzene; b) toluene; c) ethylbenzene; d) m,p-xylene and e) o-xylene.
Figure 5.6 $f_c$ influence on chromatographic peak width at half max ($w_{1/2}$) of µPID (channel D) data acquisition for 10 ppm BTEX sample. Error bars are 3.5% of the measured value. a) Benzene; b) toluene; c) ethylbenzene; d) m,p-xylene and e) o-xylene.
Figure 5.7 – $f_c$ influence on chromatographic separation resolution ($R_s$) of µPID (channel D) data acquisition for 10 ppm BTEX sample. a) $R_s$ between benzene and toluene peak; b) $R_s$ between benzene and ethylbenzene peak; c) $R_s$ between ethylbenzene and m,p-xylene peak; d) $R_s$ between m,p-xylene and o-xylene peak. Error bars are 2.7% of the measured value as detailed in Appendix A.
Figure 5.8 – $f_c$ influence on chromatographic signal-to-noise ratio $SNR$ of channel D data acquisition for 10 ppm BTEX sample. Error bars are 7.4 % of the measured value (error calculation detailed in Appendix A). a) Benzene; b) toluene; c) ethylbenzene; d) m,p-xylene and e) o-xylene.
5.3 GC-µPID Response Curve and Detection Limit

Using the dilution experiment described in Section 4.6 and injecting 200 µL of sample through a sampling loop, a calibration curve for the GC-µPID response (for each peak) was obtained and shown in Figure 5.9 for concentrations ranging from 1 ppm to 10 ppm of BTEX. The peak heights are calculated from the average of 2 consecutive experiments for each concentration. The height error is 6.5 % as calculated in section 5.2 and the concentration error is obtained by the same method presented in section 4.6 yielding a maximum value of 7.3 %. The response for this range of BTEX concentration is not linear, as shown in Figure 5.9.

The concentration detection limit ($C_{DL}$) can be estimated using Equation 4.15 and the signal corresponding to the lowest concentration injected (1 ppm). Considering the noise for the digitally smoothened signal (0.3 pA), the detection limits for the four peaks are presented in Table 5.2. Notice that the detection limit for toluene is approximately 4 times higher than when the detector was tested with direct injection. This can happen because when the GC system is used the concentration of the sample spreads and reaches the detector at a lower level.

Some commercial GC-PID systems have detection limit 100 times lower than the value presented for the gas analyser in this work. However, the µPID presented in this thesis is still a working prototype and some changes can be done to improve the detection limit in the future. Some solutions for a better detection limit include: improvement of electronics with less influence of noise; improvement of UV lamp technology developing a flexible waveguide to enable ionization chamber with more improved design of the microchannel (more curves, higher electrode and illumination area).
Figure 5.9 – Calibration curve for GC-µPID (channel D) chromatograph peaks with samples of BTEX at concentration ranging from 1 to 10 ppm and 30 V applied on the electrodes. a) Benzene; b) toluene; c) ethylbenzene; d) m,p-xylene; e) o-xylene.
Table 5.2 – Detection limit for each species in ppb. Error of 8.9 %.

<table>
<thead>
<tr>
<th></th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethylbenzene</th>
<th>m,p-Xylene</th>
<th>o-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.L. [ppb]</td>
<td>73</td>
<td>138</td>
<td>308</td>
<td>262</td>
<td>254</td>
</tr>
</tbody>
</table>

5.4 Other Channels and Commercial PID

Experiments with GC-µPID were also performed for channels A, B, C and a commercial portable PID (Baseline MOCON, piD-TECH eVx Green, part number 045-010), the technical specifications of the latter are detailed in Appendix D. The commercial PID tested is not the same one originally used with the GC from In’Air Solutions because the original commercial PID had a measurement range (0.5 ppb to 2 ppm) lower than the sample concentrations applied to test the µPID (1 ppm to 10 ppm); therefore, it would not be able to read the sample at the same concentration levels injected into the µPID. Figure 5.10 and 5.11 show the chromatographs with 10 ppm BTEX sample for all microchannels and the commercial PID, respectively. The conditions of the tests in Figure 5.10 and 5.11 are the same in terms of gas sample concentration, GC parameters (flow and temperature) as the experiments presented in Figure 5.2d. However, for Figure 5.10, $f_c$ value is fixed and equal to 0.3 Hz. The signal shows that, for the µPID, the benzene peak is higher compared to all other peaks. Retention time for µPID and commercial PID are essentially the same with a difference lower than 1 %.

On the commercial PID, the m,p-xylene peak is the highest compared to the other peaks. This means that the µPID has a higher relative sensitivity to benzene than the commercial PID. Figure 5.12 shows the peak height for all channels and all five chromatographic peaks. The dependence of the toluene peak height ($h$) on the design of the channel is similar to the result presented for direct injection in Section 4.2, showing a consistency of the results. The $h$ for ethylbenzene has a lower value only for
channel A and for m,p and o-xylene the peak height don’t show variation from channel B to C.

The detection limits of BTEX for all channels and commercial PID are displayed in Figure 5.13. Since only the 10 ppm BTEX signal level was measured, the detection limit is calculated assuming a linear response curve with zero intercept. For the microchannels, since the noise considered for the detection limit calculation is the same (0.3 pA), according to Figure 5.12 it is evident that the detection limit magnitude will follow the order $\left( C_{DL} \right)_{CH_A} > \left( C_{DL} \right)_{CH_B} > \left( C_{DL} \right)_{CH_C} > \left( C_{DL} \right)_{CH_D}$. The detection limit for channel D calculated by this way reach values of 72, 127, 429, 316 and 448 ppb of benzene, toluene, ethylbenzene, m,p-xylene and o-xylene, respectively. Notice also that the detection limit of benzene for the µPID channels B, C and D are better compared to the commercial PID (157 ppb).

