Multi-tool formaldehyde measurements in simulated and real atmosphere for indoor air monitoring

Laura Chiappini, R. Dagnelie, M. Sassine, Faustina Fuvel, Sébastien Fable, T.H. Tran-Thi, C. George

Multi-tool formaldehyde measurement in simulated and real atmospheres for indoor air survey and concentration change monitoring.

Laura CHIAPPINI[1*], Romain DAGNELIE[2], Maria SASSINE[3], Faustina FUVEL[1], Sébastien FABLE[1], Thu-Hoa TRAN-THI[2], Christian GEORGE[3]

[1] INERIS (Institut National de l'Environnement Industriel et des Risques) Parc technologique Alata BP2 F-60550 Verneuil-en-Halatte

[2] CEA Saclay 91191 Gif-sur-Yvette

[3] IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, UMR5256, 2 avenue Albert Einstein, 69626 Villeurbanne cedex

*Corresponding author: laura.chiappini@ineris.fr,
INERIS (Institut National de l'Environnement Industriel et des Risques) Parc technologique Alata BP2 F-60550 Verneuil-en-Hal
Tel : 00 33 44 55 65 89
Fax : 00 33 44 55 63 02

Abstract

Formaldehyde is of particular health concern since it is carcinogenic for human and ubiquitous in indoor air where people spend most of their time. Therefore, it is important to have suitable methods and techniques to measure its content in indoor air.

In the present work, four different techniques have been tested in the INERIS exposure chamber and in indoor environments in comparison to a standard active method: passive sampling method based on the reaction of 2,4-dinitrophenylhydrazine (DNPH) with formaldehyde, two on-line continuous monitoring systems based on fluorescence and UV measurements and a portable commercialised analyser based on electrochemical titration. Two formaldehyde concentrations, about 10 and 25 µg m^{-3} were generated in an exposure chamber under controlled conditions of temperature, relative humidity and wind speed to simulate real conditions and assess potential influence on passive sampling and continuous systems response. Influence of sampling periods on passive sampling has also been evaluated. The real atmosphere experiments have been performed in four different indoor environments: an office, a furniture shop, a shopping mall and residential dwellings in which several potential formaldehyde sources linked to household activities have been tested.

The analytical and sampling problems associated with each measurement method have been identified and discussed. An overall agreement between each technique has been observed and continuous analyzers allowed for formaldehyde concentrations change monitoring and secondary formation of that pollutant observation.

Introduction

Formaldehyde is one of the major indoor air pollutants due to its human health effects, it has been classified in group 1 (human carcinogen) by the International Agency for Research on Cancer (IARC, 2004), and its various emission sources. These sources can be either continuous like resins used for wood manufacture products (Brown, 1999; Loh et al., 2006), or intermittent such as cigarette smoke and combustion processes. Formaldehyde can also be formed as a secondary product from Volatile Organic Compounds (VOCs) oxidation such as terpenes (Bonn et al., 2002; Wolkoff et al., 2008) which are widely used in domestic cleaning products and air fresheners (Nazaroff and Weschler, 2004). Usually much higher than outdoor concentrations, indoor formaldehyde levels can consequently reach rather high values like 125 µg m^{-3} in residential environments (Zhang et al., 1994) and be of health concern. In French dwellings, average formaldehyde levels vary from 3 µg m^{-3} to 60 µg m^{-3} (Observatory on Indoor Air Quality (OQAI), 2006).

Since people spend most of the time in indoor environments, it is essential to be provided with reliable and accurate analytical techniques to assess their exposure to formaldehyde. Therefore many techniques have been developed for formaldehyde measurements and among them indirect methods, based on formaldehyde derivatisation, for concentration monitoring and population exposure survey and on-line continuous methods for source emissions and concentration variation monitoring.

As for indirect method, there are two international standards methods for formaldehyde measurement in indoor environments, respectively for active sampling (ISO 16000-3:2001, 2001) and passive sampling (ISO 16000-4:2001, 2004). Both are based on the reaction of the carbonyl function with 2.4-DinitroPhenylHydrazine (DNPH) to form an UV emitting chromophore, hydrazone. They are widely used for formaldehyde measurement (Andreini et al., 2000; Bates et al., 2000; Gillett et al., 2000; Hanoune et al., 2006; Huynh and Vu-Duc, 2002; Marchand et al., 2006). Another standard procedure (Nash, 1953), the aceyl acetone method based on the Hantzsch reaction is also widely applied. It has been compared to DNPH active sampling by Salthammer and Mentese, 2008 who have shown a good agreement between both techniques for formaldehyde measurement.

Many other derivatisation agents have been tested on other sampling medium such as passive sampling based on CENT (O-(4-cyano-2-ethoxybenzyl)hydroxylamine) (Onishi et al., 2007), Fluoral-P derivatisation which is formaldehyde specific and UV detection (Pinheiro et al., 2004), PFBHA (2.3.4.5.6- PentaFluoroBenzylHydroxylAmine) derivatisation followed by Solid Phase Micro Extraction (SPME) (Koziel et al., 2001) or thermodesorption and gas chromatography detection (Ho and Yu, 2002).

Other issues linked to formaldehyde monitoring are the identification of its sources and the evaluation of its secondary contribution to total indoor air concentration. Continuous on-line measurements appear to be a good way to characterize sources and assess reactive chemistry phenomenon. The in-situ spectrometric methods such as Fourier Transform Infrared Spectroscopy, FTIR (Hak et al., 2005), Differential Optical Absorption Spectroscopy, DOAS Cardenas et al., 2000 or Tunable Diode Laser Absorption Spectroscopy, TDLAS (Sauer et al., 2001) are very sensitive and specific but expensive and cumbersome and not adapted to indoor measurement. Since few commercialized techniques are available for on-line formaldehyde measurement (The AEROLASER®, Bell et al., 2000; Wisthaler et al., 2008, and the INTERSCAN®) many techniques are being developed in many research laboratory such as a portable system based on photodetection (Toda et al., 2005) or an analyzer based on fluorimetry detection (Eom et al., 2008).

