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REAL-TIME MONITORING OF GASEOUS FORMALDEHYDE USING A MICROFLUIDIC DEVICE

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ABSTRACT

A new analytical method based on microfluidic device for formaldehyde detection was previously developed and patented. Its principle is based on three distinct steps: 1) gaseous formaldehyde uptake into an aqueous solution through an annular flow[1]; 2) reaction at 65°C with a specific derivative agent and 3) fluorimetric detection of the reaction product, i.e. DDL. The uptake yield of gaseous formaldehyde in aqueous solution was around 90-100 % in the optimized conditions. Our laboratory researches lead finally to a 4 kg fully automatic instrument having a response time of 10 min, a temporal resolution of 2 seconds and a detection limit of 1 µg m^{-3}.
Our formaldehyde microanalyser was then deployed during two field campaigns, one in a junior high school recently built equipped with a modern ventilation (MERMAID campaign), one in a couple of elementary schools using natural ventilation (IMPACT'AIR campaign). The microanalyser operated continuously for 2 and 5 weeks respectively to monitor changes in formaldehyde concentrations in the studied room, according to the building's ventilation periods or natural ventilation, respectively.
The resulting formaldehyde concentrations varied in the ranges 2 - 25 and 1 – 55 µg m^{-3} for MERMAID and IMPACT'AIR campaigns, respectively. In both cases, the data obtained with the novel microanalyser were in excellent agreement with those measured with the ISO 16000-3 reference method (active sampling on DNPH cartridges). In addition, our microanalyser allowed to measure fast variations of formaldehyde concentration, showing that our micro-device is suitable to monitor formaldehyde concentrations in near real time.
Our studies highlighted the temporal variations of indoor formaldehyde concentration were highly correlated to the ventilation periods. In addition, the IMPACT'AIR campaign showed the influence of furniture and occupants on the level of formaldehyde in the two investigated classrooms located in two different schools, taking as reference the same empty room.

KEYWORDS
Microfluidic analytical method – portable formaldehyde microanalyser – Indoor field measurements

1. INTRODUCTION

Formaldehyde is a major pollutant of indoor air due to its multiple sources: materials, combustion, painting, etc. (Paolacci et al., 2007, Kim et al., 2010). Several studies have shown that indoor

formaldehyde concentrations are 2 to 15 times higher than those measured outdoor, and may vary typically between 10 to 100 µg m^{-3} (Marchand et al., 2008, Kim et al., 2013, Wang et al., 2010). From 2004 Formaldehyde is considered as a carcinogenic compound for human by the International Agency for Research on Cancer (IARC, 2004 and 2006). Consequently, French formaldehyde guideline values were suggested: 10 µg m^{-3} for long term exposure and 50 µg m^{-3} for two hours (AFSET, 2007). Besides, French recommendations aim at limiting formaldehyde concentrations in public buildings to 30 µg m^{-3} by 2018 (French Decree n°2015-1000). The reference method ISO16000-3 (ISO: Indoor Air-Part 3), recommended by air monitoring agency (ASTM International, 2009), uses a DNPH-cartridge sample with an analysis by HPLC/UV visible which is time-consuming and involves a laboratory treatment with bulky instruments. Many alternative methods, oriented towards real-time and in-field detection, have been developed. Reagents which react with Formaldehyde to produce color change on the detection element have been considered as the key feature for those methods. Miniature and portable systems have been developed (Toda et al, 2005, Toda et al., 2012, Allouch et al., 2013). Nevertheless, fully autonomic and continuous monitoring was not possible since the reaction on the solid detection element was not reversible. In addition, the resolution of such sensors was usually not as good as needed to detect the very low Formaldehyde concentrations recommended by the legislature.
In this context, we recently reported the development and the optimization of a novel portable micro-device (Guglielmino et al., 2014) based on three steps strongly coupled to each other: 1) the uptake of gaseous Formaldehyde into an aqueous solution, 2) the selective Formaldehyde derivatization by reaction with Fluoral-P at 65°C, 3) the analysis of the reaction product by fluorescence. This analytical method combines precision, selectivity and fast analysis in a single miniaturized and portable, 4 kg, instrument with large reagent autonomy. The system is fully controlled by homemade software and exhibits response and resolution time of 10 minutes and 2 seconds respectively.
Our formaldehyde microanalyser was then deployed during two field campaigns, one in a junior high school recently built equipped with a modern ventilation (MERMAID campaign) (Schoemaecker et al., 2014), one in a couple of elementary schools using natural ventilation (IMPACT'AIR campaign). The microanalyser operated continuously for 2 and 5 weeks respectively to monitor changes in formaldehyde concentrations in the studied room, according to the building's ventilation periods or natural ventilation, respectively.
The MERMAID and IMPACTAIR field campaigns were taking place during the winter holydays from February 23rd 2015 until March 6th 2015 and from February 16th until March 20th 2016, respectively. In the MERMAID campaign, the ventilation system aimed to ensure a good Air Exchange Rate (more than 2 h^{-1}) to provide healthier atmosphere inside classrooms.