The $w_{1/2}$ is compared on Figure 5.14 for the microchannels and the commercial PID. For benzene, the commercial PID has a negative impact on the peak, yielding a slightly larger benzene peak (15 % larger than the channel D, for example). However, for toluene and ethylbenzene, the peak width has no conclusive difference from the microchannels and the commercial PID, because the average differences uncertainties are all overlapped. The xylenes (m,p,o-xylene) are sharper for the commercial PID.
Figure 5.10 – Chromatographs for 10 ppm BTEX injection using different microchannel designs. a) Channel A; b) channel B; c) channel C; d) channel D.
Figure 5.11 – Chromatograph for 10 ppm BTEX injection using the commercial PID (Baseline MOCON miniPID green, 045-010). Details of the commercial PID on Appendix D.
Figure 5.12 – Chromatographic peak height ($h$) for all channels of the µPID with a 10 ppm BTEX sample with 30 V on the electrodes: a) benzene, b) toluene, c) ethylbenzene, d) m,p-xylene and e) o-xylene.
Figure 5.13 – Estimated concentration detection limit ($C_{DL}$) for all microchannels (30 V) and commercial PID with a 10 ppm BTEX sample: a) benzene, b) toluene, c) ethylbenzene, d) m,p-xylene and e) o-xylene. Detection limit error is 8.9% and its calculation is explained in Appendix A.
Figure 5.14 – Chromatographic peak width at half max ($w_{1/2}$) for all channels and commercial PID with a 10 ppm BTEX sample and 30 V on electrodes: a) benzene, b) toluene, c) ethylbenzene, d) m,p-xylene and e) o-xylene.
5.5 Influence of the Ionization Chamber Volume on the Chromatographic Peaks

As mentioned in Chapter 1, the sample concentration band is close to infinitesimal at the beginning of the separation column but it spreads as it moves through the column. Therefore, each compound reaches the detector with a longitudinal concentration gradient and Figure 5.15 illustrates this process. Further spreading is added depending on the detector chamber volume.

![Concentration band spread](image)

Figure 5.15 – Concentration band spread when sample moves through the separation column.

The chromatographs are estimation of the concentration profile of the sample leaving the separation column and they can be presented as a function of volume, instead of time, if the sample flow rate used in the analysis is provided. The measured flow rate at the end of the column is 2.39 mL/min and the chromatograph as function of volume is presented in Figure 5.16a.

Figure 5.16b shows that the benzene concentration profile is spread across ~600 µL. As an example, if a PID has an ionization chamber of 100 µL, it means that the signal emitted by the PID will result from the concentration of sample inside the ionization chamber, which is an average of the sample concentration within a 100 µL interval of the concentration profile (as indicated in Figure 5.16b). Therefore, the volume of the ionization chamber acts as the size of the window of a moving average filter on the original concentration profile. Considering the chromatograph in Figure 5.16a as close
as possible to the original concentration profile, Figure 5.16c illustrates the change in chromatograph peak shape with the ionization chamber volumes 1, 50, 200 and 300 µL.

The $V_c$ for the µPID (all channels) and the commercial PID are too small compared to the volume of the peaks (~40 smaller than the volume of the peak at half height). Therefore, their chamber’s size cause no significant change in width especially for the wider peaks. To illustrate that, Figure 5.16d shows the dependence of the benzene and toluene peaks depletion for chamber volumes up to 300 µL.

The peak quality depletion is measured by the relative decrease in peak height ($h_{fall}$) and the relative increase in peak width at half max ($w_{rise}$), both variables are presented as percent values in Figure 5.16d. For the ionization chamber volume of the channel D, which has the largest chamber volume between the channel designs ($V_c = 6.7$ µL), the $h_{fall}$ and $w_{rise}$ for the benzene peak are 0.2 and 0.1 %, respectively. This helps to explain why the $w_{1/2}$ did not present significant variation for the four channels, as presented in Figure 5.14. If a commercial PID with ionization chamber of 200 µL is used in the portable GC, the peak height of benzene would be reduced ~15 %, increasing the detection limit of the analyser. Notice that the toluene peak needs a larger chamber to cause significant depletion, since it is already broader than benzene due to its longer elution time in the GC column.
Figure 5.16 – Chromatograph peak quality depletion due to ionization chamber volume increase. a) Chromatograph as function of volume for 10 ppm BTEX considering result with channel D to mimic the original chromatogram; b) original benzene peak; c) benzene peak depleted due to chamber volume increase (up to 300 µL); d) benzene and toluene peak quality depletion ($h_{fall}$ and $w_{rise}$) as function of $V_c$. 
5.6 GC-µPID Signal with Preconcentrator

The preconcentrator (PC), as explained in Chapter 1, can improve the sensitivity and consequently decrease the detection limit of the gas analyser. An experiment with a PC prototype (developed under the MIGRATE project framework) was performed as an attempt to improve the detection limit of the GC-µPID [71]. The PC uses an adsorbent to trap the sample (at ambient temperature ~25 °C) and a heating system to release the concentrated sample into the gas analyser. The sampling flow rate for the preconcentration process was 5 mL/min and the desorption temperature was ~340 °C. The PC was integrated into the sampling loop as indicated in Figure 5.17.

![Figure 5.17 – GC sampling loop with preconcentrator integrated.](image)

Unfortunately, the preconcentrator prototype suffered a contamination problem even before the tests with the µPID. This is identified by an unwanted peak measured by the experiment with nitrogen. After a series of purges with nitrogen, a 5 ppb BTEX sample is injected into the gas analyser with the preconcentrator.

