

PORTABLE MICROFLUIDIC ANALYSER FOR CONTINUOUS MONITORING OF FORMALDEHYDE IN INDOOR AIR



At a time when pollution has become a major public health concern, reliable monitoring techniques for air quality must be available. Formaldehyde is a pollutant found mainly in indoor air. It is present in concentrations 2 to 15 times higher than those in outdoor air, with values typically ranging from 10 to 100 $\mu\text{g m}^{-3}$ [1]. A wide variety of formaldehyde sources are present indoors: building and furnishing products, household products, domestic combustion, etc. Formaldehyde is also present in many products due to its disinfectant and conservation properties.

Formaldehyde has irritating effects on the respiratory system and eye mucosa, and its involvement in allergic asthma, is well known [2]. The International Agency for Research on Cancer classified it as carcinogen in 2004. Health agencies recommended thus to reduce exposure to lowest feasible concentration: values of 19.7 $\mu\text{g m}^{-3}$ (16 ppb) (NIOSH^a) and 30 $\mu\text{g m}^{-3}$ (24.4 ppb) (ANSES^b) for long term exposure while occupational exposure limits are set at 243 $\mu\text{g m}^{-3}$ (300 ppb) (over 8 h) and 487 $\mu\text{g m}^{-3}$ (600 ppb) (over 15 min) under EU Directive 2019/983. Rapid, sensitive, easy-to-use, and robust continuous analysis techniques need to be developed to democratise the formaldehyde monitoring.

1. Materials and methods

In this section, we will describe the formaldehyde monitoring analytical system (microF), the gas generators and the set-up for the evaluation of the microF performance regarding humidity exposition and its use in a field campaign.



Figure 1: MicroF: Microfluidic formaldehyde analyser

1.1. MicroF

The microF (Figure 1) is a portable microfluidic formaldehyde analyser commercialised by Chromatotec. It was first developed and patented by a research team at ICPEES^c (CNRS^d and University of Strasbourg). As represented in Figure 2, this device is based on the continuous detection of 3,5-diacetyl-1,4-dihydrolutidine (DDL), a product of the reaction of formaldehyde with fluoral-P (or acetylacetone solution). The air sample and liquid reagent solution flow at a constant rate through the micro-F. Both gas and liquid phases are co-injected into a 530 μm ID capillary column. Due to the high solubility of formaldehyde, the aqueous solution traps all the gaseous formaldehyde. After degassing, Fluoral-P reacts specifically with formaldehyde in an oven set at 65°C for about 3.5 min, ensuring the full conversion of formaldehyde into DDL, which is a fluorescent molecule. The DDL is excited by a LED at 415 nm and the fluorescent light is collected at 530 nm by a photomultiplier and then amplified. The fluorescence is therefore proportional to the formaldehyde concentration [3].

1.2. Humidity and gaseous formaldehyde generation

Whereas humidity is omnipresent in air, this parameter is often overlooked by analysers' manufacturers. To assess the humidity impact on the analysis of formaldehyde by the microF, a mixture of controlled humidity and formaldehyde concentration was required. Humidity was generated from distilled water contained in a bottle in which a microporous tube was immersed. Nitrogen flowed in the microporous tube and water was evaporated at the interface into the flow, resulting in a mixture of air at controlled humidity. This humidity generator was described and used by Becker et al. [4] Gaseous formaldehyde was generated using a paraformaldehyde permeation tube. The permeation tube was placed in an oven and heated at 60°C. The system was supplied by a constant flow of nitrogen (60 mL min^{-1}) and generated formaldehyde at a fixed concentration of 339 $\mu\text{g m}^{-3}$. It was further diluted with humid or dry nitrogen, producing concentrations between 50 and 152 $\mu\text{g m}^{-3}$ at 8% or 50% relative humidity (RH) [5]. Both formaldehyde and water gaseous flows combined in a mixing chamber to which the microF sampling inlet was connected. In these studies the standard method ISO 16000-3 was used as a reference to monitor formaldehyde concentration [6].

