



HAL
open science

Performance of the Radiello®Diffusive Sampler for Formaldehyde Measurement: The Influence of Exposure Conditions and Ozone Interference

J. Vignau-Laulhere, H. Plaisance, Pierre Mocho, K. Raulin, Y. Bigay, V. Desauziers

► To cite this version:

J. Vignau-Laulhere, H. Plaisance, Pierre Mocho, K. Raulin, Y. Bigay, et al.. Performance of the Radiello®Diffusive Sampler for Formaldehyde Measurement: The Influence of Exposure Conditions and Ozone Interference. *Analytical Methods*, 2015, 7 (13), pp.5497-5503. 10.1039/c5ay00996k . hal-02129494

HAL Id: hal-02129494

<https://hal.science/hal-02129494>

Submitted on 2 Nov 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Performance of the Radiello® diffusive sampler for formaldehyde measurement: the influence of exposure conditions and ozone interference

Jane Vignau-Laulhere,^{ab} Hervé Plaisance,^b Pierre Mocho,^c Katarzyna Raulin,^a Yves Bigay^a and Valérie Desauziers^{*b}

The radial diffusive standard sampler Radiello® filled with Florisil impregnated with 2,4-dinitrophenylhydrazine (DNPH) was evaluated with the goal of survey monitoring the formaldehyde concentration in indoor air for a 4.5 day sampling time. A Radiello® sampler provides measurements with a relative standard deviation of repeatability comprised between 1.5 and 4.0%, a high sampling rate assessed to 98.7 ± 2.8 mL min⁻¹ under standard conditions (temperature: 19.9 ± 0.5 °C and relative humidity: $52.9 \pm 3.2\%$) and a detection limit of $0.5 \mu\text{g m}^{-3}$ for a 4.5 day sampling time. The influence of three environmental factors (temperature (T°), relative humidity (RH) and ozone concentration (O_3)) on the sampling rate was also evaluated in an exposure chamber following a fractional design of the experiment at two factor levels (low and high). Temperature is found to be the factor leading to the most significant variation of the sampling rate with an effect of +1.8% per °C. From the fractional design of the experiment, a model was set up for expressing the sample rate of Radiello® as a function of significant factors and the uncertainty on the sampling rate was assessed to 11.9% under the domain of tested conditions.

Introduction

Among indoor air pollutants, volatile organic compounds (VOCs) are of particular interest due to their abundance in indoor air and their adverse effects on health.¹ A study conducted from 2003 to 2005 by the French observatory of indoor quality (OQAI) in 567 dwellings reports that formaldehyde is the most abundantly detected VOC with a mean concentration of $19.6 \mu\text{g m}^{-3}$.² 22% of the dwellings exceed the upcoming French regulation threshold of $30 \mu\text{g m}^{-3}$ for long-term exposure. Another national campaign was conducted in France from 2009 to 2011 in 316 day-care centers and primary schools giving an average concentration of $15.7 \mu\text{g m}^{-3}$ fairly close to that found in the previous campaign on dwellings.³ Among these buildings receiving children, eight of them exhibited formaldehyde concentrations close to $50 \mu\text{g m}^{-3}$ and were subjected to a diagnostic of emission sources. More than 29 potential sources of formaldehyde were identified in each investigated room with higher emissions from building materials compared to furnishing materials. The main source of formaldehyde in most

rooms came from false ceilings made of wood products.⁴ Today, in France a monitoring of two toxic VOCs is considered in some buildings such as nurseries, schools and retirement homes receiving vulnerable people. The sampling scheme requires two measurement periods of 4.5 days (summer and winter). Several techniques exist for measuring formaldehyde in air: chemical sensors,^{5,6} electrical sensors,⁷ SPME derivation with *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine,^{8,9} and reaction with dansylhydrazine.¹⁰ The one that was the most selected for this monitoring is the radial diffusion Radiello® sampler because of a high sampling rate which makes the quantification of low formaldehyde concentrations for a sampling time of 4.5 days possible.