Among all these techniques, the ability of four have been tested in the INERIS exposure chamber and in various indoor environments in comparison with the standard active method sampling on Sep-Pack cartridges: two on-line continuous monitoring systems based on fluorescence (Paolacci et al., 2007) and UV measurements, a portable commercialized analyzer based on electrochemical titration (INTERSCAN®) and passive sampling methods on Radiello® cartridge based on the reaction of 2,4-dinitrophenylhydrazine (DNPH) with formaldehyde. Even if this latest has been widely used (Andreini et al., 2000; Bates et al.,

2000; Clarisse et al., 2003) formaldehyde uptake on passive samplers depends on many environmental parameters (temperature, relative humidity, wind speed…), sampling time or formaldehyde concentration which cannot be controlled as well as flow rate for active sampling and whose influence on formaldehyde uptake rate has to be addressed.

Therefore this paper on the one hand points out some parameters which have to be taken into account when measuring formaldehyde in indoor environment with passive samplers and on the other hand emphases the need to be provided with continuous measurement method specially to discriminate formaldehyde primary and secondary emissions, identify sources and consequently better reduce them.

Experimental

Description of formaldehyde concentration measurement instruments

Table 1 overviews the instruments used for this study and tested in simulated and real atmosphere conditions.

Both off-line methods, active and passive sampling, were based on Dinitrophenylhydrazine (DNPH) reaction, solvent extraction and HPLC-UV analysis which were carried out using a ternary gradient (acetonitrile/water/THF - water/acetonitrile – acetonitrile) HPLC-system from Dionex Corporation (Voisins Le Bretonneux, France) equipped with a multiwavelengths UV/VIS detector operating at 365 nm for formaldehyde detection. The analytical column was an ALTIMA (C18, 150*3mm, 3 µm) purchased from Altech (Toronto, Ontario) and the separation was carried out with a solvent flow rate of 0.6 ml min^{-1}.

Active sampling tubes were Sep-Pack® cartridge purchased from Waters (Guyancourt France). The air flow through the cartridges was set to 1 L min^{-1}, controlled with a flow controller Gillibrator® before and after each sampling. The total sampled volume is also controlled with a gasmeter. A KI ozone filter was used to prevent negative artifacts linked to hydrazone ozonolisis (Bates et al., 2000). Sampling lasted a few hours so that they could cover the whole passive tube exposure time period.

Passive sampling tubes were Radiello® chemiadsorbing cartridge code 165 (introduced in the blue diffusive body code 120-1) purchased from The Fondazione Salvatore Maugeri (FSM, Padova, Italy). Two sampling times were tested: 8 and 48 hours. The sampling flow rate was the value given by the FSM: 99 mL min^{-1}. This sampling rate varies as a function of the temperature as expressed by the following equation (as determined by FSM): $Q_k=(K/298)^{0.35}$ where Q_K is the sampling rate at the temperature K and Q_{298} is the reference value at 298 K. Therefore, temperature is monitored throughout the whole exposure time.

Detection limits for both active and passive methods have been determined based on the standard procedure NF ISO 11843-2, 2000 (table 1). They are given in µg m^{-3} for each performed sampling time.

The continuous analyzer developed by the CEA-Saclay laboratory is based on the use of nanoporous transparent matrices made via sol-gel processes and doped with a colorimetric agent, Fluoral P and the fluorescence reaction product fast detection. The use of an exposure in a pulsed mode allows a 7 hours monitoring with a 10 minutes frequency. The calibration range is 1 to 200 ppb of HCHO within 0 to 60% of relative humidity. The interference of water implicates the use of a dessicant above 60% of humidity. A detailed presentation of the technique is given in Paolacci et al., 2007. Detection limit given in Table 1 corresponds to the lowest concentration which can be measured by the instrument and is part of the calibration curve.

The other continuous analyzer was completely fulfilled in IRCELYON laboratory. It is based on formaldehyde trapping in a 3-Methylbenzthiazolinone-2-Hydrazone (MBTH) solution in acid media by means of a turning coil sampler tube through which air and aqueous solution flow concurrently *(*François et al., 2005; Lee and Wang, 2004; Sauer et al., 2003*)*, derivatisation with a blue cation UV detected by light reflection through a capillary. Liquid core waveguide LCW (810µm i.d) Teflon® AF- 2400 tube (Biogeneral, San Diego, CA) was used as an innovative optical cell combining long optical path and minor volume for high sensitivity *(*Genfa and Dasgupta, 1989*)*. The detection limit given in Table 1 has been determined as four times the background noise.

The portable commercialized INETRSCAN® 4000 series analyzer, based on electrochemical titration with a few tens of second time response, was purchased from Interscan Corporation

(Chatsworth, Canada). The detection limit given in Table 1 is the value given by the company.

Simulated atmosphere (exposure chamber) experiments.

A 150 L Pyrex exposure chamber was used to test, under controlled conditions of temperature, relative humidity and wind speed, the formaldehyde monitoring technique presented here above. A full description of the exposure chamber is given in Gonzalez-Flesca and Frezier, 2005. The chamber operating conditions were 20°C, 50 % relative humidity, 1 m s^{-1} wind speed. This wind speed velocity has been chosen because it ensures the atmosphere homogeneity in the chamber. Moreover, even if wind speed is supposed to be very low in indoor environments, it can reach values such as 0.3 m s^{-1} in unventilated workplaces (Baldwin and Maynard, 1998) and can be significant in air exhaust system equipped places.