2. MATERIALS/METHODS

The two analytical techniques used during the field campaigns are described below.

2.1. Reference method ISO 16000-3 based on the formaldehyde uptake on DNPH cartridge

The reference ISO 16000-3 method for the formaldehyde detection is based on active sampling using 2,4-Dinitrophénylhydrazine (DNPH) cartridge (Waters, Sep-Pak) followed by the analyses using the high performance liquid chromatography with UV detection (HPLC-UV) (ISO, Indoor Air-Part 3, 2001, ASTM International, 2009). This method allows to quantify all aldehydes present in ambient air. Air samplings were realized with two automatic sampling devices, namely DNPH MP4V and DNPH MP8V, composed of mass flow controller, gas pump and 4 or 8 solenoid valves and operating at 500 and 1000 mL min^{-1} respectively. Once sampling achieved, DNPH cartridges were eluted with 2 or 3 mL of Acetonitrile (Sigma Aldrich, 99.8%). 20 µL of the resulting hydrazone solution was then injected and analyzed by HPLC/UV where hydrazone were separated through a non-polar C18 column and detected at 360 nm (Salthammer et al., 2010; Marchand et al., 2008). Aldehydes concentrations were determined using an external calibration. This offline method is not formaldehyde specific, very time consuming and requires busy and expensive equipment.

2.2. Formaldehyde micro-analyzer based on microfluidic device

The analytical method recently developed in our laboratory to quantify gaseous formaldehyde was detailed in our previous work (Guglielmino et al., 2014) and is therefore briefly described here. This analytical method is based on three highly coupled steps (Guglielmino et al., 2014; Guglielmino et al., 2015): 1) the uptake of gaseous formaldehyde into an aqueous solution; 2) the chemical reaction between formaldehyde and a selective derivative agent, i.e. fluoral-p, via the Hantzsch mechanism (Eisner et al., 1972); and 3) the fluorescence detection of the reaction product, i.e. 3.5-diacetyl-1.4-dihydrolutidine (DDL).
Air sampling was conducted by a mass flow controller with a dynamic range of 0-20 mL min^{-1} placed before a mini air pump to obtain a constant gas flow injected coaxially into the uptake capillary of 530 µm ID (see Figure 1). At the same time, the liquid reactant is continuously injected at 17 µL min^{-1} by a micro peristaltic pump through a specific Tee into the same uptake capillary (Guglielmino et al., 2014). The coinjection of both gas mixture and the fluoral-p solution into a capillary permits to obtain a biphasic flow. Depending on gas and liquid flows ratio, three different flows regimes can be obtained: bubble, slug and annular flow. Guglielmino et al. (2014) shown that the annular flow allows to improve the uptake of gaseous formaldehyde into the fluoral-p solution leading to an uptake yield of more than 70%. The optimal gas and liquid flow were found to be 20 mL min^{-1} and 17 µL min^{-1} respectively.

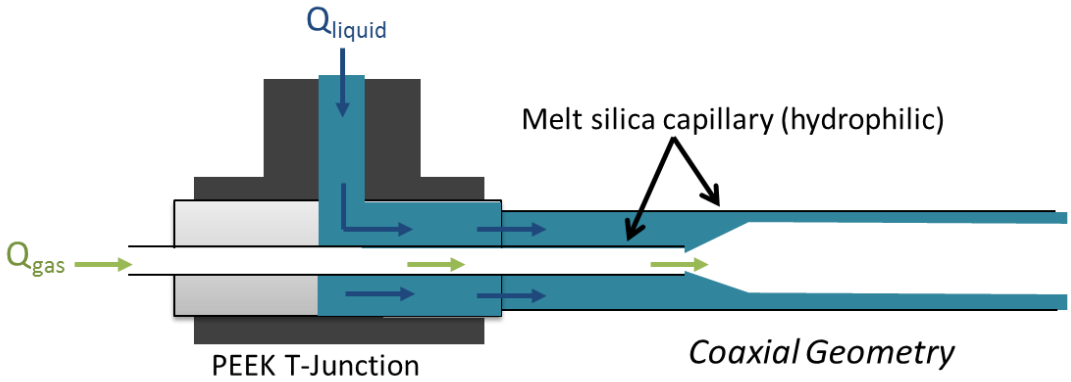

Figure 1: Scheme of the microfluidic cell, to obtain a diphasic (gas and liquid) flow.