This technique is based on passive sampling and trapping by derivatization of carbonyl compounds on a cartridge coated with 2,4-dinitrophenylhydrazine (DNPH) and solvent extraction (NF ISO 16000-3, 2002). Several studies have shown that the methods performed either by active (pumped) or passive sampling using DNPH as the trapping agent could be influenced by environmental factors such as temperature, relative humidity and the presence of ozone.^{11,12} Negative interference caused by the presence of ozone in air has been reported.¹³ Ozone reacts with DNPH and DNPhydrazone derivatives to form 2,4-dinitrophenol, 2,4-dinitroaniline and 1,3-dinitrobenzene.¹⁴ For active sampling, this underestimation was proven even at low concentrations,^{15,16} leading to the development of many different scrubbers for use in combination with active

^aEthera, 7 Parvis Louis Néel, 38040 Grenoble Cedex 9, France

^bPôle RIME-C2MA, Ecole des Mines d'Alès, Hélioparc, 2 Avenue Pierre Angot, 64053 Pau Cedex 9, France. E-mail: valerie.desauziers@mines-ales.fr; Fax: +33559306368; Tel: +33559309992

^cLaboratoire Thermique Énergétique et Procédés, Université de Pau et des Pays de l'Adour, BP 7511, 64075 Pau, France

sampling. For passive sampling, the results reported in the literature are more contradictory. Bates *et al.*¹⁶ conclude that the magnitude of ozone interference is comparable for both passive and active samplers based on the results of the tests in an exposure chamber with short exposure durations (<24 hours) and various concentrations of formaldehyde (10–100 $\mu\text{g m}^{-3}$) and ozone (0–600 ppb). Recent studies^{11,18} reported that ozone interference may be low or even negligible compared to other environmental factor effects when DNPH-based passive samplers are exposed to atmospheres containing relatively low ozone levels (below 100 ppb) representative of most indoor situations. Mabilia *et al.*¹⁸ showed that temperature is the most influential environmental factor in the case of a DNPH-based passive sampler Analyst® and has a positive influence on its sampling rate. Concerning a Radiello® sampler, little information is available about the influence of environmental factors on the measurement of formaldehyde. Besides the Radiello® sampler, other diffusive devices based on the trapping by derivatization of carbonyl compounds with DNPH like the passive sampler Analyst®,¹⁸ the cartridge for the simultaneous determination of ozone and carbonyl,¹⁹ passive version of the Waters Sep-Pak XPoSure sampler,¹⁷ and the passive sampler UME^X manufactured by SKC Inc. exist. The reaction with DNPH is the trapping method most commonly used for passive sampling of formaldehyde.

The objectives of this study are to assess some method performance parameters (sampling rate, detection limit, repeatability and uncertainty on the sampling rate) and the influence of environmental factors for an exposure time of 4.5 days.

Materials and methods

Passive sampler Radiello®

The radial diffusive sampler Radiello® (code 165) (Fondazione Salvatore Maugeri, Padova, Italy) used in this study consists of a microporous polyethylene cylinder 16 mm in diameter, 55.5 mm length (46.5 mm available for the diffusion), 1.7 mm wall thickness and 25 μm pore size (Fig. 1, modified from Pavilonis *et al.*, 2013 (ref. 20)).