Formaldehyde was introduced in the chamber with a 10 ppm gaseous standard. Relative humidity and pollutant concentration are controlled by diluting with zero air. Each gas (zero air, formaldehyde, humid air) flow rate introduced in the chamber is controlled by a mass flow controller. The formaldehyde concentrations were set to about 10 µg m^{-3} to simulate low formaldehyde levels usually measured in indoor air, and about 25 µg m^{-3} to simulate medium indoor concentration levels. It should be pointed out that accurate formaldehyde generation in the chamber, based only on the controlled dilution system is not possible because of dilution in water or chamber walls losses. That is why the real generated concentration is often bellow the theoretical concentration and is controlled with active samplings on DNPH cartridges. These concentration conditions will be referred to as "low" and "high experimental conditions" respectively. Gaseous standard mixture was purchased from Air Liquide (Mitry-Mory, France). For each experiment, 6 passive Radiello® tubes and one used as a blank were introduced in the chamber meanwhile the other techniques were connected on the chamber. Two Radiello® exposure times have been tested, 8 and 48 hours, to evaluate the influence of sampling periods on passive sampling. For each condition of exposure time and concentration, two experiments have been performed. About 8 to 10 hours of active samplings on Sep-Pack® cartridges were carried out to cover the whole passive tubes exposure period and the measurement of continuous monitoring systems.

Blank experiments (sampling on the exposure chamber with each technique except passive tubes which have to be introduced in it) have been carried out without any formaldehyde injected into the chamber.

The exposure chamber experiments conditions as well as instruments deployed are given in table 2.

Real atmosphere (indoor environments) experiments.

The same methodology has been employed in real indoor atmospheres: an office, a furniture shop, a shopping mall and dwellings. In the kitchen and living room of one of the dwellings, several potential formaldehyde sources have been tested: use of cleaning products and ironing respectively. Table 3 describes the different indoor environments and the technique deployed.

Results and discussion

Exposure chamber experiments: standard methods results

A comparison between active and passive sampling for formaldehyde measurements are presented on table 4 in which passive and active measurements, the ratio measure on blank for Radiello sampling tube and the difference between active and passive are given.

One of the main observations is the high level of blank corresponding to low "Measure/Blank" ratio, which can be linked to a high difference between active and passive measurement. Indeed, for low exposure time (8 h) and low concentration conditions (~10 µg m^{-3}) even for 48 H exposure time, this ratio is about 2 to 5, below an insurance quality ratio which can be chosen equal to at least 10 to ensure a representative and quantitative measurement. However, for high concentration conditions and 48 h exposure time, this ratio tends to become satisfactory so is the difference between concentrations measured by each method (- 7 % and – 16 %).

These results suggest that the Radiello sampling tubes should not be used for low exposure time experiments (8 h) whatever the concentration level is, and for 48 h exposure time when concentration levels are low. They also suggest that on the one hand, some work should be done to improve Radiello passive tubes levels of blank, and that on the other hand cautions should be taken during storage and transport to minimize sources of contaminations.

Exposure chamber experiments: continuous methods results

In figure 1, formaldehyde concentration evolution in the exposure chamber, as measured by each method at their original time resolution, the UV and fluorescence continuous measurement techniques, passive and active sampling techniques, is shown. The mean concentration on the whole experiment period measured by each method is also given. This is an example of one day formaldehyde monitoring on the exposure chamber under "high experimental conditions". On this particular day, the passive sampling tubes were introduced in the exposure chamber, requiring its opening and consequently causing a formaldehyde concentration decrease.

In figure 1, the ability of both continuous analyzers to measure this concentration decrease can be observed. However, the UV analyzer response to that decrease is not immediate. The time delay of about an hour can be explained by the instrument memory effect and its analysis time resolution (20 min).

Besides, because of the different instruments measurement intervals, each of the continuous data set was integrated and average formaldehyde concentrations were calculated on a common time scale to enable their comparison with standard methods. Mean concentrations are given in figure 1: before the chamber opening and therefore the passive tubes introduction in the chamber, the mean concentration measured by the two continuous methods (18,4 and 15,8 µg m^{-3} for UV and fluorescence respectively) and the active method (16,8 µg m^{-3}) was 17 µg m^{-3} with a relative standard deviation of 8 %. After the chamber opening, the mean concentration measured by the two continuous methods (12,2 and 12,2 µg m^{-3} for UV and fluorescence respectively) and the standard methods (14,3 and 17,8 µg m^{-3} for active and passive respectively) was 14 µg m^{-3} with a relative standard deviation of 18 %. Therefore, a good agreement can be observed with satisfactory standard deviation between each technique equal before and after the chamber opening.

Indoor environment experiments: standard methods results

A comparison between active and passive sampling for formaldehyde measurement is presented on Table 5.
As for exposure chamber experiments, passive tubes high levels of blank can affect formaldehyde measurement resulting in an important difference between active and passive methods (from - 15 to 34 %). A good agreement is observed between both techniques when the measure/blank ratio becomes high enough. This difference is very low (from – 4 to – 1 %) in comparison with the values measured during exposure chamber experiment (from -37 to 17%) as shown in table 4 and the campaign in the shopping mall (from – 34 to -15 %). The main difference between these two sets of experiments is the wind speed. Indeed, in the exposure chamber, a wind speed of 1 m s^{-1} was simulated and in the shops, an air exhaust system was operating whereas there was no mechanical ventilation in the private houses.

This wind speed could explain the passive sampler over-estimation of formaldehyde concentrations. It has indeed been shown that Eddy diffusion caused by air turbulence at the entrance of the sampling tube can lead to a shortening of the diffusion path length and therefore a positive artifact (Sekine et al., 2008).