The aqueous solution containing both fluoral-P and formaldehyde pass through an oven maintained at 65°C, permitting to achieve the full reaction in less than 3 minutes at 65°C. Finally, the fluorescence of DDL was excited by a LED centered at 415 nm and then collected on a photomultiplier coupled to a 530±40 nm band pass filter. The fluorescence signal was also amplified and averaged on two seconds.
Within these conditions the analytical set-up has a temporal resolution of two seconds and a response time of ten minutes. Its detection limit was estimated to about 1 µg m^{-3} (S/N =3) (Guglielmino et al., 2014). With 100 mL of liquid reactant, its autonomy reaches 98 hours, i.e. 4.1 days. The analytical instrument is 45 cm length, 33 cm wide and 15 cm height corresponding to a weight of 4kg including both reactant and trash bottles. This analytical system is standalone, fully controlled by homemade software which ensured real time analysis and concentration calculation. Finally, its low weight and size, its low reagent consumption insure a high level of wearing and autonomy comfort for the user.

3. RESULTS

3.1. MERMAID field Campaign

Once all instruments installed, indoor air sampling began for two consecutive weeks and instruments worked continuously. During measurements, doors and windows of the classroom were closed and nobody was allowed to enter inside the investigated classroom except for opening the windows. Ventilation conditions were preprogrammed for the whole day. The temperature inside the studied room

varied between 19 and 26°C and the humidity ranged from 20 to 40% when windows were closed and reaches up to 60% when windows were opened for one hour.
Different variations of formaldehyde concentrations were observed depending on the ventilation state. Indeed, significant variations were measured between periods with and without ventilation, showing the effect of the ventilation and the micro-analyzer performances. Formaldehyde concentrations varied between 2 and 25 µg m^{-3} depending on the ventilation status. Figure 2 corresponds to a focus on the variation of formaldehyde concentration for Tuesday 3rd March and Wednesday 4th of March with the ventilation periods of the building drawn in grey on this graph. The concentration decreased very quickly after the beginning of the ventilation period. However, at least 30 minutes of ventilation is compulsory to reach and stabilize the smaller formaldehyde concentration, i.e. 10 µg m^{-3} for March 3rd 2015.When ventilation stopped, formaldehyde concentration increased to reach a maximum (18 µg m^{-3} for March 3rd 2015 nights) after about two hours.

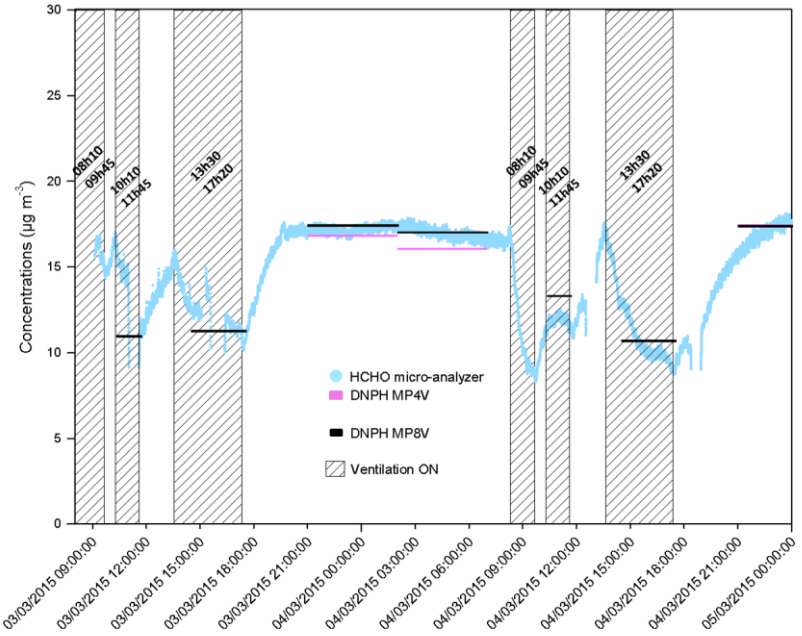

Figure 2: Variation of gaseous formaldehyde concentrations between Tuesday, 3 march 2015 and Wednesday, 4 march 2015 as a function of ventilation system status; Comparison between reference ISO 16000-3 method and our formaldehyde microanalyser.