Two cellulose acetate caps are soldered with an epoxy adhesive to the cylinder ends. A stainless steel net coaxial cylindrical cartridge (60 mm length, 5.8 mm wall thickness, and 16 mm in diameter) filled with 900 mg of 35–50 mesh Florisil

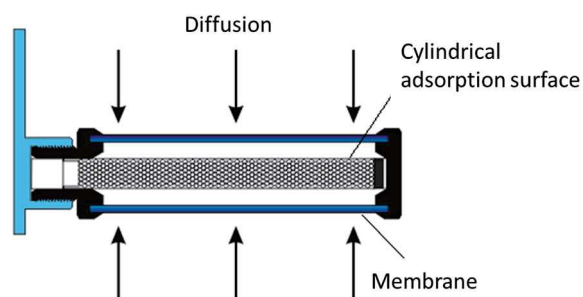


Fig. 1 Passive sampler Radiello®.

impregnated with 2,4-DNPH is inserted into the porous cylinder.²¹ Consequently, there is a great diffusion area, which facilitates the trapping of gas compounds on the cartridge, giving an uptake rate of at least two times higher than the axial devices.²² The diffusive path length is 18 mm, and it is opaque to light; it is suited to the sampling of light-sensitive compounds. This cartridge is selective to aldehydes sampling. For exposure, the Radiello® sampler is screwed on a plane cellulose acetate support. The molecules of formaldehyde diffuse through the cylindrical membrane towards the cartridge and react with DNPH to form the corresponding hydrazone. The hydrazone amount is extracted with 3 mL of acetonitrile and analysed by HPLC according to the method described later. Fondazione Salvatore Maugeri (FSM) gives a sampling rate value (SR_{298}) of 99 mL min^{-1} at $T = 298$ K for formaldehyde and an equation correcting the effect of temperature on the sampling rate (SR); this produces a variation of $\pm 1\%$ for a 10 $^{\circ}\text{C}$ variation from 25 $^{\circ}\text{C}$:²¹

$$\text{SR} = \text{SR}_{298} \left(\frac{T}{298} \right)^{0.35} \quad (1)$$

It is given as being invariant with humidity in the range 15–90% at 25 $^{\circ}\text{C}$. The interference of ozone is not appreciable below 100 ppb. For an ozone concentration higher than 100 ppb, an equation correcting the sampling rate is given:

$$\text{SR}_{298} = 99 - 0.02[\text{O}_3] \quad (2)$$

Exposure chamber experiments

To determine the sampling rates of two passive samplers under various environmental conditions, batches of 6 diffusive samplers are placed in a dynamic exposure chamber in which the formaldehyde concentration ($[\text{HCHO}]$), temperature (T°), relative humidity (RH) and ozone concentration ($[\text{O}_3]$) are controlled. The dynamic system is schematically represented in Fig. 2.

It consists of a glass exposure chamber of 50.9 L, flushed by clean air produced by a compressor and is dried and chemically filtered in an air purifier (Claind, Lenno, Italy). The first air flow is produced by paraformaldehyde permeation tubes Dynacal® (VICI Metronics, Washington, USA) placed in an oven manufactured by Calibrage (Saint Chamas, France) and composed of dry air with a stable formaldehyde concentration. A second air flow comes from a humidifier system consisting of bubblers filled up with water and flushed with purified air. A third air flow supplies dry air for dilution and adjusting humidity. A last air flow comes from a homemade ozone generator and a dilution bench producing dry air containing ozone at ppb levels. These four airflows are regulated by mass flow controllers. They are mixed at the chamber inlet, generating various test atmospheres controlled in formaldehyde and ozone concentrations and humidity. The open airflow is regulated between 15 and 20 L min^{-1} . The exposure chamber is placed in an air-conditioned room at regulated temperature (20 ± 1 $^{\circ}\text{C}$ and 30 ± 2 $^{\circ}\text{C}$).

