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MICROFLUIDIC SENSING OF AIRBORNE FORMALDEHYDE: TOWARDS ON-CHIP INTEGRATION

Daniel Măriuța[1,2], Lucien Baldas[2], Stéphane Colin[2], Christine Barrot-Lattes[2],
Stéphane Le Calvé[3,4], Jan G. Korvink[1] and Jürgen J. Brandner[1]

[1]Karlsruhe Institute of Technology, Institute of Microstructure Technology, Campus Nord, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[2]Institut Clément Ader (ICA), Université de Toulouse, CNRS, INSA, ISAE-SUPAERO, Mines-Albi, UPS, Toulouse France
[3]University of Strasbourg, Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES), Group of Atmospheric Physical Chemistry, Strasbourg France.
[4]In'Air Solutions, 1 rue Blessig, Strasbourg, France

KEY WORDS

Contact sensing, Micro-fabrication, On-chip membrane-based gas-liquid contacting, CMOS-based fluorescence sensing

ABSTRACT

1. INTRODUCTION

Indoor pollution concentrations are known to be up to five times higher than outdoors [1]. People spend generally 90% of their time indoor, and approximately 3,8 million people die yearly from causes related to the exposure to indoor pollution [2]. Among all the indoor pollutants, volatile organic compounds (VOCs) are of particular interest due to their high level of toxicity. One of the VOCs that raises increased concern is formaldehyde, a compound that is supposed to be carcinogenic and mutagenic [3], [4]. Formaldehyde is largely used in the fabrication of building materials, household products, and resins for wood products. There are research projects looking for a none harmful formaldehyde alternative in the form of bio-based platform chemical 5-HMF (5-Hydroxymethylfurfural) [5], but meanwhile, the formaldehyde industrial consumption is continuously growing. Detection devices existing today are far from being cost-effective, ultra-portable, stable and fast, making the detection process of formaldehyde difficult and limited.

This project aims to explore the miniaturization possibilities towards the lab-on-a-chip integration of the real-time detection of low concentrations of formaldehyde. The detection principle is based on the Hantzsch reaction coupled to the fluorescence optical detection microfluidic method, described in [6]. A prototype concept is here proposed, aiming to embed the detection process inside a modular palm-hand device. For a better understanding and control of the involved parameters, formaldehyde trapping and derivatization are assigned to a sub-device, named Gas-Liquid Micro-Contactor, and the fluorescence detection system to another sub-system, named Optical Detector (Figure 1). A micro-machined polymer chip, embedding a flat hydrophobic membrane, stands for continually contacting a gas and a liquid microflow, using an overlapping network of two meandering channels. The interest here is to study the feasibility of enabling enhanced and efficient formaldehyde trapping using relatively cheap on-chip membrane-based polymer chips. The optical detection sub-system targets the development of a miniaturized device for the fluorescence intensity quantification based on the contact sensing and the CMOS-based fluorescence sensing in low interrogation volumes, down to the nanoliter range.

