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# Development and comparison of three analytical systems for detection and quantification of formaldehyde and other aldehydes for process, indoor and ambient air emissions

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## INTRODUCTION

Among indoor air pollutants, **aldehydes** are of particular interest due to their impact on human health. **Formaldehyde** is often the most abundant aldehyde in the air and also the most studied due to its potential role in allergic diseases and its carcinogenic properties. French regulations recommend a limit of **10 µg/m<sup>3</sup>** for **chronic exposure** to formaldehyde by 2023<sup>1</sup>. US EPA method for quantification of formaldehyde requires an 8h sampling on **DNPH cartridges**. However, given the importance of providing results at higher frequency, there is a need of faster and reliable methods for the quantification of formaldehyde at low ppb levels. In this work, we compare 3 different systems: an Automatic Gas chromatograph equipped with thermodesorption unit and flame ionization detector (auto-TD-GC-FID), a transportable microdevice based on the derivatization of formaldehyde for continuous fluorimetric detection and a transportable high-performance liquid chromatography (HPLC) system using 2,4-dinitrophenylhydrazine (DNPH) sampling tubes.

## Auto-TD-GC-FID

The Auto-TD-GC-FID (Fig 1) is a system allowing continuous monitoring of formaldehyde and some other low molecular weight compounds in ambient air. This system is designed to avoid coelution and carry over. Figure 2 shows the different steps for the measurement of formaldehyde:

- i. Sampling of the analytes on a specific trap.
- ii. Separation of heavy compounds in the pre-column.
- iii. CO<sub>2</sub> by-passes the methanizer.
- iv. Methanization of formaldehyde and FID detection.

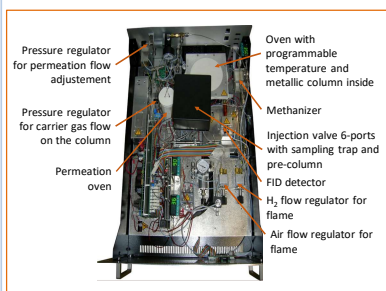


Figure 1: Description of the Auto-TD-GC-FID for the formaldehyde detection and measurement.

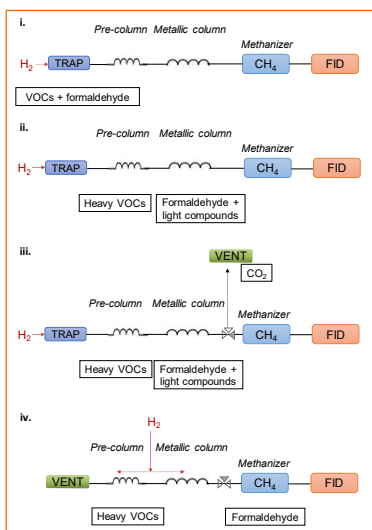


Figure 2: Operating principle of the Auto-TD-GC-FID for the detection and measurement of formaldehyde.

## Field Measurements:

One of our analyzer is located in an university campus in Beijing, China for the monitoring of outdoor ambient air. Figure 3 presents the trend of the formaldehyde concentration over 5 days. Figure 4 (A) and (B) show the chromatograms obtained respectively for an ambient air analysis and for an internal calibration.

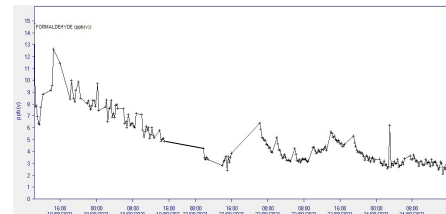


Figure 3: Formaldehyde monitoring in outdoor air from 09/18/2021 to 09/24/2021.

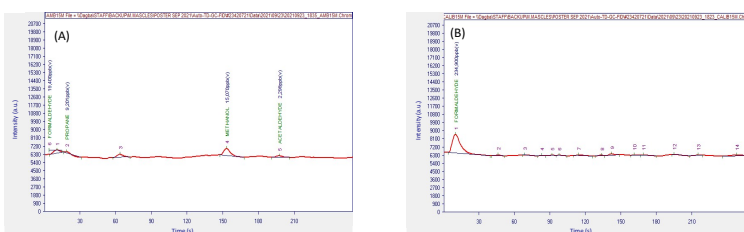


Figure 4: (A) Chromatogram obtained for an ambient air analysis. – (B) Internal calibration with a formaldehyde permeation tube.

This device allows the **continuous monitoring** of formaldehyde in **near real-time** thanks to a short cycle time of 15 minutes. The method detection limit (MDL) is around **1 ppb** which makes it very suitable for indoor and outdoor measurements. Performances and calibration of the analyzer are easily checked thanks to **internal calibration** with a certified formaldehyde permeation tube.

## Microfluidic Device

This microanalyzer is a portable and compact instrument weighing less than 4 kg (Fig 5). This device operates according to 3 steps (Fig 6)<sup>2</sup>:

- i. Uptake of gaseous formaldehyde into an aqueous acetylacetone solution.
- ii. Chemical reaction between formaldehyde and acetylacetone (Hantzsch mechanism).
- iii. Fluorescence detection of the reaction product (DDL).