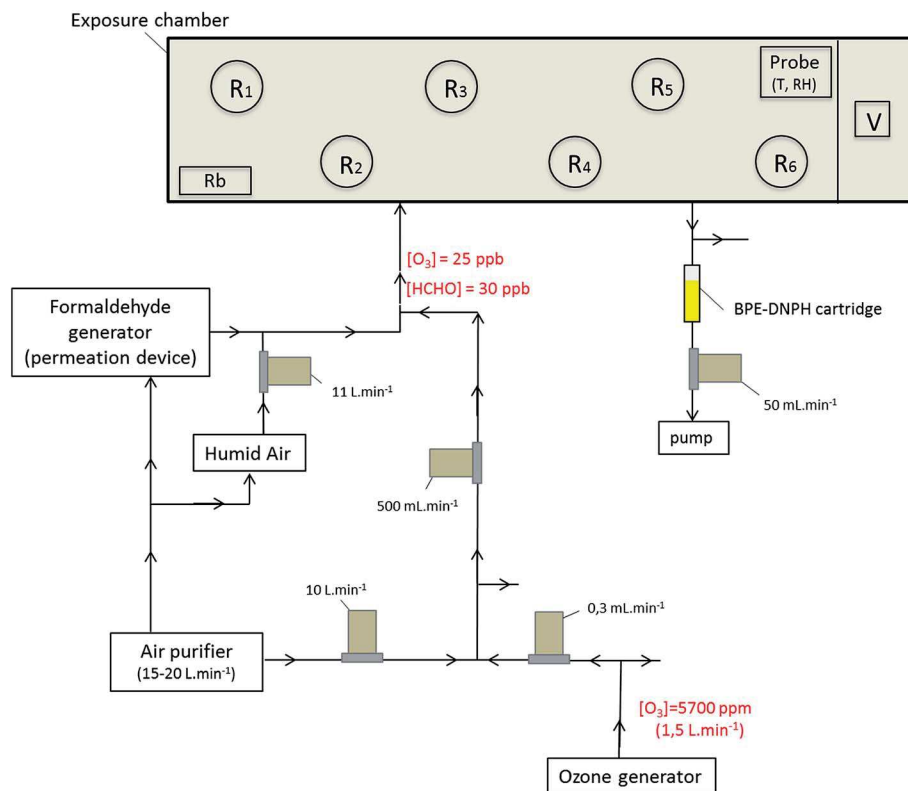


Fig. 2 Layout of the exposure chamber: ■ = mass flow controller, R_n = Radiello® cartridges, R_b = Radiello® blank cartridge, and V = fan.

The temperature and relative humidity in the exposure chamber are continuously monitored and recorded by means of multi-function probes. The sampling duration chosen is 4.5 days because monitoring of a formaldehyde set-up in France in some buildings receiving vulnerable people is based on two measurement periods of 4.5 days (summer and winter). The formaldehyde and ozone concentrations in the exposure chamber are monitored by successively pumped 24 and 48 hour samples on dual-bed 1,2-bis(2-pyridyl)ethylene/DNPH (BPE/DNPH) cartridges (Sigma-Aldrich, Saint Louis, MO, USA) (Fig. 3) developed by Uchiyama.²³ The active samplings cover a full sampling duration.

Air samples are drawn through the cartridge first through the BPE and then through the DNPH. Ozone is sampled by reaction with BPE contained in a first bed to produce pyridine-4-aldehyde. Airborne formaldehyde passes through the BPE without trapping and is trapped in the second bed by reaction with DNPH. DNPH and carbonyl DNPH hydrazones are not influenced by ozone because of effective trapping by the BPE. The sampling flow rate was regulated to 50 mL min⁻¹ with a mass

flow meter and checked before and after each pumped sample with a gas flow meter (DryCal DC-Lite, Butler, NJ, USA). Preliminary tests showed that in this configuration, no breakthrough occurs under the conditions tested in the exposure chamber. The cartridges are extracted in the reverse direction to air sampling with 3 mL of a mixture composed of 30% of dimethyl sulfoxide (DMSO) and 70% of acetonitrile with an added aliquot of phosphoric acid (0.085% (v/v)). Acetonitrile (>99.9%) and DMSO (>99.7%) were supplied by Sigma-Aldrich (Saint Louis, MO, USA), and phosphoric acid was provided by Carlo Erba Reagents (Val de Reuil, France). A solvent passing through the BPE-DNPH cartridge washed DNPH into the BPE bed where it reacted with pyridine-4-aldehyde and formed the corresponding hydrazone.¹⁹ The amounts of formaldehyde and pyridine-4-aldehyde are determined by HPLC according to the method described in the paragraph "HPLC analysis".