2. GAS-LIQUID MICRO-CONTACTOR

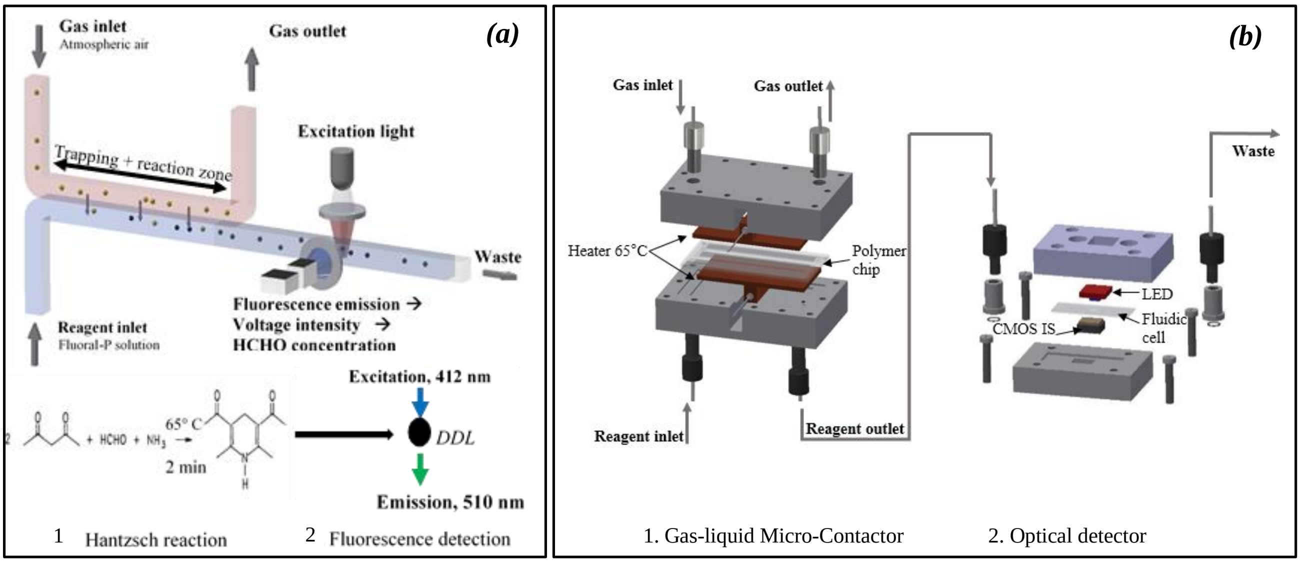


Figure 1. (a) Formaldehyde detection methodology; (b) Prototype device exploded view

Micro-fabrication of polymer chips for efficient gas-liquid interaction is a subject of interest in a large variety of fields, especially in the lab-on-a-chip domain [7]. Disposable polymer chips propose relatively cost-effective and ultra-portable alternatives for applications well-established for properly working in laboratory conditions, but lacking in portability and autonomy for long-term remote applications.

Here, the poly (methyl methacrylate) (PMMA) polymer is considered due to the fact that it does not release formaldehyde up to 80°C temperature and it is not known as a formaldehyde absorbent. PMMA does not react with Fluoral-P reagent solution and has a good optical clarity. These properties make this polymer the perfect candidate for integration of formaldehyde detection based on the Hantzsch reaction and optical sensing into a chip.

The polymer chip concept hosts a network of two overlapping meandering micro-channels, one channel being assigned to the liquid stream and the other one to the gas stream. They are milled with very good precision (±5μm) on two 1 mm thickness PMMA sheets (Figure 2.b). Two different double-sided commercial-available hydrophobic ePTFE membranes (Aspire® QP955 and Aspire® QL217) were considered for being on-chip integrated and further tested. They have a reference pore diameter of 200 nm and the contact angle is 120° [8]. A vacuum chunk was used to maintain the horizontality of the PMMA sheets, in order to avoid its wavy form and assure a constant depth of the channel over the length. The two meter long overlapping channels have: (a) 400 μm × 200 μm cross section for the gas carrying channel and (b) 100 μm × 200 μm cross section for the liquid carrying channel.

The microfluidic sealing of the chip was realized using solvent-enhanced femtosecond laser welding. A hot embossing procedure was previously tested, but failed since the very thin ePTFE layer (30 μm thickness) of the membrane melted during the process. Two interior strips (Figure 2, (b)) were designed on the PMMA gas sheet, in order to enforce the mechanical resistance of the structure which is important when pressure drop is considered. The hydrophobic membrane was precisely cut by a CO_2 laser (Figure 2, (c)) to fit the pocket on the PMMA gas sheet. The gas-liquid contacting chip is integrated in between two upper and lower holders (Figure 3). The holders are micro-machined in polyether ether ketone (PEEK) which was chosen due to its low thermal conductivity of 0.25 $\frac{W}{m^2K}$. They host fluidic leakage-free connections for gas (Swagelok, SS-100-1-1, 1/16) and liquid (N-333, Idex-HS) streams, the flat copper foils thermally controlled by cartridge heaters (Watlow, C1A-9602, 30 W power, 24V voltage) in order to heat up the fluid streams insi – the temperature found to be optimal for the Hatzsch reaction, and O-rings (Parker, 6-1735 E540-80, 0.7 × 0.5 mm) – one for each fluidic inlet/outlet – that assure the leakage-free condition when the chip is clamped in between the holders.