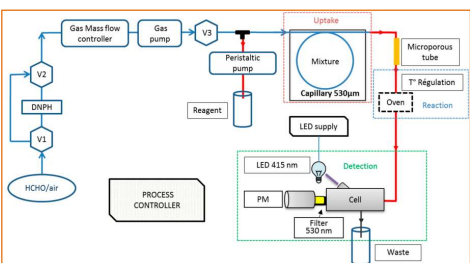


Figure 6: Operating principle of the microanalyzer<sup>3</sup>.

## Field Measurements during the MERMAID project<sup>3,4</sup>:

- Field campaign in a classroom located in a low energy school.
  - Formaldehyde (and other aldehydes) monitoring for 2 weeks, according to the ventilation periods.
- Figure 7 shows the variations of gaseous formaldehyde during a typical day. Results are compared to those obtained with the ISO 16000-3 reference method (i.e. active sampling on DNPH cartridges).

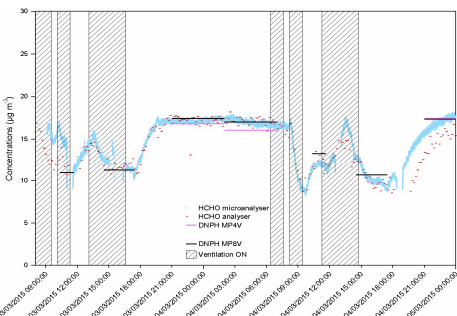


Figure 7: Gaseous formaldehyde concentration as function of time, demonstrating lower concentrations during ventilation periods. Comparison of 3 analytical methods.



Figure 5: Formaldehyde microanalyzer.

This microfluidic analytical method is **sensitive, accurate and precise** and allows a **near real-time** measurement of formaldehyde. Its MDL is around **1 ppb** which is well adapted to the monitoring of formaldehyde in indoor and outdoor air.

## UHPLC DNPH method

This work is based on the reference method for the measurement of aldehydes, i.e., DNPH-tube sampling, coupled to an offline HPLC/UV analysis. The goal is to adapt this reference method on a transportable, on-line analyzer. Two types of methods are being studied and developed:

- High pressure method: formaldehyde and other aldehydes are separated in isocratic mode. Figure 8 shows the chromatogram obtained for the separation of the aldehydes-DNPH derivates at high pressure:

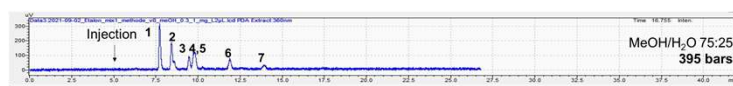


Figure 8: Separation of various aldehydes at high pressure.

- Simplified, low pressure method: the separation of aldehydes is studied at low pressure, in isocratic mode. Figure 9 presents the chromatogram obtained at low pressure (< 50 bars):



Figure 9: Separation of various aldehydes at low pressure.

These two methods (high and low pressure) are directly adaptable on our transportable HPLC system (Fig 10 (A) and (B)):

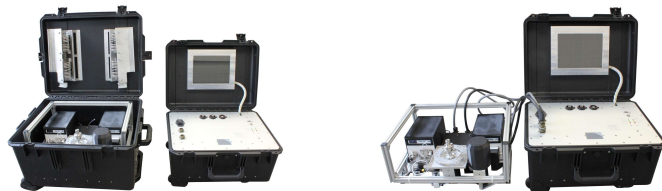


Figure 10: Transportable HPLC system: (A) Analytical system inside its transport case – (B) Analytical system outside its transport case.

The reference DNPH-based method can thus be adapted onto **transportable systems**. As shown in the chromatograms, these systems allows the measurement of formaldehyde as well as other aldehydes and can be used at high and low pressure, depending on the need.

## CONCLUSION AND PERSPECTIVES

Three different systems have been studied and compared for the analysis of formaldehyde. First, the Auto-TD-GC-FID allows a **continuous, on-line and near real-time** monitoring of formaldehyde thanks to a short cycle time of **15 minutes per analysis**. The MDL around **1 ppb** makes it suitable for the measurement of formaldehyde in outdoor and indoor air. This system is equipped with an **internal calibration** which enables to check the stability of the system and make adjustments if necessary. This method only needs power supply and does not require any solvent for its operation which is also a huge advantage compared to the reference method. The microfluidic device can also be used for a **fast, sensitive, accurate and precise** measurement of formaldehyde in outdoor or indoor air. This system has also the advantage of being **portable** (compact and light). In parallel of these two systems, developments on **transportable HPLC** based on the reference method (i.e. DNPH-tube sampling coupled to an offline HPLC/UV analysis) are being made. Two systems are under elaboration for the analysis of various aldehydes: high and low pressure. Finally, the three methods presented here all have their own advantages. Because of their complementarities, the proposed solutions can cover a very broad spectrum of applications and customer needs.

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