HPLC analysis

The extracts of Radiello® and active cartridges were analysed with a common protocol by HPLC on a Varian ProStar 310 (9050) with a UV/Vis detector (Varian, CA, USA) at 349 nm. Simultaneous analysis of formaldehyde and pyridine-4-aldehyde hydrazones was carried out using Ascentis RP-Amide, 5 µm particle size, 250 mm × 4.6 mm i.d. columns (Supelco, Bellefonte, PA, USA). The mobile phase was composed of acetonitrile/MilliQ water (34/66 (v/v)) at a flow rate of 2 mL min⁻¹ and the injection volume was 20 µL. More details on the analysis method are given by Uchiyama *et al.*¹⁹

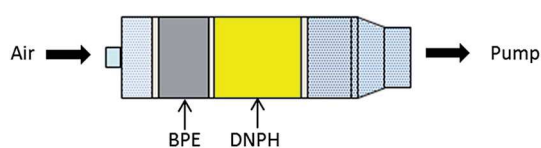


Fig. 3 BPE/DNPH cartridges.

Design of experiments

The aim of the fractional factorial design is to identify parameters and their combination that influence the sampling rate of Radiello®. The sampling rate was first assessed under the standard conditions, $T = 20\text{ }^{\circ}\text{C}$, $\text{RH} = 50\%$, $[\text{FA}] = 25\text{ ppb}$ and without ozone. The sampling rate obtained for these standard conditions is taken as a reference value. In order to assess the sampling rate of Radiello® under various exposure conditions, a test program was done in the exposure chamber following a design of experiments with three environmental factors (temperature, relative humidity and ozone). It has the advantage of evaluating the influence of several factors and their interactions with a minimum of experiments.²⁴ A fractional factorial design with three factors at two levels was chosen for each of these three factors: temperature (20–30 °C), relative humidity (20–80%) and ozone concentration (0–25 ppb). In our case, a 2^3 fractional factorial design was considered. The experiments were performed in the exposure chamber described in the paragraph “Exposure chamber experiments”.

Results and discussion

Nominal sampling rate obtained under standard conditions

To assess the sampling rate under standard conditions, two series of six Radiello® were exposed in the exposure chamber for 4.5 days according to the conditions in the paragraph “Exposure chamber experiments”. The standard conditions were: temperature = $19.9 \pm 0.5\text{ }^{\circ}\text{C}$, relative humidity = $52.9 \pm 3.2\%$ and formaldehyde concentration = $26.1 \pm 0.2\text{ ppb}$. The results are summarized in Table 1. This nominal sampling rate of Radiello® ($\text{SR}_{\text{nominal}}$, mL min^{-1}) was calculated according to the following equation:

$$\text{SR}_{\text{nominal}} = \frac{m_{\text{HCHO}} - m_{\text{blank}}}{[\text{HCHO}]_{\text{Active}} \times t} \quad (3)$$

where $[\text{HCHO}]_{\text{Active}}$ is the weighted time average concentration determined by active samplings ($\mu\text{g m}^{-3}$), m_{HCHO} is the sampled amount of formaldehyde (μg), m_{blank} (μg) is the background amount of formaldehyde in a closed cartridge and t is the sampling duration (min).

These two first test series confirm the high sampling rate of the passive sampler (99 mL min^{-1}), characteristic of its radial

shape. The mean sampling rate ($98.7 \pm 2.8\text{ mL min}^{-1}$) is close to the value of 98.4 mL min^{-1} provided by FSM. The repeatability of replicate measurements under standard conditions was comprised between 1.8 and 3.3% expressed in terms of Relative Standard Deviation (RSD).