Indoor environment experiments: continuous methods results and secondary formaldehyde formation monitoring

The three continuous analyzers have been tested in the indoor environments and have shown a good agreement with the active sampling method.
Standards techniques, active and passive formaldehyde measurement and both continuous in development analyzers, IRCE-UV and CEA-fluo, have been tested in an office as shown in figure 2. It presents one day formaldehyde monitoring in an office with formaldehyde concentration decrease due to door opening during the day. The office door was closed the day before the beginning of the experiment to ensure the stability of the atmosphere. It was eventually opened during the experiment day since the temperature in the room was rising because of all the functioning apparatus.
Before the office door opening at about 2 PM, a good agreement between each technique can be observed with a relative standard deviation equal to 6 %. Moreover, the formaldehyde decrease linked to door opening is properly monitored by each continuous analyzer. However, after the door opening, a formaldehyde concentrations underestimation of about 25 % in comparison with active sampling can be observed for the CEA Fluo analyzer. Indeed, in the morning, before 2 PM, CEA analyzer measurements were carried out in an atmosphere with ~ 60 % of relative humidity. Meanwhile, the nanoporous thin film, which is hydrophilic, was filled with water. After that, the film cannot dry properly by exposure to the "after 2 PM atmosphere" which still contain 50 % relative humidity

Another series of indoor experiments have been led with the portable commercialized analyzer INTERSCAN® to check for its capacity to measure formaldehyde.
These experiments took place in two different dwellings, in the office and living room of the first one, in the living room and kitchen of the second one. INTERSCAN® measurements were compared to active measurement. Even if the portable commercialized analyzer provides brief measurement of a few tens of seconds and Sep-Pack® a few hours integrated measurement, the formaldehyde concentrations in the rooms could be considered as constant since no particular activity was carried out and no door or windows have been opened. Whenever the comparison was made, results from both techniques were similar with relative standard deviation ranging from 7 to 22 %. As an example, for the house office experiment, measured concentrations where 26 and 28 $\mu g\ m^{-3}$ by Sep-Pack and INTERSCAN® respectively, while for one of the house dining room experiments, they were 38 and 35 $\mu g\ m^{-3}$.
Last experiment was also carried out with the portable commercialized analyzer INTERSCAN® to monitor the potential formaldehyde formation following domestic activities (ironing, household…). First experiment concerned ironing and was performed in the living room where the background formaldehyde concentrations were about 40 $\mu g\ m^{-3}$. When living the stirrer a few minutes on the stirring table consequently heating the table protecting foam, the INTERSCAN® could measure a formaldehyde concentration increase to about 90 $\mu g\ m^{-3}$ showing the ability of the analyzer to measure concentration variations. It also enlightens the potentiality of such material to emit formaldehyde when heated.
Eventually, an experiment took place in a kitchen where the formaldehyde concentration background was about 40 $\mu g\ m^{-3}$ as monitored by Sep-Pack® and INTERSCAN®. Then, cleaning products have been used. A table was cleaned and no formaldehyde concentration increase has been immediately observed. A few minutes later, the windowpanes have been washed with a glass cleaner and no change in formaldehyde concentration could be observed with the analyzer. 15 minutes after the cleaning products use, an increase of formaldehyde concentrations in the kitchen could be monitored by the analyzer as shown in

figure 3. This may result from chemical reaction between airborne pollutants such as terpenes (limonene) widely used in such housekeeping products (Nazaroff and Weschler, 2004), and Ozone (Bonn et al., 2002; Weschler, 2006; Wolkoff et al., 2008), enlightening formaldehyde secondary formation as already observed by Solal et al., 2008. It can be observed in figure 3 that formaldehyde reaches a very high concentration value of about 200 µg m^{-3}. Such a concentration does not seem to be really realistic and should not correspond to formaldehyde measurement only. Indeed, further studies should be carried out to evaluate the selectivity of the portable commercialized analyzer on the one hand and try to identify and quantify all the secondary products formed from limonene reaction on the other hand.

Indoor environment experiments: formaldehyde measured concentrations

As it can be seen in the summarizing table (table 6), mean formaldehyde concentrations measured in indoor environments range from 40 to 54 µg m^{-3}. These values can be compared for example to ATSDR minimum risk level value of 50 µg.m^{-3} for a zero to 15 days exposure in relation to eyes and nose irritation (ATSDR, 1999) and OEHHA chronic reference exposure level of 3 µg.m^{-3}, for more than a year exposure in relation to respiratory and eye irritations (OEHHA, 1999). In France, guide values have been set to help survey formaldehyde in indoor environments, on the basis of toxicological data and usual formaldehyde concentrations measured indoor (HCSP, 2009). As an example, in 2009, the value of 30 µg m^{-3} has been set as an urging value to set up actions to improve air quality.
All the mean formaldehyde values measured indoor during the experiments presented here are above these values, enlightening the imperious need to be provided with efficient technique to survey this pollutant concentrations, indentify sources and reduce them.

Conclusion
This work aimed at studying the ability of passive sampling tubes and different continuous analysers in comparison to active sampling, to measure formaldehyde in indoor environments.
A comparison of the results given by the standard active and passive methods and the three continuous formaldehyde monitoring systems has shown a general good agreement between each technique with standard deviations ranging between 7 and 25 %. Continuous on-line analyzers have been able to measure formaldehyde concentration changes even if their response can be altered by memory effects for the UV analyzer and relative humidity for the florescence analyzer. The negative influence of water on formaldehyde measurement could be overcome by the use of anhydrous filter which is being tested.
Particular attention should be addressed when measuring low formaldehyde concentrations with passive Radiello® diffusion tubes during low exposure time because of the high blank level. Some work should be done to improve Radiello® passive tubes levels of blank and cautions should be taken when storing and caring the sampling tubes to minimize the contamination sources.
Another parameter which could influence formaldehyde adsorption on passive sampler would be the wind speed. Further investigations should be carried out to improve knowledge on such phenomena which could be significant indoor when air exhaust systems are used or when draught are caused by windows opening for instance.
Besides, the cleaning product use clearly shows formaldehyde secondary formation probably linked to terpene ozonolysis. Such experiments should be repeated since the relative contributions of primary and secondary emissions in indoor air remain very difficult to quantify but essential to reduce formaldehyde concentrations.
Revealing formaldehyde measurement method weaknesses on the one hand and showing high concentrations indoor that can be attributed to both primary and secondary sources; this work enlightens the urgent need to be provided with efficient active and passive methods for

formaldehyde indoor concentration monitoring and population exposure survey, and on-line continuous techniques for source emissions and concentration variation monitoring.