During a standard ventilation day such the 4th March, the ventilation was switched ON at 8:10 am for the beginning of the class and the formaldehyde concentration decreased immediately from the maximum reached during the night (17 µg m^{-3}) down to 9 µg m^{-3} in 95 min. Then, the ventilation system was switched OFF during the morning break. Even if the break time was very short (25 minutes), the formaldehyde concentration increased to about 12 µg m^{-3} (see Figure 2). This increase was more pronounced during the lunch break. Next, the ventilation system was again switched ON and the formaldehyde concentration decreased again until about 10 µg m^{-3}. The ventilation was finally switched OFF for the night and formaldehyde concentration increased to reach approximately the formaldehyde concentration reached the day before.
To validate the new formaldehyde micro-analyser performances in real conditions, results were compared to the reference ISO 16000-3 method where two automatic sampling devices were used namely DNPH MP4V and DNPH MP8V.
As shown in Figure 2 and 3a, formaldehyde concentrations were simultaneously measured with the micro-analyzer (µHCHO), and with the two automatic sampling devices to collect air on DNPH cartridges, for 3rd and 4th March (figure 2) and between the 26th and 28th of February (figure 3a), respectively.
Alternatively to the controlled ventilation, the windows were opened twice for about 1 hour each time at 4:15 PM.