Leakage free condition was tested at 10 µL/min reagent flow rate. After six minutes of continuous streaming, leakage occurred near the connector. The chip was verified and it could be observed that the liquid filled in approximately one third the length of the two meters meandering channels. It could also be observed that the laser bonding of the chip failed, most probably due to the high pressure induced by the hydraulic resistance on the side filled in with water. A chip with a shorter meandering channel length is considered for the following tests.

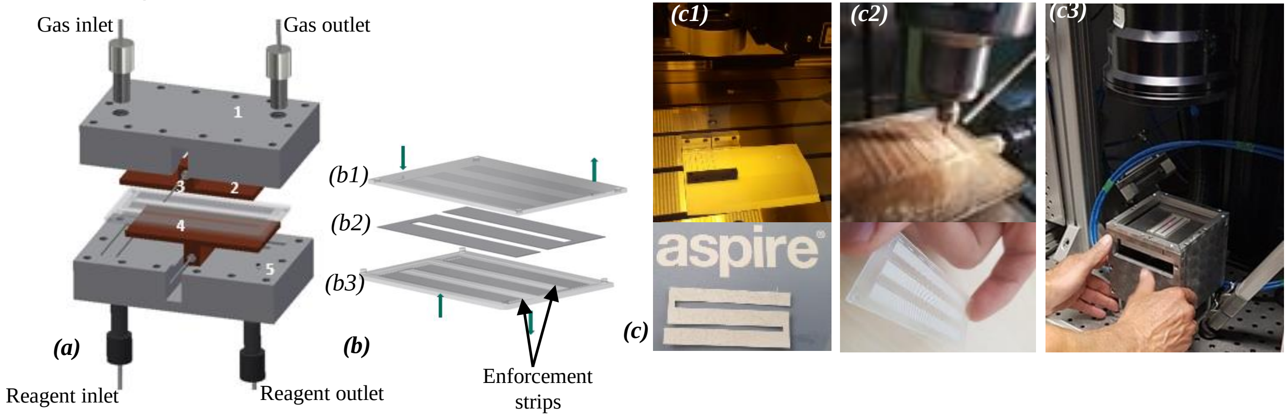


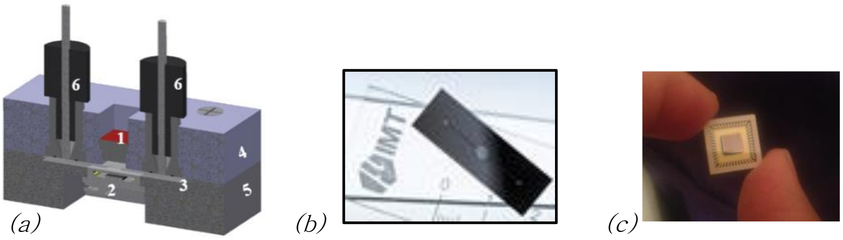
Fig. 2. (a) (1) – Holder. (2) – Copper layer. (3) – Cartridge heater. (4) – Gas-liquid contacting chip. (5) – O-ring. (b) Gas-liquid contacting chip, exploded view: (b1) – Gas layer, (b2) – Double-sided membrane, (b3) – Liquid layer. (c) Fabrication steps of the gas-liquid chip contactor: (c1) CO_2 laser membrane cut. (c2) Meandering channels micro-milling process. (c3) Solvent-based laser welding.