Acknowledgement

References

Andreini B.P., Baroni R., Galimberti E. and Sesana G. (2000) Aldehydes in the atmospheric environment: evaluation of human exposure in the north-west area of Milan. Microchemical Journal 67:11-19

ATSDR (1999) Agency for Toxic Substances and Disease Registry , Toxicological Profile for Formaldehyde. U.S. Department of Health and Human Services. Public Health Service. http://www.atsdr.cdc.gov/.

Baldwin P.E.J. and Maynard A.D. (1998) A Survey of Wind Speeds in Indoor Workplaces. Ann Occup Hyg 42:303-313

Bates M.S., Gonzalez-Flesca N., Sokhi R. and Cocheo V. (2000) Atmospheric volatile organic compound monitoring. Ozone induced artefact formation. Environmental monitoring and assesment 65:89-97

Bell W. *et al.* (2000) A pilot study of formaldehyde monitoring in ambient air. NPL Report COEM S36

Bonn B., Schuster G. and Moortgat G.K. (2002) Influence of water vapour on the process of new particle formation during monoterpene ozonolysis. Journal of Physical Chemistry A. 106:2869-2881

Brown S.K. (1999) Chamber Assessment of Formaldehyde and VOC Emissions from Wood-Based Panels. Indoor Air 9:209-215

Cardenas L.M. *et al.* (2000) Intercomparison of formaldehyde measurements in clean and polluted atmospheres. Journal of Atmospheric Chemistry 37:53-80

Clarisse B. *et al.* (2003) Indoor aldehydes: measurement of contamination levels and identification of their determinants in Paris dwellings. Environmental Research 92:245-253

Eom I.Y., Li Q.Y., Li J.Z. and Dasgupta P.K. (2008) Robust hybrid flow Analyzer for formaldehyde. Environmental Science & Technology 42:1221-1226

François S., Perraud V., Pflieger M., Monod A. and Wortham H. (2005) Comparative study of glass tube and mist chamber sampling techniques for the analysis of gaseous carbonyl compounds Atmos Environ 39:6642-6653

Genfa Z. and Dasgupta P.K. (1989) Fluorometric measurement of aqueous ammonium ion in a flow injection system. Analytical Chemistry 61:408-412

Gillett R.W., Kreibich H. and Ayers G.P. (2000) Measurement of Indoor Formaldehyde Concentrations with a Passive Sampler. Environmental Science & Technology 34:2051-2056

Gonzalez-Flesca N. and Frezier A. (2005) A new laboratory test chamber for the determination of diffusive sampler uptake rates. Atmospheric Environment 39:4049-4056

Hak C. *et al.* (2005) Intercomparison of four different in-situ techniques for ambient formaldehyde measurements in urban air. Atmospheric Chemistry and Physics 5:2881-2900

Hanoune B., Lebris T., Marchand C. and Le Calvé S. (2006) Formaldehyde measurments in libraries: comparison between infrared diode laser spectroscopy and a DNPH-derivatization method. Atmospheric Environment 40:5768-5775

HCSP (2009) High Council for Public Health, Guide values for indoor air quality management: formaldhyde. http://www.hcsp.fr/

Ho S.S.H. and Yu J.Z. (2002) Feasibility of collection and analysis of airborne carbonyls by on-sorbent derivatization and thermal desorption. Analytical Chemistry 74:1232-1240

Huynh C.-K. and Vu-Duc T. (2002) Intermethod comparisons of active sampling procedures and analysis of aldehydes at environmental levels. Analytical and Bioanalytical Chemistry 372:654-657

IARC (2004) Overall evaluation of carcinogenicity to humans, formaldehyde (50-00-0). The IARC monographs series 88:

ISO 16000-3:2001 (2001) Indoor air - Part 3 : determination of formaldehyde and other carbonyl compounds - Active sampling method. Standard, ISO 16000-3:2001 (2001-09-01):

ISO 16000-4:2001 (2004) Indoor air - Part 4 : determination of formaldehyde - Diffusive sampling method. Standard, ISO 16000-4:2004 (2004-05-15):

Koziel J.A., Noah J. and Pawliszyn J. (2001) Field sampling ann ddetermination of formaldehyde in indoor air with solid-phase microextraction and on-fiber derivatisation. Environmental Science & Technology 35:1481-1486

Lee S.-C. and Wang B. (2004) Characteristics of emissions of air pollutants from burning of incense in a large environmental chamber. Atmospheric Environment 38:941-951

Loh M.M. *et al.* (2006) Measured concentrations of VOCs in several non-residential microenvironments in the United States. Environmental Science & Technology 40:6903-6911

Marchand C., Bulliot B., Le Calvé S. and Mirabel P. (2006) Aldehyde measurments in indoor environments in Strasbourg (France). Atmospheric Environment 40:1336-1345

Nash T. (1953) The colorimetric estimation of formaldehyde by means of the Hantsch reaction. Biochemical Journal 55:416-421

Nazaroff W.W. and Weschler C.J. (2004) Cleaning products and air fresheners: exposure to primary and secondary air pollutants. Atmospheric Environment 38:2841-2865

NF ISO 11843-2 (2000) Capability of detection, Part 2: Methodology in the linear calibration case. Standard, NF ISO 11843-2:2000

Observatory on Indoor Air Quality (OQAI), National survey: indoor air quality in French dwellings. (2006).