Blank values and the detection limit

The blank values were determined for 9 closed cartridges placed in the exposure chamber during the tests. The mean blank value and its standard deviation were equal to $0.31 \pm 0.13\text{ }\mu\text{g}$. Using the standard deviation of the blank and the nominal sampling rate of $98.7\text{ }\mu\text{g m}^{-3}$ found previously, the detection limit (DL) defined as three times the standard deviation of blanks was $0.50\text{ }\mu\text{g m}^{-3}$ for a 4.5 day sampling time. This detection limit is suitable for monitoring the concentration in indoor air. Furthermore, a similar value (DL = $0.60\text{ }\mu\text{g m}^{-3}$ for a duration of one week sampling time) was reported for this diffusive sampler in the OQAI study.²

Influence of environmental factors on the sampling rate

The effects of several environmental factors, temperature, humidity, ozone and their interactions on the sampling rate were evaluated. One set of six samplers were exposed in the exposure chamber for 4.5 days under each condition as described in the paragraph “Design of experiments”, and the sampling rates of the sampler (SR_{exp}) were calculated using eqn (3). The whole results obtained under various exposition conditions are summarized in Table 2.

The run 7 has a formaldehyde concentration slightly upper to the target value of 30 ppb. This can be caused by slight deviations in the generation/dilution system. However, this has no consequence on the estimate of the sampling rate because only the $[\text{HCHO}]_{\text{Active}}$ measurements are considered in the calculation of the sampling rate. Repeatability for eight sets expressed in RSD is comprised between 1.5 and 4.0%. No environmental condition appears to be responsible for an increase of RSD. The range of experimental sampling rates enclose the nominal value of 98.7 mL min^{-1} found under standard conditions and the estimates of the sampling rate under the conditions tested are relatively close to or in agreement with those of FSM. However, temperature appears as the

Table 1 Results of two series of Radiello® exposed for 4.5 days under standard conditions. $[\text{HCHO}]_{\text{Radiello}}$ is the average concentration calculated applying the sampling rate corrected from the temperature influence given by FSM ($\text{SR}_{\text{FSM Radiello}}$) and $[\text{HCHO}]_{\text{Active}}$ is the weighted time average concentration determined from successively pumped 24 and 48 hour samples on BPE/DNPH cartridges. The active samplings cover a full sampling duration of 4.5 days

Run order	T° ($^{\circ}\text{C}$)	RH (%)	$[\text{HCHO}]_{\text{Active}}$ (ppb) ($n = 3$)	$[\text{HCHO}]_{\text{Radiello}}$ (ppb) relative standard deviation (%) ($n = 6$)	$\text{SR}_{\text{nominal Radiello}}$ (mL min^{-1})	$\text{SR}_{\text{FSM Radiello}}$ (mL min^{-1})
1	19.7 ± 0.7	52.8 ± 2.5	25.9	26.0 3.6	99.1 ± 3.6	98.4
2	20.1 ± 0.2	52.9 ± 2.8	26.2	27.4 1.9	98.2 ± 1.9	98.4
				Average (standard deviation)	98.7 (2.8)	

Table 2 Results of the fractional design for Radiello® with T° , RH and O_3 as potential influence factors. $[HCHO]_{\text{Radiello}}$ is the average concentration calculated applying the sampling rate corrected from the temperature influence given by FSM (SR_{FSM} Radiello) and O_3 and $[HCHO]_{\text{Active}}$ are the weighted time average concentrations (ozone and formaldehyde) determined from successively pumped 24 and 48 hour samples on BPE/DNPH cartridges. The active samplings cover the full sampling duration of 4.5 days. Significant differences between SR_{exp} and SR_{FSM} at a confidence level of 95% according to t -tests are reported in bold