Figure 5.18a and 5.18b show the chromatograph for the injection of nitrogen and 5 ppb of BTEX, respectively. Since the preconcentrator is applied in this operation, the separation process was adapted and is 8 min longer compared to the separation process without the preconcentrator. During the purge test with nitrogen (Figure 5.18a), it is possible to identify the contamination peak, which hides the benzene signal when the 5 ppb BTEX sample is injected.
Figure 5.18b shows the peaks corresponding to the 5 ppb BTEX injection. The pattern of the last three peaks, corresponding to ethylbenzene, m,p-xylene and o-xylene, can be recognized starting at \( t = 700 \) s. However, the ethylbenzene and o-xylene signal heights are close to the noise level with \( SNR < 3 \). This means that only toluene and m,p-xylene are detectable for this experiment. Nonetheless, this shows the potential to a low detection limit when the \( \mu \)PID is used in a portable GC equipped with a preconcentrator.

![Graph](image)

Figure 5.18 – Chromatograph for GC-\( \mu \)PID equipped with a preconcentrator. Using channel D at 30 V. a) Purge with nitrogen; b) 5 ppb BTEX sample analysis.

**5.7 Conclusions**

Chapter 5 presented the characterization of the \( \mu \)PID when integrated with the In’Air Solutions gas analyser. Initially, the best cut-off frequency for the low-pass first order RC filter was evaluated for channel D. The results showed that 0.3 Hz is the best \( f_c \).
value yielding the best signal-to-noise ratio while still maintaining good resolution between the peaks. The response curve was obtained by introducing a range of BTEX mixture concentration from 1 to 10 ppm into the GC. The response curve is shown as a function of the peak height. The benzene peak provides the most linear dependence on concentration; however, all other peaks present a loss of sensitivity as lower concentrations (< 5 ppm) are introduced into the gas analyser. The detection limits ($C_{DL}$) obtained for all compounds, considering the lowest noise (0.3 pA) are: 73 ppb, 138 ppb, 308, 262 and 254 for benzene, toluene, ethylbenzene, coelluted m-/p-xylene and o-xylene, respectively.

The four channels were tested with the GC prototype and compared with a commercial PID. The peak height dependence for the 10 ppm toluene injection in the GC-µPID for all channels is similar to the result obtained for the direct injection of 100 ppm of toluene in all channels, showing a consistency in the results. For the benzene peak, the channels B, C and D have better detection limit, this might be a consequence from the better relative sensitivity to benzene of the µPID when compared to the commercial PID, which has better relative sensitivity to the m,p-xylene peak. Regarding the peak width at half max, the microchannels are better compared to the commercial PID for the benzene peak; however, for the reminder peaks, the commercial PID is either better or equally sharp as the microchannels. No significant better separation resolution was observed between the microchannel designs.

The volume of the separated compounds leaving the column of the GC prototype is much higher (approximately 100 times higher) than the ionization chamber volume of the four channel designs. The analysis performed on the influence of the ionization chamber volume on the chromatogram shows that, for the sharpest peak in the chromatogram (benzene), the fall in peak height and broadening of the peak from channel A to D is 0.2 % and 0.1 %, respectively. This explains why no significant variation in peak width was observed for the tests with GC-µPID using the four different microchannels. A consequence of this is that the portable GC has the potential to reduce the volume of the sample without a negative impact in the chromatogram quality.
When the GC-µPID had a preconcentrator integrated to the sampling process, the detection limit reached low ppb level for toluene (~5 ppb), even though the PC was suffering contamination. This shows that the µPID has a potential for further reduction in the detection limit when integrated to a fully working PC in the future. However, the detection limit of lab based commercial PIDs is 100 times lower than the $C_{DL}$ obtained for the GC-µPID including the PC in the sampling loop.

Future improvements should be done in the µPID design to reach a detection limit lower than the values established by the EU (1.6 ppb). Suggestions to achieve that involve: the implementation of more stable electronics, including a miniaturized amplifier and Faraday cage; the development of a UV light waveguide that enables different channel geometries that are not limited by the 6 mm commercial UV lamp illumination diameter; also, an improvement in the channel by developing a design with even higher electrode and illumination area.
Chapter 6  Conclusions & Recommendations

6.1 Conclusions

This chapter provides the main conclusions obtained from this thesis in light of the objectives described in Section 1.4. This work reported the design, fabrication and characterization of a µPID prototype for VOC analysis. The device was developed to be modular and contain a flow-through ionization chamber with low volume (~1 µL). The characterization was performed with and without a GC prototype. Future recommendations are also presented in the end of this chapter.

6.1.1 Recent Miniaturized PIDs

- The ionization chambers of the µPIDs developed in the last decade are ~100 times smaller compared to the commercial PID. Besides, while commercial PIDs can have flow-through or membrane ionization chamber, most µPIDs present flow-through chambers. As a consequence, the ionization chamber fill time of µPIDs can be ~100 times faster than the commercial PIDs.
- All µPIDs using a lamp as ionization source had 10.6 eV commercial UV lamps implemented in their design, which had enough energy to detect the most common VOCs. In contrast to that, the D-µPIDs used helium as auxiliary gas for the plasma to generate photons with energy high enough to ionize N₂ and O₂ samples. The auxiliary gas flow was either parallel or perpendicular to the sample flow.
- Some µPIDs designed the ionization chamber as a microchannel, which makes them more compatible for the integration with a microfluidic gas analyser. The
work of Akbar et al. (2015) [56] even produced the separation column and PID in the same chip. For some designs, the signal electrodes were the vertical walls of the microchannels. Materials used for the electrodes include conductive silicon, conductive silicon covered with CNT or Ag-NW and metal (Ti/Au).