OEHHA (1999) Office of Environmental Health Hazard Assessment, Determination of Chronic Reference Exposure Level for Airborne Toxicants. Chronic Toxicity Summary.

Formaldehyde. http://www.oehha.ca.gov/

Onishi M., Sekine Y., Sugihara K., Kitasaka K. and Shimajiri H. (2007) A passive sampler for the determination of carbonyl compounds in indoor air employing O-(4-cyano-2-ethoxybenzyl)hydroxylamine as reactive adsorbant. Journal of Health Science 53:413-422

Paolacci H. *et al.* (2007) A ppb formaldehyde gas sensor for fast indoor air quality measurement. Sensors and transducers 82:1423-1430

Pinheiro H.L.C., de Andrade M.V., de Paula Pereira P.A. and de Andrade J.B. (2004) Spectrofluorimetric determination of formaldehyde in air after collection onto silica cartridges coated with Fluoral P. Microchemical Journal 78:15-20

Salthammer T. and Mentese S. (2008) Comparison of analytical techniques for the determination of aldehydes in test chambers. Chemosphere 73:1351-1356

Sauer C.G., Pisano J.T. and Fitz D.R. (2003) Tunable diode laser absorption spectrometer measurements of ambient nitrogen dioxide, nitric acid, formaldehyde, and hydrogen peroxide in Parlier, California. Atmospheric Environment 37:1583-1591

Sauer F., Beck J., Schuster G. and Moortgat G.K. (2001) Hydrogen peroxide, organic peroxides and organic acids in a forested area during FIELDVOC'94. Chemosphere - Global Change Science 3:309-326

Sekine Y., Watts S.F., Rendell A. and Butsugan M. (2008) Development of highly sensitive passive sampler for nitrogen dioxide using porous polyethylene membrane filter as turbulence limiting diffuser. Atmospheric Environment 42:4079-4088

Solal C., Rousselle C., Mandin C., Manel J. and Maupetit F., VOCs and formaldehyde emissions from cleaning products and air fresheners. *Indoor Air Confernence*, Copenhague, Denmark (2008).

Toda K., Yoshioka K.-I., Mori K. and Hirata S. (2005) Portable system for near-real time measurement of gaseous formaldehyde by means of parallel scrubber stopped-flow absorptiometry. Analytica Chimica Acta 531:41-49

Weschler C.J. (2006) Ozone's impact on public health: Contributions from indoor exposures to ozone and products of ozone-initiated chemistry. Environ Health Perspect 114:1489-1496

Wisthaler A. *et al.* (2008) Technical note: intercomparison of forùmaldehyde measurments at the atmosphere simulation chamber SAPHIR. Atmos Chem Phys 8:2189-2200

Wolkoff P. *et al.* (2008) Acute air effects of ozone-initiated d-limonene chemistry: importance of gaseous products. Toxicology letters 181:171-176

Zhang J., Lioy P.J. and He Q. (1994) Characteristics of aldehydes: concentrations, sources, and exposures for indoor and outdoor residential microenvironments. Environ. Sci. Technol. 28:146-152

Table 1 : Overview of the instruments and their characteristics deployed for the study

Method	Naming	Detection principle	Time resolution	Detection limit $\mu g\ m^{-3}$
Active sampling	Sep-Pack ® cartridge	DNPH derivatization HPLC analysis	1 - 8 h	0.02 - 0.2
Passive sampling	Radiello® Cartridge	DNPH derivatization HPLC analysis	8 – 48 h	0.07 – 0.4
Continuous analyzer	IRCE UV analyzer	UV detection	5 min	0.2
Continuous analyzer	CEA Fluo analyzer	Fluo detection	10 min	0.4
Continuous sensor	INTERSCAN®	Electrochemical detection	A few tens of seconds	5

Table 2 : Exposure chamber experiments description

Concentration condition	Number of experiment	Exposure time	Deployed techniques
Low	2	8 h	Radiello® Sep-Pack®
High	2	8 h	Radiello® Sep-Pack®
Low	1	48 h	Radiello® Sep-Pack® IRCE UV analyzer CEA Fluo analyzer
Low	1	48 h	Radiello® Sep-Pack® INTERSCAN®
High	1	48 h	Radiello® Sep-Pack® IRCE UV analyzer CEA Fluo analyzer
High	1	48 h	Radiello® Sep-Pack® INTERSCAN®

Table 3 : Indoor environment experiments description

Indoor environments	Exposure time	Deployed techniques
Shopping mall	8 h	Radiello® Sep-Pack®
Furniture shop	8 h	Radiello® Sep-Pack®
Firm office	48 h	Radiello® Sep-Pack® IRCE UV analyzer CEA Fluo analyzer
House office	48 h	Radiello® Sep-Pack® INTERSCAN®
House dining room	48 h	Radiello® Sep-Pack® INTERSCAN®
House living room	48 h	Radiello® Sep-Pack® INTERSCAN®
Kitchen Household activities	~1 h	INTERSCAN®

Table 4: Mean formaldehyde concentrations measured on the exposure chamber for different experimental condition and exposure time by active and passive sampling.

Concentration condition	Exposure time	Passive (μg m^{-3})	Measure/Blank	Active (μg m^{-3})	Difference Active-passive (%)
Low	8 h	7.6	2	5.2	-37
Low	8 h	8.7	2	5.6	-42
High	8 h	25.8	4	20.3	-24
High	8 h	24.1	3	19.9	-19
Low	48 h	6.7	5	7.9	17
Low	48 h	11.4	6	7.5	-41
High	48 h	17.8	15	16.7	-7
High	48 h	32.7	52	27.7	-17

Table 5 : Mean formaldehyde concentrations measured in each indoor environment by active and passive sampling.