Run order	T° ($^\circ\text{C}$)	RH (%)	O_3 (ppb) ($n = 3$)	$[HCHO]_{\text{Active}}$ (ppb) ($n = 3$)	$[HCHO]_{\text{Radiello}}$ (ppb) relative standard deviation (%) ($n = 6$)	SR_{exp} Radiello (mL min^{-1})	SR_{FSM} Radiello (mL min^{-1})
1	20.1 ± 0.4	18.1 ± 1.6	0	33.2	33.8 4.0	100.3 ± 4.0	98.4
2	18.9 ± 0.6	78.7 ± 2.4	0	27.7	22.0 3.3	105.1 ± 2.0	98.3
3	28.7 ± 0.3	22.7 ± 1.6	0	31.2	39.9 2.2	127.5 ± 3.0	99.4
4	28.5 ± 0.2	86.1 ± 1.4	0	28.3	31.0 3.4	108.9 ± 3.7	99.4
5	19.1 ± 0.3	16.0 ± 1.8	23.5	27.5	24.8 2.7	88.9 ± 2.4	98.3
6	19.6 ± 0.4	83.9 ± 1.9	26.7	27.5	27.7 3.5	99.1 ± 3.4	98.4
7	28.1 ± 0.2	20.4 ± 3.3	24.7	40.4	55.1 3.5	125.8 ± 4.4	99.4
8	28.2 ± 0.2	87.1 ± 0.8	22.1	31.3	40.4 1.5	115.6 ± 1.9	99.4
Full average (standard deviation)						108.9 (13.4)	

parameter which has the most effect on the sampling rate. Indeed, a net increase of +25% in the sampling rate is obtained for both tests (125.8 and $127.5 \text{ mL min}^{-1}$) at high temperature. As against the application of equations correcting the effect of temperature proposed by FSM is not conclusive, it results in little changes to the sampling rate that is not correlated with changes in experimental rates recorded depending on exposure conditions.

In order to reveal the factors and their interactions that influence the sampling rate of Radiello®, experimental data were fitted by a multilinear regression equation deduced from the factorial design method (Table 3).

In this model, the factors were previously standardized so that the variation extent of each factor is the same. To transform the factor value (Fi) to the standardized factor value (Fi_{stand}), the following equation was applied:

$$Fi_{\text{stand}} = \frac{(2Fi - (Fi_{\text{max}} + Fi_{\text{min}}))}{((Fi_{\text{max}} - Fi_{\text{min}}))} \quad (4)$$

where Fi_{max} and Fi_{min} are the maximum and minimum of factor i . The standardized factor i (Fi_{stand}) varies between -1 and 1 .

Two factors (T° and RH) and two interactions ($T^\circ\text{RH}$ and $T^\circ O_3$) have significant influence on the sampling rate. Temperature appears as the factor having the highest influence. From regression analysis, a model can be set up for expressing the sample rate of Radiello® as a function of 4 significant factors. The model obtained, with standardized factors, is given in the following equation:

$$SR = 112.0 + 12.4T_{\text{stand}}^\circ - 2.7RH_{\text{stand}} - 6.0T_{\text{stand}}^\circ RH_{\text{stand}} + 3.0T_{\text{stand}}^\circ O_{3\text{stand}}, R^2 = 0.95 \quad (5)$$

The results of the fractional factorial design show that the sampling rate of Radiello® is mainly influenced by temperature (+1.8% per $^\circ\text{C}$) and to a lesser degree by relative humidity (-0.1% per %RH) and two interactions ($T^\circ\text{RH}$ and $T^\circ O_3$) with variations of -0.54% per $^\circ\text{C}$ %RH and 0.96% per $^\circ\text{C}$ ppb O_3 , respectively.