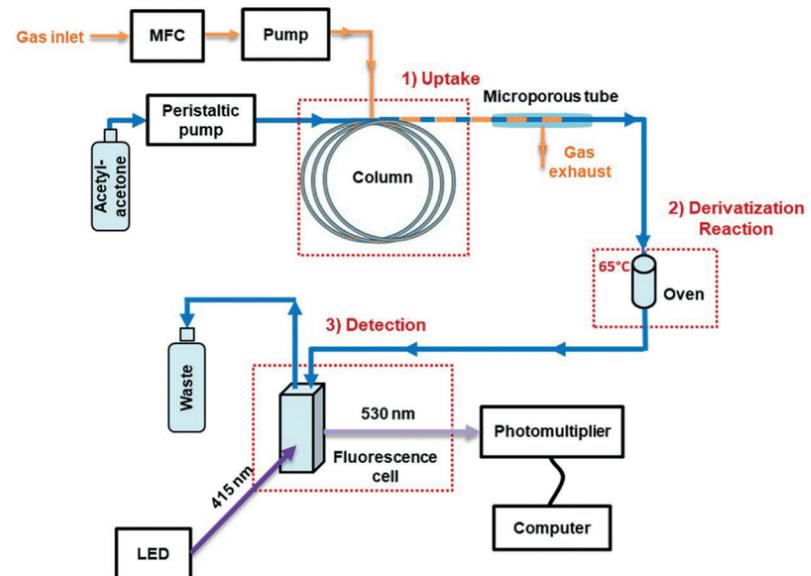


Figure 2: Scheme of the microF showing the sampling, the uptake, the reaction, and the detection steps (adapted from [3]).

1.3. Measurements of formaldehyde in a French public school

An indoor study was carried out in two elementary schools in the city of La Rochelle (France) both constructed between 1965 and 1974. The classroom selected in the first school was rectangular, with a volume of 187 m^3 and located on the first floor. It was occupied by 25 students of 9-11 years old. Ventilation was done with manual opening of the windows only. A CO₂ detector (LUM'Air) was used to monitor CO₂ in the room as a confinement indicator. The objective of the campaign was to quantify formaldehyde in schoolroom, identify its sources and assess the effect of different ventilation scenarios, i.e., usual school aeration procedure, aeration according to the CO₂ level and aeration instructions given by the French Indoor Air Quality Observatory (OQAI).

2. Results and discussion

2.1. The microF: a micro-analyser not affected by humidity.

Formaldehyde is highly soluble, so that many instruments dedicated to formaldehyde can be potentially affected by the presence of humidity. Various formaldehyde concentrations in the range 50–152 $\mu\text{g m}^{-3}$ was generated either in dry conditions or at a relative humidity of 8% (green triangle shapes) 50% (blue circle shapes). MicroF response (i.e., fluorescence intensity) was plotted as function of formaldehyde concentration determined by the DNPH reference method (Figure 3).

Whatever the humidity, the calibration curves in both conditions were identical, showing that water in the air does not have an impact on the measurements of HCHO by microF. It has also been

^aNIOSH: National Institute for Occupational Safety and Health (American federal agency)

^bANSES: French Agency for Food, Environmental and Occupational Health & Safety (French government agency)

^cICPEES: Institute of Chemistry and Processes for Energy, Environment and Health

^dCNRS: French National Centre for Scientific Research

shown in a previous study that the other aldehydes react 1000–10,000 times more slowly with Fluoral than formaldehyde, which means that they cannot interfere [7]. MicroF is thus an interference-free analyser, specific to formaldehyde and able to measure the range of concentration from 1 to 1000 $\mu\text{g m}^{-3}$, covering formaldehyde levels in domestic and professional environments.

2.2. The microF: a tool for continuous real-time formaldehyde monitoring

An example of airborne formaldehyde monitoring performed in a French primary school over 5 weeks is shown in Figure 4.