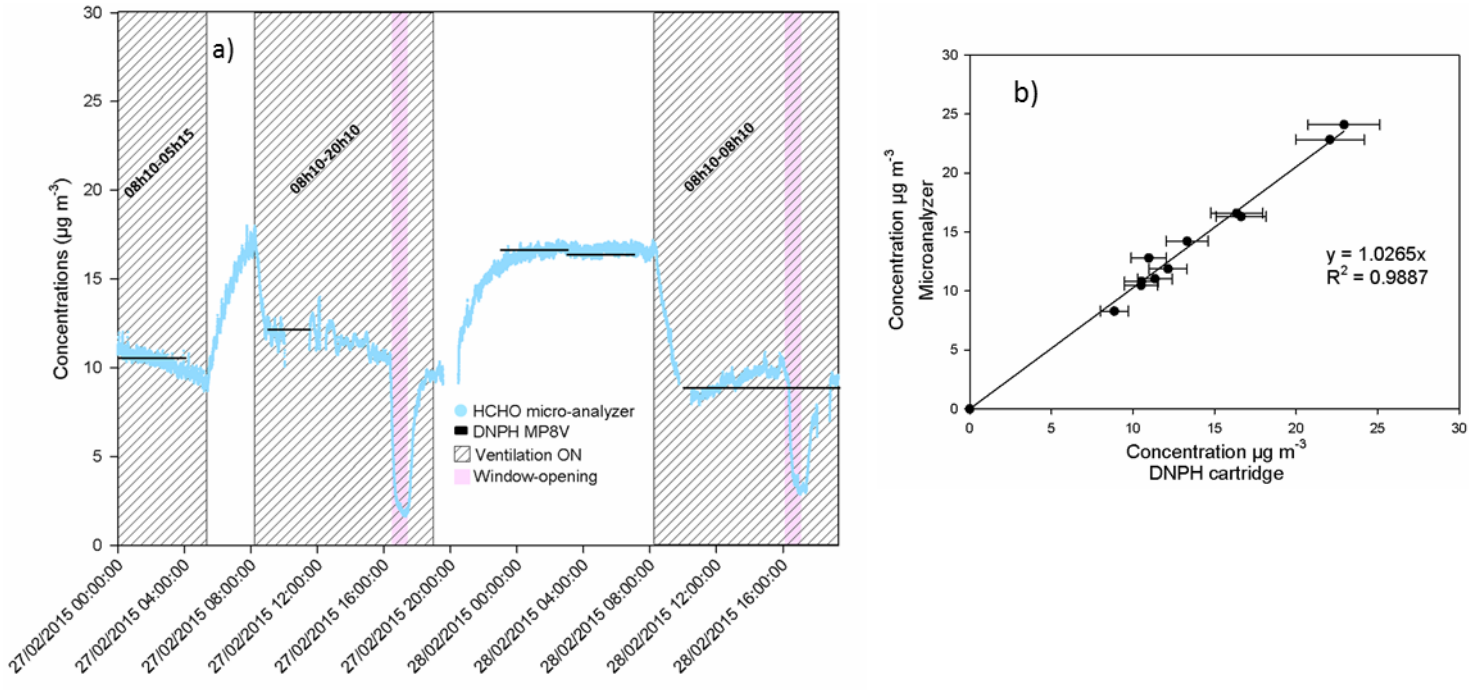

Figure 3: a) Variation of gaseous formaldehyde concentrations between Friday, 27 February 2015 and Saturday, 28 February 2015 as a function of ventilation system status and window-opening. Comparison with another analytical method for gaseous formaldehyde quantification: the reference ISO 16000-3 method where one automatic sampling device were used namely DNPH MP8V b) Inter-comparison of formaldehyde concentration provided by our micro-analyzer with those obtained with DNPH cartridges, between the 26th and the 28th of February.

3.2. IMPACT'AIR field Campaign

Once all instruments installed, indoor air analysis began for five consecutive weeks and instruments worked continuously. During the weeks 1 and 2, the classroom was respectively empty and contained the furniture without any people, permitting to quantify the contributions of either building materials (week 1) or furniture (week 2). Then for the three last weeks, the classroom was normally occupied by the schoolchildren to study the impact of human activity and aeration on air quality and particularly on formaldehyde concentrations. More precisely, during the last three weeks, three ways of aeration were used:

- Week 3: occupants used usual aeration in relation to what was practiced in the school;
- Week 4: specific time aerations were applied according to the recommendations suggested by the French Institute of indoor air quality;
- Week 5: People opened the windows when the CO_2 concentrations were high according to some light indicators.

The resulting measurements are shown in Figure 4 for the 5 weeks

Results were again compared to the reference ISO 16000-3 method where two automatic sampling devices were used. As shown in Figure 4, formaldehyde concentrations were simultaneously measured with the micro-analyzer (µHCHO), and with the two automatic sampling devices to collect air on DNPH cartridges. The correlation between both analytical techniques is shown in Figure 5.

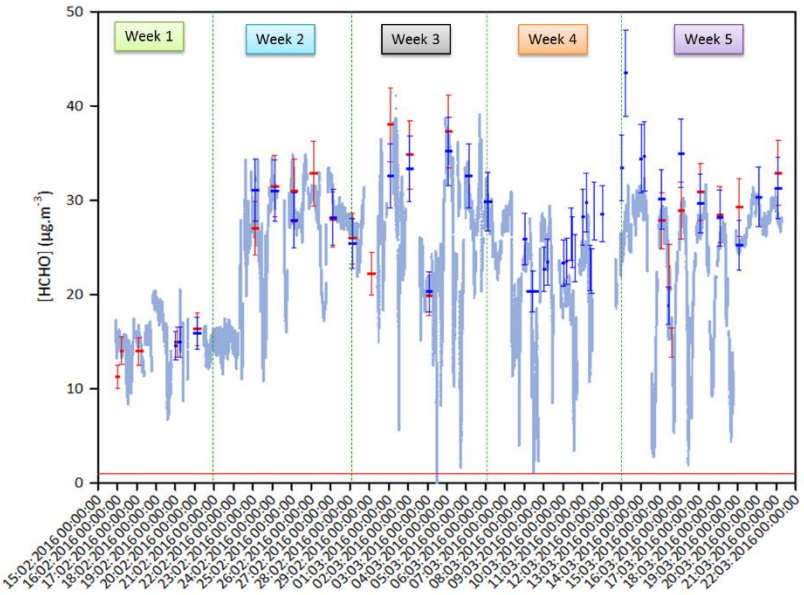

Figure 4: Variation of gaseous formaldehyde concentrations between Monday, 16 February 2016 and Saturday, 20 March 2016 and Comparison with DNPH reference ISO 16000-3 method.