- Most miniaturization of recently developed PIDs was performed with silicon and glass as main materials in combination with lithography based fabrication techniques, including DRIE, wet etching, laser etching, drop casting, e-beam evaporation, PECVD, lithography evaporation and lift-off, anodic bonding, gluing and dicing.

- Lithography based fabrication has high performance for miniaturization; however, it requires expensive installation with clean rooms. Moreover, most fabrication methods use a photomask which is expensive and can limit the flexibility of fabrication because every time a new design needs to be tested, a photomask for the fabrication of the new design needs to be produced.

- Reported performances for the µPIDs include response time as fast as 78 ms for 1 mL/min carrier gas flow rate and a detection limit of ppt level for benzene. Some publications mentioned detection limit in mass units without disclosing the volume used; therefore their detection limit could not be directly compared to detection limits in “parts per” units.

6.1.2 Design

- While most µPIDs mentioned in the literature are fabricated using silicon-based fabrication techniques, this work showed a simpler design using micromilling and electrical discharge machining as manufacturing techniques. The main materials for the construction of the prototype were PMMA, copper and PVC.

- The design presented did not use any glue or bonding process, making it modular and facilitating component replacement, such as UV lamp and electrodes. This contrasts with the state of the art, which had the components fixed. The modular design also benefited the cost of the experiments performed for this thesis, because it allowed to replace the microchannel design, and use
different geometries. Moreover, the modular design also allowed the same UV lamp to be used even when the microchannel was replaced, which is important since the lamp is relatively expensive (~120 euros). In a design where the parts are fixed, a different UV lamp would have to be used for each microchannel geometry.

- The ionization chamber design presented in this thesis was a microchannel (flow-through chamber) that had different geometries. Therefore, it was possible to evaluate the influence of the geometry on the performance of the prototype. The volumes of the ionization chamber ranged from 1.1 to 6.7 µL.

- The microchannels geometries were designed within the UV lamp illumination diameter, which is 6 mm. Therefore, the microchannel design is limited by the commercial UV lamps available.

- The width of the microchannel was limited by the electrical discharge machining fabrication and also by the copper structural stability. The design presented as channel D had close to the maximum permissible electrode area and illumination area. This is a disadvantage of the design presented in this work compared to other µPIDS fabricated by DRIE, which can have an aspect ratio of 1:50 (width and depth) for the microchannel.

- The copper electrodes did not fit precisely on the bottom PMMA, which caused channel width deviation from the nominal value up to 13%.

- Leakage was observed for flow rates ranging from 0.5 – 20 mL/min and can vary from 8 to 28 % depending on the microchannel design and flow rate used. Channel D resulted in the highest leakage and channel B had the lowest leakage.

- A shell made of PVC protected the sensor user from the UV light exposure and enabled the world-to-chip connections (electronic and fluidic).

- The design enabled the µPID integration with the portable GC analyser from In’Air Solutions.

- Two different coatings were successfully applied to the top surface of the copper electrodes: PMMA and DLC. PMMA was fabricated by spin coating yielding a 5 µm thick layer and DLC was fabricated by PECVD with 1 µm thick layer. For
an effective fabrication of the DLC layer, titanium was used as an adhesive layer between the copper and the DLC.

6.1.3 Results: Direct Injection of the Gas Sample into the $\mu$PID

- The $\mu$PID results show good signal repeatability with low error (3.5 %).
- The current signal measured during the injection of toluene can range from 0.2 to 3.2 nA and has a response time lower than 1 s for all channels.
- A comparison between the $S_r$ of channel A and B showed that an increase in illumination area had more impact in the signal than a decrease in channel width, considering the dimensions used in the channel design.
- The higher baseline level for channel A compared to channel B can be due to larger portion of the electrode being hit by UV light, causing an increase in current by the photoelectric effect.
- Increasing the illumination area and electrode area is key to enhance the signal rise according to the measurements observed for all the channels tested.
- Lamp deterioration can cause significant drop in signal rise (~3 times lower) for the $\mu$PID. However, no perceivable signal change was measured when replacing a used electrode for a new one.
- The 5 $\mu$m thick PMMA coating did not cause any signal improvement. Some hypothesis to explain this behaviour are: 1) PMMA at 5 $\mu$m is not effective at blocking photons; 2) Photons reaching electrode walls, which are uncovered by the PMMA, are enough to generate the photoelectric effect that creates the same noise and baseline level observed in the signal without the PMMA; 3) Other noise sources had more impact on noise compared to the photoelectric effect.
- As expected, higher voltage led to a higher signal. However, the signal increase with voltage is not linear. From 0 to 5 V the highest increase in signal is found and from 5 to 30 V the voltage sensitivity drops; however, 30 V is still useful since it allows a more stable signal due to a higher $S_p$. All the microchannels tested in this work have the same signal variation with voltage.
From 1 to 100 ppm of toluene, the detector response was approximately linear with $r^2$ from a linear fit of 0.99, for the two response tests performed.

The detection limit depends on the sensitivity and noise level of the detector signal. Considering the highest sensitivity (24.3 pA/ppm) and lowest noise observed (0.3 pA), the detection limit for toluene was 37 ppb.

A change in the position of the detector had little influence in the signal and the response change is smaller than the measurement error.

A direct injection of nitrogen with high humidity yielded a signal ~100 times higher than the highest signal with toluene 100 ppm.