During the first week, the room was empty from furniture. The analyser measured concentrations in the range of 7.8–40.9 $\mu\text{g m}^{-3}$ with an average of $29.5 \pm 5.0 \mu\text{g m}^{-3}$. It showed that building materials emit a significant amount of formaldehyde. Subsequently, during the second week, formaldehyde concentration was monitored in the furnished classroom. The concentration levels were in the range of 18.8–56.4 $\mu\text{g m}^{-3}$, with an average concentration from 29.5 ± 5.0 to $33.8 \pm 5.2 \mu\text{g m}^{-3}$. During the 3rd, 4th and 5th week, concentrations measured were in average $31.0 \pm 6.9 \mu\text{g m}^{-3}$ (range 8.9 to 48.1 $\mu\text{g m}^{-3}$), $27.4 \pm 6.3 \mu\text{g m}^{-3}$ (3.4 to 40.1 $\mu\text{g m}^{-3}$), and $25.6 \pm 7.7 \mu\text{g m}^{-3}$ (6.4 to 41.3 $\mu\text{g m}^{-3}$), respectively. It corresponds to users following either: the usual ventilation protocol of the school, ventilation according to CO_2 levels (windows opening when CO_2 concentration reach 1700 ppm), and ventilation according to Observatoire de la qualité de l'air intérieur (Observatory of indoor air quality) instructions (windows opened for approximately 30 min before and after class, every 2 h of class). MicroF was able to monitor formaldehyde concentrations in indoor air for several weeks and successfully reported concentration changes within 10 minutes, which cannot be highlighted with the off-line DNPH method.

3. Conclusion

In this article, we present a portable cost-effective solution for the measurement of formaldehyde concentration in the air. The analyser is free from potential interferences: whether other aldehydes as it has been demonstrated before, or humidity as it has been shown here. It shows a high sensitivity to the ambient formaldehyde level, with a detection limit as low as 1 $\mu\text{g m}^{-3}$, enabling precise measurements of concentration in the indoor air (in private housing or public places). Furthermore, this sensitivity extends its utility for outdoor air analysis. It notices rapid changes of concentration within a 10-minute timeframe.

The on-line microF analyser provides precise time concentration change, as opposed to the reference method which gives averaged values (usually over 1 hour or more) after off-line analysis with sedentary laboratory equipment after manual elution of DNPH tube. The microF can autonomously monitor differences between night and day, events of window opening or specific activities involving formaldehyde emission in the air. People's exposure can then be assessed accurately and potentially minimised by taking appropriate measures.

Since it is portable, it can be moved during an analysis to investigate either one room or different rooms in a same building in order to spatially map concentration levels and potentially identify the various formaldehyde sources. Additionally, thanks to its microfluidic configuration, it has an extremely low reagent consumption, so that 4.1 days of analysis can be carried out with only 100 mL of reagent.

Regarding the different formaldehyde uses, applications of the analyser can include advanced diagnostics for indoor environments and monitoring of employee's exposure in industries for food-processing, construction materials, cosmetics and even hospital in thanatopraxy and anatomic pathology services, etc.

4. Bibliography

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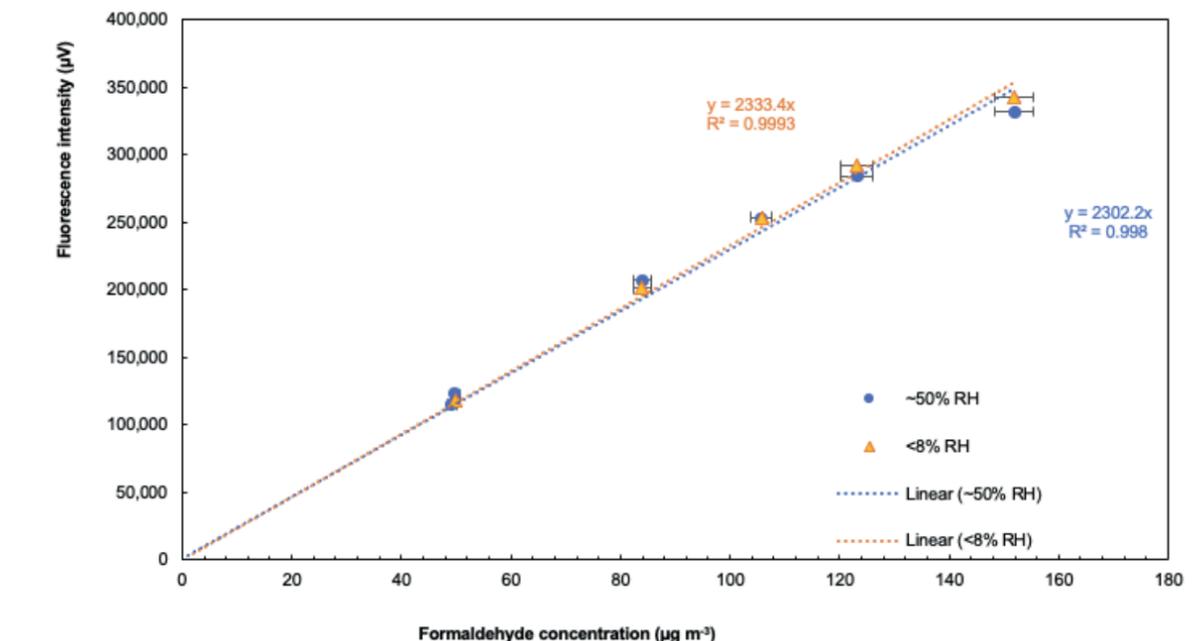