3. OPTICAL DETECTION SYSTEM

In contact sensing, the samples are placed in close proximity of the sensor surface without intermediate optics. Due to the short distance between the sensor and the sample, the optical loss can be small. The CMOS technology enables on-chip detection and signal processing, significantly reducing size and power consumption [9].

The optical detection sub-system here proposed combines the contact sensing and CMOS fluorescence sensing in low interrogation volumes (600 nL - 5 µL), in order to develop a robust, low-power, and sensitive micro-detector. Geometry of the fluidic interrogation chambers (Figure 3, c) was optimized in such a way to assure an uniform flow velocity [10]. The fluidic cells (Figure 3, c) were fabricated from two 1 mm thickness glass layers (Schott AF32). Fabrication of the interrogation cells was performed at LAAS Toulouse in the framework of the French National Nanofabrication Network Renatech. Two 4 inch glass wafers (Schott AF32) were used. The first wafer (fluidic wafer) was cleaned with oxygen plasma at 800 W for 5 minutes. Afterwards, a 200 µm SU8 coating was added and baked using the EVG 120 equipment. The masks were then used to expose the wafer to UV light, using the Suss MA6 gen4 equipment, in order to create the desired channeling geometry. The SU8 developer was used to remove the exposed parts, followed by a hard-bake at 125°C for 1 minute with ramping. The second glass wafer (cover wafer) was firstly laminated with a Photec 2040 dryfilm for protecting the glass during piercing. The piercing was made with sand-blasting, procedure followed by rinsing and cleaning with acetone and DI water. The wafer was cleaned with oxygen plasma at 800 W for 5 minutes, before adding a SU8 10 µm coating (Suss spincoater) and before being baked (hot plate). The fluidic and cover wafers were bonded together using Nanonex nanoimprint equipment by applying uniform pressure. An AZ 4562 photoresist coating was added using a spincoater as a protection layer before dicing the wafer in six different fluidic cells which were then rinsed and cleaned with DI water.

Commercially-available LEDs (Roithner Lasertechnik GmbH, VL415-5-15, 10-16 mW, viewing angle 15°) and CMOS image sensors (Anitoa® USL24) have been used. The Anitoa® ULS24 CMOS image sensor was specially developed for spectroscopic measurements and possesses a signal-to-noise ratio larger than 13 dB at its 3.0×10^{-6} lux detection threshold. The linearities of the CMOS image sensor over the integration time ($y = 247.82x - 348.26$, $R^2 = 0.9848$) and over the light intensity ($y = 16.209x + 106.38$, $R^2 = 0.9968$) were calculated experimentally, exposing the CMOS image sensor to different light intensities and measuring the photon counts. The upper and the lower holders are 3D printed. The prototype will be tested in a configuration possessing a bandpass filter (Midwest, BP525-R10). As well, a second round of interrogation fluidic cells made from PMMA are considered to be fabricated using micro-milling and hot embossing procedures. Results observed from parallel testing should prove the viability of PMMA material for optical detection of formaldehyde.



(a) *(b)* *(c)*

Fig. 3. (a) Longitudinal cross-section: (1) – LED, (2) – CMOS sensor, (3) – disposable fluidic cell, (4) – upper holder, (5) – lower holder. (b) Glass fluidic cell. (d) – Anitoa ULS 24 CMOS image sensor

4. CONCLUSION

Successful development of a micro-total-analysis system for the continuous detection of the low-limits gaseous formaldehyde is highly desired since this possibly carcinogenic substance largely used in the fabrication of household products is continually released indoors. In this work, a laboratory prototype was developed based on the Hantzsch reaction coupled to the optical fluorescence detection method, and composed of two sub-devices: a gas-liquid micro-contactor relying on a disposable PMMA gas-liquid contacting chip that uses as separation medium a hydrophobic polymer membrane, and a fluorescence optical detection system combining the contact sensing of a disposable glass interrogation fluidic cell with the CMOS-based spectroscopy. After the successful fabrication of the sub-systems, further results are expected in order to experimentally prove the concept.

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