### 6.1.4 Results: GC-µPID

- The low pass first order RC filter cut-off frequency that causes best signal-to-noise ratio for all the chromatographic peaks was 0.3 Hz. Therefore, this value was applied for the data acquisition of the µPID with GC. For $f_c \leq 0.3$ Hz, the noise level did not change, but the signal height, peak width and chromatograph resolution were depleted.
- Repeatability of peak height and peak width at half max were 6.5 and 3.5 %, respectively.
- The response curve obtained for 1 to 10 ppm BTEX sample when using the channel D showed non-linear behaviour, especially for the last three peaks. Decreased sensitivity was observed for the lowest concentrations. The concentration detection limit for benzene, toluene, ethylbenzene, m,p-xylene and o-xylene peaks were 73, 138, 308, 262 and 254 ppb.
- The toluene 10 ppm peak height (GC-µPID) for different channel designs (A, B, C and D) followed the same trend observed for the 100 ppm toluene signal rise during the sample direct injection experiments, showing the results consistency.
- For benzene and toluene, the detection limit of the channel D was lower than the commercial PID, reaching values of 72 and 127 ppb in the microchannel, when calculated with a single point linear fit (10 ppm point). The commercial
PID showed a higher relative sensitivity to the last three peaks (o,m,p-xylene and ethylbenzene) compared to the µPID.

- There was no significant change in peak width for the microchannels, because the error bars were overlapped. This is probably because the volume of their chambers had similar value in the same order of magnitude (~1 µL). Moreover, this value was much smaller than the volume of the sample.

- The preconcentrator used with the GC prototype had contamination issues and because of them it hid the benzene peak from the chromatograph. However, it was still possible to say that the toluene peak was detected, since its height was ~3.\(N\). Therefore, it is possible to see the potential of low ppb level detection limit of the GC-µPID when it is used with a preconcentrator.

- The detection limit of the GC-µPID (when combined with the PC) is 100 times higher than the commercial lab based GC-PID detection limit. The prototype also does not have detection limit lower than the limit of benzene exposure recommended in some EU countries (0.64 ppb). Despite all that, the modular µPID developed in this work can still serve in applications that do not require extremely low detection limits, since it provides a design that enables further portability of the whole GC system making the gas analysis process local-based instead of lab-based.

### 6.2 Recommendations

- Develop a portable amplifier for the µPID. This will enable the detector to be integrated into a portable gas analyser for field analysis. The commercial portable PID has a very compact electronics system, future efforts can be done to implement similar electronics design with portable circuits in the µPID.

- Develop a more versatile UV light source to be integrated into a range of microchannel geometries and sizes. An option for that is to develop a waveguide that can change its shape according to the microchannel design needs.
Develop solutions to mitigate leakage. A possible solution is to modify the bottom shell and bottom PMMA to contain more O-ring pockets, after a rigorous evaluation and identification of the main leakage spots. Observations in this thesis suggest that the leakage occurred mainly in the electrode holes on the bottom PMMA and between the copper electrode and top and bottom PMMA surface. Another possibility is to implement an O-ring between the bottom and top PMMA surrounding the copper electrodes.

Verify the effectiveness of other electrode coatings against noise generation and the photoelectric effect. For that, a better isolation of external noise sources is necessary, so that the photoelectric effect is isolated and its influence on the detector can be quantified precisely.

Evaluate the gradual change in signal due to a range of humidity levels in order to obtain a humidity-signal response curve. Develop suitable humidity filters into the gas analyser.

Increase robustness of wiring connections and Faraday cage effectiveness to reduce noise. Electromagnetic noise perturbations can be mitigated using a more compact Faraday cage.

Evaluate the µPID in a µGC system where the sample volume is smaller than the sample volume used in the test with the portable GC prototype. With a smaller sample volume the importance of the ionization chamber volume will be emphasized.

Use the µPID in a µGC equipped with a pre-concentrator. Integrating the main components of the GC system in a chip will allow a better portability with possible improved detection limit. A further step can involve the modular fabrication of other GC components such as the separation column and preconcentrator.
References


[35] D.C. Locke, C.E. Meloan, Study of the Photoionization Detector for Gas


References


Appendix A: Uncertainties

A.1 Uncertainty: Direct Injection Detection Limit

The expanded uncertainty of the detection limit (in parts per units) is obtained from

\[ U(C_{DL}) = t \cdot u(C_{DL}). \] (A.1)

Considering that the detection limit is calculated from Equation 4.15:

\[ \left( \frac{u(C_{DL})}{C_{DL}} \right)^2 = \left( \frac{u(N)}{N} \right)^2 + \left( \frac{u(a)}{a} \right)^2, \] (A.2)

where \( u(N) \) is estimated from the error of signal rise \( (S_r) \) and \( u(a) \) is the standard uncertainty obtained in the linear regression for the slope of the linear fit. The maximum error found for the detection limit in the direct injection tests is 3.5 \%; therefore all error displayed in Figure 4.19 are assumed for this value.

A.2 Uncertainty: Signal-to-Noise Ratio (SNR)

The signal-to-noise error is obtained from its expanded uncertainty:

\[ U(SNR) = t \cdot u(SNR). \] (A.3)

Since \( SNR \) is calculated from the ratio of the peak height and signal noise, the standard uncertainty of the signal-to-noise ratio can be calculated from
\[ \left( \frac{u(SNR)}{SNR} \right)^2 = \left( \frac{u(h)}{h} \right)^2 + \left( \frac{u(N)}{N} \right)^2. \]  
(A.4)

Where \( u(h) \) derives from the 6.5 % error from peak height and \( u(N) \) from the 3.5 % error of noise. The relative error calculated for the \( SNR \) is \( \sim7.4 \% \) of the measured value.