Figure 3: Calibration curves obtained with the microF in laboratory-controlled setting in dry ($\text{RH}<8\%$) and humid conditions ($\text{RH}=50\%$)

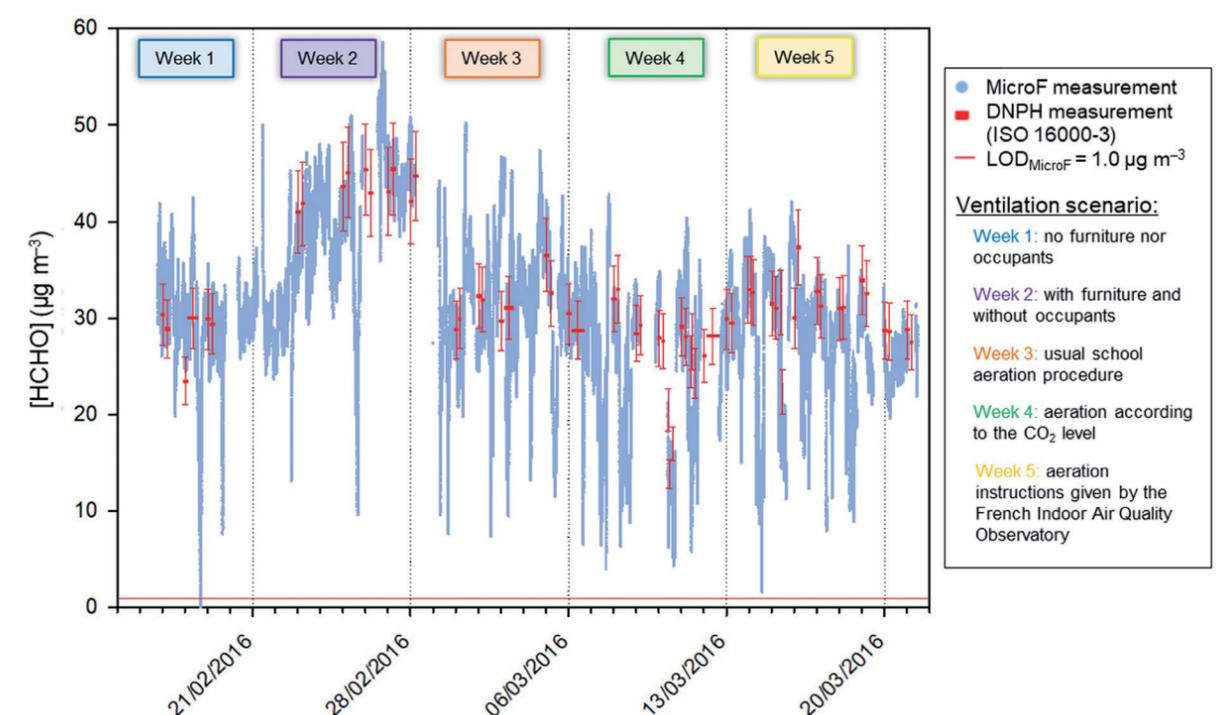


Figure 4: Formaldehyde concentration evolution during five consecutive weeks in a French primary school. The data are obtained with either an on-line formaldehyde microanalyser operating with a time resolution of 2 seconds (raw data, blue) or the DNPH reference (adapted from [8]).

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