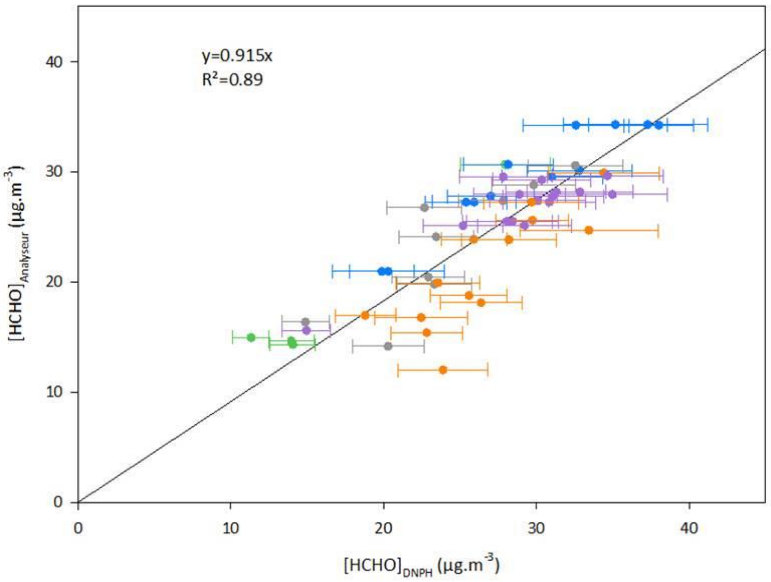

Figure 5: Inter-comparison of formaldehyde concentrations provided by our formaldehyde microanalyzer with those obtained with DNPH cartridges during five weeks (Lavoisier school).

4 DISCUSSION

4.1. MERMAID Field campaign

During the five weeks inside the classroom, formaldehyde was always detected and its concentration in the range 2-25 µg m^{-3}, was strongly influenced by the natural ventilation status.

Correlation between formaldehyde concentration and ventilation status

The efficacy of the building ventilation was proved with the very quickly decrease of formaldehyde concentrations after the ventilation starts (see figure 2). Indeed, concentrations are divided by two during ventilation period. In addition, after long ventilation period, the increase of formaldehyde concentration

is slower than before and the maximum reached the night is lower, i.e. 25 µg m^{-3} for February 26th nights (see Figure 3a) and 17 µg m^{-3} after long ventilation period for March 3rd nights (see Figure 2).
Besides, it is important to underline that the effect of the outdoor air supply on indoor formaldehyde concentration is significantly more efficient than ventilation (Figure 3a) and led to decrease formaldehyde concentration down to 2 µg m^{-3} in less than 30 minutes. Indeed, the three windows were opened at 16:15 for one hour the February 27th and 28th. After closing the windows, the formaldehyde concentration increased slowly to reach the initial concentration of about 10 µg m^{-3}.

Comparison of formaldehyde concentrations measured by different techniques

Results obtained by both analytical techniques are in very good agreement as shown in figures 2, 3a and 3b. For instance, figure 3b shows an excellent correlation of our micro-analyser data obtained in the measured concentration range 8 -24 µg m^{-3} (between the 26th and 28th of February) with those found with DNPH cartridges. Indeed, the slope of 1.03 indicates an average deviation of 3 % between both techniques.
In addition, the microfluidic instrument can measure very rapid changes in formaldehyde concentrations such as during the window opening as observed on Figure 3a while reference method ISO 16000-3 can only provide an average concentration over its chosen sampling time, i.e. few tens of minutes or several hours.

4.2. IMPACT'AIR Field campaign

During the five weeks field campaign inside the classroom, formaldehyde concentration ranged roughly between 0 and 40 µg m^{-3}. The resulting formaldehyde concentration measured in week 1 can be attributed to building materials emissions. As illustrated in Figure 4, the formaldehyde concentration increased significantly from the first week to the second week, exhibiting the significant contribution of furniture to the formaldehyde concentration.
In addition, the average concentrations obtained for the 3 next weeks were not really different compared to those measured in the second week. Nevertheless, if we consider only the time where the schoolchildren are present, the average formaldehyde concentration decreases in the range 20 – 40 % for weeks 3 to 5 compared to the second week. Such observation highlight the benefits of ventilation which reducing the real level of formaldehyde exposure.
Finally, an excellent agreement between formaldehyde measurements obtained either with the new formaldehyde microanalyser or with the DNPH reference method, was observed again (see Figure 5) confirming the robustness of this new microdevice on a long time experiment.

5. CONCLUSIONS

The results obtained in this work show that the new analytic method based on microfluidic device is extremely sensitive, accurate and precise for quantification of formaldehyde in ambient air.
Our microfluidic analytical method allows to quantify over a long period of time the formaldehyde in near real time and to highlight very fast temporal variation of formaldehyde concentration in air.
Using this temporal resolution of 2 s, the resulting detection limit of our formaldehyde micro-analyzer is around 1 µg m^{-3} which is adapted to monitor formaldehyde in indoor air. In addition, the sensitivity can be improved when the time resolution is increased from 2 to 60 s. Indeed, a time-resolution of 60 s would be sufficient for the major part of applications.

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