A.3 Uncertainty: Separation Resolution \((R_s)\)

The expanded uncertainty of the separation resolution is obtained from

\[ U(R_s) = t \cdot u(R_s). \]  
(A.5)

Since \( R_s \) is calculated from Equation 5.1, the standard uncertainty of the separation resolution, \( u(R_s) \), can be obtained from

\[ \left( \frac{u(R_s)}{R_s} \right)^2 = \left( \frac{u(\Delta t_r)}{\Delta t_r} \right)^2 + \left( \frac{u(w_{av})}{w_{av}} \right)^2. \]  
(A.6)

The \( u(\Delta t_r) \) is considered zero because there is no relevant error source associated with the time measurement. \( u(w_{av}) \) stems from the combined uncertainty of two \( w_{1/2} \) measurements. The maximum error found for the measured \( R_s \) values is \( \sim2.7 \% \).

A.4 Uncertainty: GC-\( \mu \)PID Detection Limit

The detection limit estimated for GC-PID results derive from a linear fit using a single signal point; therefore

\[ C_{DL} = \frac{3 \cdot N \cdot C}{h}. \]  
(A.7)

Where \( C \) is the concentration of the pollutant at the point measured. The expanded uncertainty is calculated by

\[ U(C_{DL}) = t \cdot u(C_{DL}), \]  
(A.8)
where

$$\left( \frac{u(C_{DL})}{C_{DL}} \right)^2 = \left( \frac{u(N)}{N} \right)^2 + \left( \frac{u(C)}{C} \right)^2 + \left( \frac{u(h)}{h} \right)^2. \quad (A.9)$$

The standard uncertainty of the noise is obtained in the same way described in Appendix A.1. The $u(C)$ is obtained from the cylinder concentration error (2 %) or from the diluted concentration error and the $u(h)$ is calculated from the error of peak height, which is 6.5 %. The error of the detection limit for all channels is estimated at ~8.9 %.
Appendix B: Leakage

Leakage was evaluated for all channels, including the influence of assembly. For each channel, the prototype was assembled and connected to the rig as in Figure 4.1. An inlet flow ($Q_{in}$) of nitrogen was set at the flow rates from 0.5 to 20 mL/min and the outlet flow ($Q_{out}$) was recorded, using the MFC2 and MFM respectively. After that, the device was disconnected from the rig and fully disassembled/assembled again to reconnect it to the rig and proceed with a repeated measurement. This procedure was performed five times for all channels (A, B, C and D).

Since the MFC2 provides a set value of inlet flow with negligible variation, it was not necessary to have its average. However, the outlet flow has variations and the leakage ($L$) is evaluated as a leakage factor ($\Delta$). Leakage is defined as

$$L = Q_{in} - Q_{out}, \quad (B.1)$$

And the leakage factor is

$$\Delta = 1 - \overline{Q_{out}}/Q_{in} \quad (B.2)$$

where $\overline{Q_{out}}$ is the average outlet flow rate from the five experiments.

Figure B.1 shows the leakage factor values for $Q_{in}$ 2 to 20 mL/min, which present error ranging from 8.7 % to 23.9 %, depending on the channel used. Results for $Q_{in} < 2$ mL/min are not shown since they have extremely high error, as presented in Figure B.2.

For the µPID, leakage factor rises with flow rate until about 10 mL/min and when $Q_{in} > 10$ mL/min a more flat behaviour is observed. The lowest leakage factor was found for channel B ($\Delta = 8 \%$). Channel D has the highest leaking rates, ranging from 25 to 28 %.
Appendix B

Figure B.1 – Leakage factor curve, represented by $\Delta$, for all microchannel designs (A, B, C and D).

B.1 Error of Leakage Factor

Each flow rate measured ($Q$) has three main uncertainty sources: resolution ($u_R$), accuracy of the mass flow controller ($u_{acc}$) and repeatability of measurements ($u_{re}$). The resolution is 0.01 mL/min and the accuracy is calculated as 0.5% of the reading and 0.1% of the full scale of the MFM. The $u_R$, $u_{acc}$ and $u_{re}$ are obtained as: 1) the resolution is divided by $2\sqrt{3}$; 2) the accuracy is divided by the $t$ of student for 95% confidence interval and infinite degrees of freedom; 3) a standard deviation is calculated from the data that yields the average from five repeatability tests. The combined standard uncertainty for the measured flow is:

$$u_Q^2 = u_R^2 + u_{acc}^2 + u_{re}^2.$$  \hfill (B.3)

The standard uncertainty for $\Delta$ can be obtained from

$$\left(\frac{u(\Delta)}{\Delta}\right)^2 = \left(\frac{u(L)}{L}\right)^2 + \left(\frac{u(Q_{out})}{Q_{out}}\right)^2.$$  \hfill (B.4)

While the error of delta is obtained from

$$U_\Delta = u_\Delta \cdot t_\Delta$$  \hfill (B.5)
Figure B.2 – Error of $\Delta$ for a range of $Q_{in}$ values.
Appendix C : MATLAB algorithms

C.1 MATLAB Code for Data Acquisition

Filename “Test_mPID_190722”

```matlab
%%%%%% TEST microPID %%%%%%%%

% Script objectives:
% 1) Acquire data from micro PID
% 2) Save data from micro PID to files
% 3) Save entry parameters
% 4) Plot data from micro PID

%% Instruction: Before start script, close all plots, clear variables and
% command window
clear all;
clc;
close all;

%% Inputs
input1='V_supply';
input2='rate';
input3='duration_in_seconds';
input4='interval_in_seconds';
input5='faraday_cage';

V_supply = 5;    %[INPUT 1] Voltage from power supply
FC='y';         %[INPUT 5] Using faraday cage or not to reduce noise?

%% Create a session
s = daq.createSession('ni');

%% Add analog input channel
a10 = addAnalogInputChannel(s,'Dev1',0,'Voltage');
a10.TerminalConfig = 'Differential';

%% Session acquisition rate and duration
```
rate = 200; %[INPUT 2]
duration_in_seconds = 1020; %[INPUT 3]

s.Rate = rate;
s.DurationInSeconds = duration_in_seconds;