Indoor environments	Exposure time	Passive (μg m^{-3})	Measure/Blank	Active (μg m^{-3})	Difference Active-passive (%)
Shopping mall	8 h	19.0	5	13.5	- 34
Shopping mall	8 h	16.6	6	11.2	- 38
Furniture shop	8 h	40.0	10	34.3	- 15
Firm office	48 h	22.2	17	27.9	23
House office	48 h	39.4	31	41.1	1
House dining room	48 h	38.6	28	37.8	- 1
House living room	48 h	57.6	42.4	55.4	- 4

Table 6 : Summarizing table giving mean formaldehyde concentrations (µg m^{-3}) and standard deviations (%) between each technique for all the experiments.

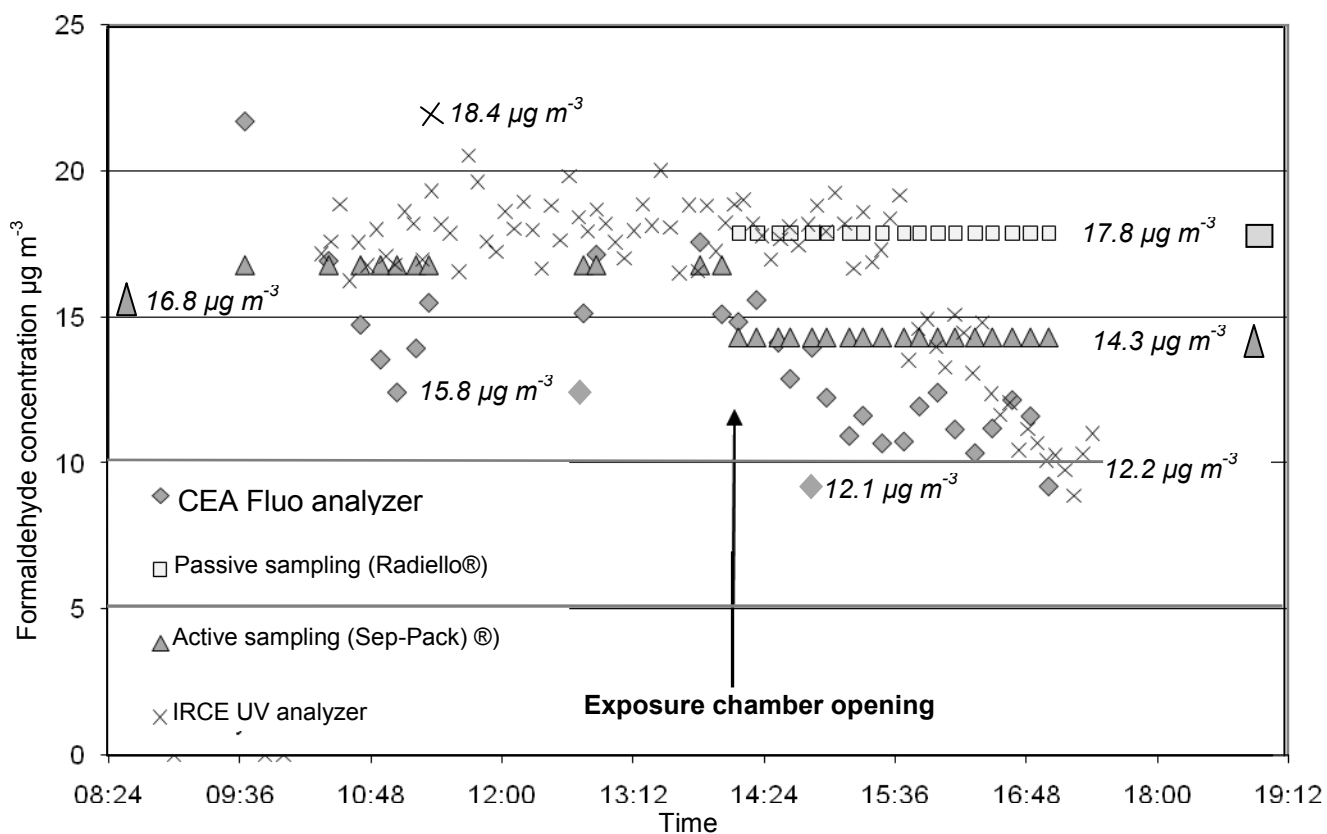| Concentration condition	Experiment time	Deployed techniques	Mean concentration µg m^{-3}	Standard deviation on between each technique %
Chamber experiments				
Low	8 h	Radiello® Sep-Pack®	6.4	27
Low	8 h	Radiello® Sep-Pack®	7	31
High	8 h	Radiello® Sep-Pack®	23	17
High	8 h	Radiello® Sep-Pack®	22	13
Low	48 h	Radiello® Sep-Pack® IRCE UV analyzer CEA Fluo analyzer	7.2	8
High before chamber opening	48 h	Radiello® Sep-Pack® IRCE UV analyzer CEA Fluo analyzer	17	7
High after chamber opening	48 h	Radiello® Sep-Pack® IRCE UV analyzer CEA Fluo analyzer	13	10
Indoor environments				
Shopping mall	8 h	Radiello® Sep-Pack®	16	27
Furniture shop	8 h	Radiello® Sep-Pack®	44	11
Firm office	48 h	Radiello® Sep-Pack® IRCE UV analyzer CEA Fluo analyzer	40	6
House office	48 h	Radiello® Sep-Pack® INTERSCAN®	40	4 (Radiello/Sep-Pack) 8 (Sep-Pack/interscan)
House dining room	48 h	Radiello® Sep-Pack® INTERSCAN®	38	1 (Radiello/Sep-Pack) 8 (Sep-Pack/interscan)
House living room	48 h	Radiello® Sep-Pack® INTERSCAN®	54	8 (Radiello/Sep-Pack) 22 (Sep-Pack/interscan)
Kitchen Household activities	~1 h	INTERSCAN®	40-200	