%% Start acquisition and return data
raw_data = s.startForeground();

%% Smoothing signal
interval_in_seconds = 0.2; %[s] %[INPUT 4]
[time, smooth_data] = smooth_sig_avg_1(rate, duration_in_seconds, interval_in_seconds, raw_data);

%% Simple mathematics
Sensitivity = 1E-9;
raw_data = raw_data*Sensitivity; % V to A
raw_data = raw_data*1E9; % A to nA
smooth_data = smooth_data*Sensitivity; % V to A
smooth_data = smooth_data*1E9; % A to nA

period = 1/rate; % period of raw sampling
raw_time = [period:period:duration_in_seconds]'; % Time vector to plot raw samples as function of time

figure
p = plot(raw_time, raw_data, time, smooth_data);
xlim([-1.5E-3 2E-3])
ylim([0 2])
p(2).LineStyle = '-';
p(2).LineWidth = 1.5;
p(2).Color = 'm';
p(2).Marker = 'o';
p(2).MarkerSize = 1;
p(2).MarkerFaceColor = 'm';
p(2).MarkerEdgeColor = 'm';
xlabel('time [s]')
ylabel('signal [nA]')

% figure
% pwelch(raw_data,[],[],[],rate)

%% Save data to .txt file
% The file writes yymmddHHMM_(raw/smooth).txt

% Directory of files:
dir_files = 'C:\0_MATLAB_laptop\Ex\';

inputs = [V_supply; rate; duration_in_seconds; interval_in_seconds]; %Create matrix
raw = [[1:1:size(raw_data,1)'] raw_time raw_data]; %Create matrix
smooth = [[1:1:size(smooth_data,1)'] time smooth_data]; %Create matrix
% Create file yymmddHHMM_inputs.txt, write and close
filename_inputs = sprintf('%s_inputs.txt', datestr(now, 'yymmddHHMM')); % File name
filename_inputs = strcat(dir_files, filename_inputs); % Put file in right folder
fileID_inputs = fopen(filename_inputs, 'w');
fprintf(fileID_inputs, '%-30s %-12.1f
%-30s %-12.1f
%-30s %-12.1f
%-10s
input1, inputs(1), input2, inputs(2), input3, inputs(3), input4, inputs(4), input5, FC
');
fclose(fileID_inputs);

% Create file yymmddHHMM_raw.txt, write and close
filename_raw = sprintf('%s_raw.txt', datestr(now, 'yymmddHHMM')); % File name
filename_raw = strcat(dir_files, filename_raw); % Put file in right folder
fileID_raw = fopen(filename_raw, 'w');
fprintf(fileID_raw, '%s
raw

%-12s %-12s
%-

%-12.1f %-12.5f %-12.8f
raw');
fclose(fileID_raw);

% Create file yymmddHHMM_smooth.txt, write and close
filename_smooth = sprintf('%s_smooth.txt', datestr(now, 'yymmddHHMM')); % File name
filename_smooth = strcat(dir_files, filename_smooth); % Put file in right folder
fileID_smooth = fopen(filename_smooth, 'w');
fprintf(fileID_smooth, '%s
smooth

%-12s %-12s
%-

%-12.1f %-12.5f %-12.8f
smooth');
fclose(fileID_smooth);

C.2 MATLAB Code for Chromatograph Evaluation

Filename “analyse_chromatograph_different_filters_v4”

%%%% PROGRAM TO ANALYZE GC-microPID ACQUIRED IN US %%%%
%%%%

%%%% INSTRUCTION %%%%
%
% 1) Select the spreadsheet
% 2) Select data columns from spreadsheet
% 3) Get chromatographic data including all peaks
%
%% Cleaning
clear; clc; close all;
%
%% Read excel and plot chromatograph
A = xlsread('for_matlab_ch3_003Hz_smooth.xlsx');
B = xlsread('for_matlab_ch3_003Hz.xlsx');

dataset = 1;
as = dataset*2-1; bb = dataset*2;
t = A(:,aa); S = A(:,bb);
t_raw = B(:,aa); S_raw = B(:,bb);

%% % Plot 30 V
figure
p = plot(t_raw,S_raw,t,S)
% title('Signal vs Time')
% Labels
xlabel('Time [s]', 'FontWeight', 'bold')
ylabel('Signal [nA]', 'FontWeight', 'bold')
% Axis limits
ylim([0.4 0.8]);
xlim([0 600]);
grid on
% Dataset specifications
p(1).LineStyle = '-'; p(1).Color = 'r'; p(1).Marker = 'none';
p(2).LineStyle = '-'; p(2).Color = 'k'; p(2).Marker = 'none'; p(2).LineWidth = 2;
% Set axis specifications
ax = gca; ax.FontSize = 12; ax.FontWeight = 'bold'; ax.LineWidth = 1.5;
% Set figure size specifications
fig = gcf; fig.Position = [200 200 750 300]

%% Select begin and end point for peak analysis
% Section of: | Benzene | Toluene | Ethylbenzene, m,p - Xylene, o - Xylene
tn = [70; 170; 170; 360; 360; 600]; % Start and end point of peak analysis [s]
n = size(tn,1); % Number of sections
% Creating vectors:
M = zeros(n,1); I = zeros(n,1);

% Initial values of indexes a and b
a = 1; b = 2;

for i = 1:(n/2)
    % Calculating indexes of start and end point
    k1 = t - tn(a,1); k2 = t - tn(b,1);
    [M(a,1),I(a,1)] = min(abs(k1)); [M(b,1),I(b,1)] = min(abs(k2));
    % Updating indexes a and b
    a = a + 2; b = b + 2;
end

%% Evaluating peaks
data_peaks = zeros(5,3); % Create matrix to store height and width of peaks

% Benzene
minprom_1 = 0.02;
[pks,locn,widths,proms] = findpeaks(S(I(1):I(2)),t(I(1):I(2)),'MinPeakProminence',minprom_1,'MinPeakDistance',2,'NPeaks',1);
figure
findpeaks(S(I(1):I(2)),t(I(1):I(2)),'MinPeakProminence',minprom_1,'MinPeakDistance',2,'NPeaks',1,'Annotate','extents');
text(locs+.02,pks,num2str((1:numel(pks))'));
data_peaks{1,1:3} = [proms(1) widths(1) locs(1)];

% Toluene
minprom_2 = 0.04;
[pks,locs,widths,proms] = findpeaks(S(I(3):I(4)),t(I(3):I(4)), 'MinPeakProminence', minprom_2, 'MinPeakDistance', 2, 'NPeaks', 1);
figure
findpeaks(S(I(3):I(4)),t(I(3):I(4)), 'MinPeakProminence', minprom_2, 'MinPeakDistance', 2, 'NPeaks', 1, 'Annotate', 'extents');
text(locs+.02,pks,num2str((1:numel(pks))'));
data_peaks(2,1:3) = [proms(1) widths(1) locs(1)];

% Ethylbenzene, m,p-Xylene and o-Xylene
minprom_3 = 0.02; baseline = S(I(5)); % Baseline
Sc3 = S(I(5):I(6)) - baseline; % Signal corrected by baseline
[pks,locs,widths,proms] = findpeaks(Sc3,t(I(5):I(6)), 'MinPeakProminence', minprom_3, 'MinPeakDistance', 3, 'WidthReference', 'halfheight');
figure
findpeaks(Sc3,t(I(5):I(6)), 'MinPeakProminence', minprom_3, 'MinPeakDistance', 3, 'NPeaks', 3, 'Annotate', 'extents', 'WidthReference', 'halfheight');
text(locs+.02,pks,num2str((1:numel(pks))'));
data_peaks(3:5,1:3) = [proms(1) widths(1) locs(1); proms(2) widths(2) locs(2); proms(3) widths(3) locs(3)];
data_peaks_total = [data_peaks(1:5,1); data_peaks(1:5,2); data_peaks(1:5,3)];

% Resolutions - Start calculation
R = zeros(4,1); % Create resolutions vector
a = 1; b = 2; % Loop indexes
% Loop to calculate resolutions
for i = 1:4
    diff = data_peaks(b,3)-data_peaks(a,3); % Update indexes
    avg = (data_peaks(b,2)+data_peaks(a,2))/2;
    R(i) = 0.589*diff/avg;
    a = a+1; b = b+1; % Update indexes
end
% Resolutions - Finish calculation
%%
Appendix D : Technical Specifications of
Commercial PIDs

Table D.1 – Technical specifications of commercial PIDs from Baseline MOCON (piD-Tech eVx) used with the portable GC from In’Air Solutions.

<table>
<thead>
<tr>
<th>Name</th>
<th>Green PID</th>
<th>Blue PID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part number</td>
<td>045-010</td>
<td>045-014</td>
</tr>
<tr>
<td>Full scale</td>
<td>10000 ppm</td>
<td>2 ppm</td>
</tr>
<tr>
<td>Detection limit</td>
<td>500 ppb</td>
<td>0.5 ppb</td>
</tr>
<tr>
<td>Weight</td>
<td>8 g</td>
<td>8 g</td>
</tr>
<tr>
<td>External dimension</td>
<td>20 mm</td>
<td>20 mm</td>
</tr>
<tr>
<td>Ionization chamber volume</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td>Ionization chamber type</td>
<td>Diffusion (membrane)</td>
<td>Diffusion (membrane)</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>0 – 300 mL/min</td>
<td>0 – 300 mL/min</td>
</tr>
<tr>
<td>Ionization chamber fill time</td>
<td>10 – 120 s</td>
<td>10 – 120 s</td>
</tr>
<tr>
<td>Common application</td>
<td>TVOC measurement</td>
<td>TVOC measurement</td>
</tr>
</tbody>
</table>
Appendix E : Technical Drawings

The following is a brief description of the drawings displayed in this appendix:

**Channel A, B, C and D:** Microchannels that fit into the bottom PMMA and constitute the signal electrodes.

**Bottom PMMA:** Structure at the bottom of the microchannel responsible to separate the positively and negatively charged electrode. It contains the inlet and outlet pores to deliver the gas sample into the microchannel.

**Top PMMA:** Structure at the top of the microchannel that fits two O-rings which positions the UV lamp at the centre of the ionization chamber.

The microchannel (A, B, C and D) combined with the bottom and top PMMA and the UV lamp compose the core of the µPID, where the ionization chamber is located.

**Bottom Shell:** Structure below the bottom PMMA that contains the fluidic connection to the ionization chamber and the electronic connection to the signal electrodes.

**Top Shell:** Structure above the top PMMA that encloses the core to protect the sensor user from the UV light emission and connects the electronics to power the UV lamp.