Figure 1 : Time series of formaldehyde concentrations during a "high experimental conditions" exposure chamber experiment. Measurements of the individual instruments are given at their original time resolution. For each method, the mean measured concentration on whole experiment period, before and after the chamber opening, is given in italic (µg m^{-3}).
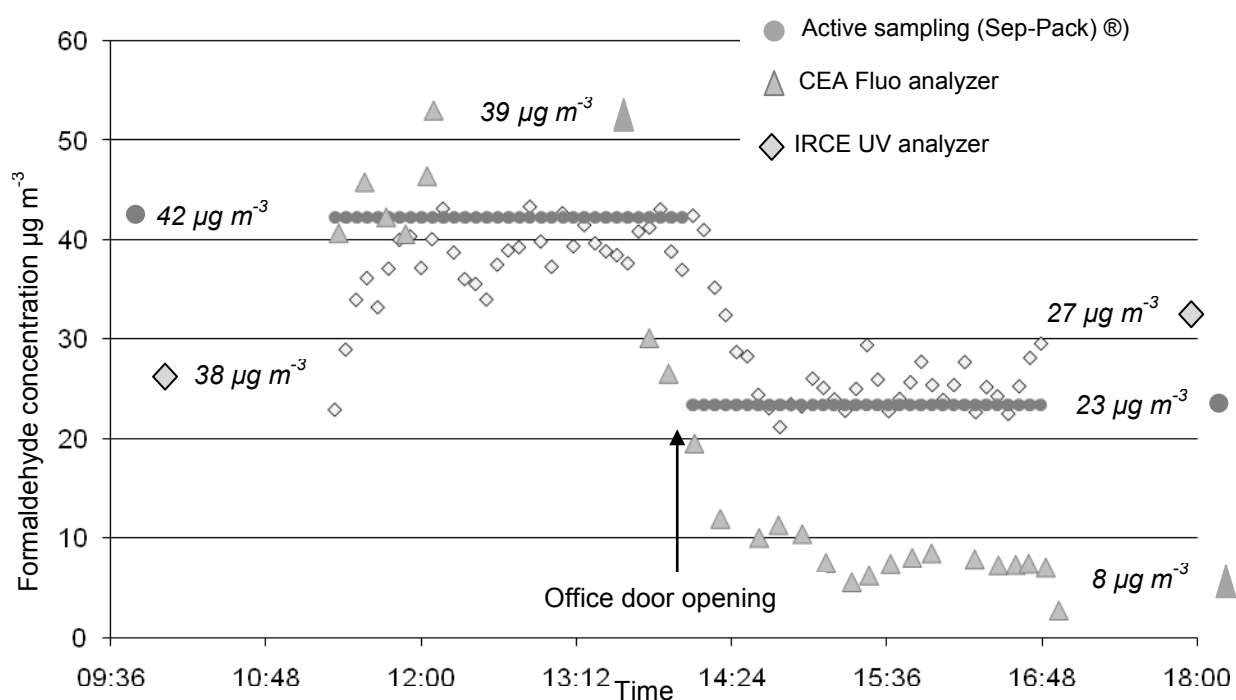
Figure 2 : **Time series of formaldehyde concentrations in an office experiment. Measurements of the individual instruments are given at their original time resolution. For each method, the mean measured concentration on whole experiment period, before and after the door opening, is given in italic (µg m^{-3}).**
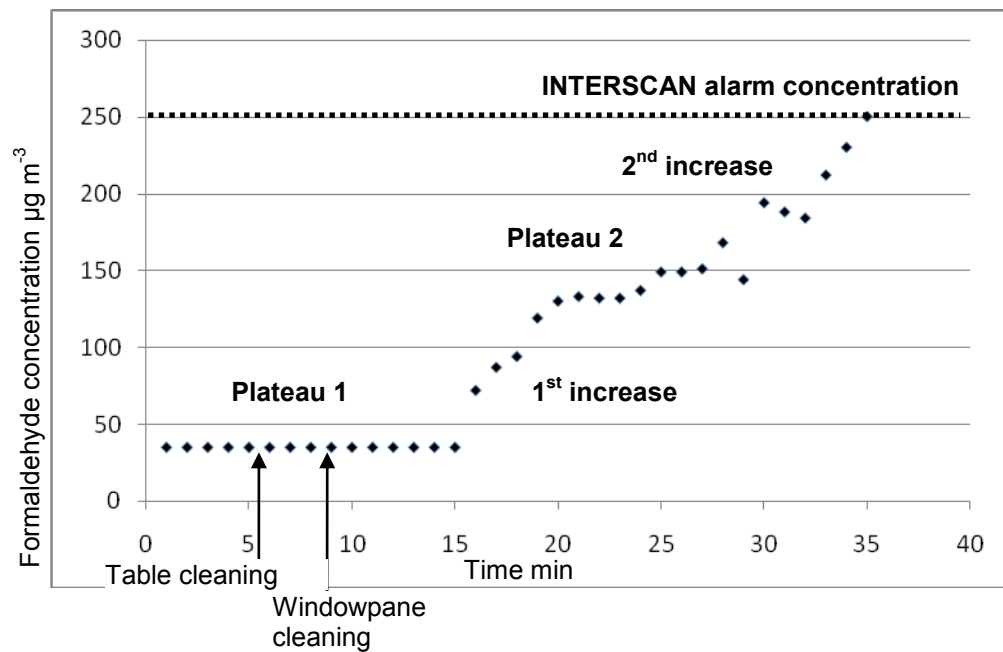
Figure 3 : Formaldehyde time series monitored by the portable commercial analyzer during the use of housekeeping products.