Table 3 Coefficients of the linear model, standard error and confidence interval of the estimated coefficients at a confidence level of 95%, t -tests (in bold, the significant effects)

Factors	Effect	Coefficient	Standard error	Low CI	High CI	t value	p value
Intercept		112.0	0.5	111.0	113.1	222.0	0.00
T°	22.1	12.4	0.3	11.3	13.5	22.6	0.00
RH	-5.3	-2.7	0.5	-3.6	-1.7	-5.8	0.01
O_3	-0.6	-0.4	0.5	-1.4	0.7	-0.7	0.48
$T^\circ\text{RH}$	11.9	-6.0	0.5	-7.0	-5.0	-11.8	0.00
$T^\circ O_3$	6.0	3.0	0.5	2.0	4.1	5.7	0.01
RHO_3	1.8	0.9	0.5	0.1	1.8	2.1	0.05
$T^\circ RHO_3$	0.1	0.1	0.5	-0.3	1.7	1.4	0.16

Considering only the dependence of the sampling rate (SR_{mod}) with temperature ($^{\circ}C$) and relative humidity (%), a more practical simplified model is proposed:

$$SR_{mod} = 4.50 + 4.48T^{\circ} + 0.91RH - 0.04T^{\circ}RH, R^2 = 0.83 \quad (6)$$

Fig. 4 shows an agreement between the experimental values of the sampling rate (SR_{exp}) found under tested environmental conditions and those given by the simplified model (SR_{mod}). This simplified model can be used to improve the accuracy of measurements taking into account some effects of environmental factors on the sampling rate.

The results of the experimental design are consistent with several studies on DNPH-based passive samplers that show temperature as the factor having the greatest effect on the sampling rate. Mabilia *et al.*¹¹ studied the influence of several factors (temperature, ozone, relative humidity and absorbent) on Analyst® passive samplers. Temperature is the factor with the greatest influence on the response. The increase of its response with temperature is around +1% per degree which is similar to that found in our study for the Radiello sampler.

For an ideal diffusive sampler, the dependence of the sampling rate on absolute temperature and pressure is governed by that of the diffusion coefficient of the analyte D ($cm^2 \text{ min}^{-1}$). The latter dependence is given by $D = f(T^{n+1}, P^{-1})$ where n is a mathematical parameter with $0.5 < n < 1.0$, and P is the pressure of the sampled atmosphere during sampling (in kPa).²⁵ Hence the dependence of the sampling rate (SR), expressed in $cm^3 \text{ min}^{-1}$ or equivalent, is $SR = f(T^{n+1}, P^{-1})$. This dependence should be of the order of 0.2–0.4% K^{-1} depending on the n value and cannot explain the increase of the Radiello sampling rate of +1.8% per degree found in our study. An assumption is that temperature could modify the sampling efficiency of formaldehyde on the cartridge and/or yield of reaction between DNPH and formaldehyde.

The results also show that no change in the diffusive sampler response clearly appears in the presence of ozone at low concentrations representative of indoors. This confirms the recent observations of authors which do not find interference relative to ozone for various DNPH-based passive samplers when ozone levels are below 100 ppb.^{11,18} A real difference exists

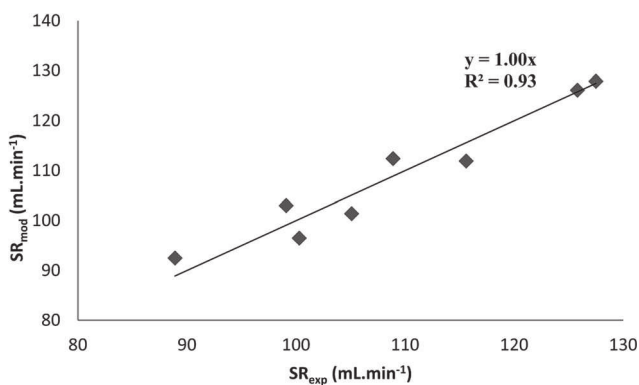


Fig. 4 Comparison between the experimental (SR_{exp}) and the theoretical (SR_{mod}) sampling rate of formaldehyde.

between passive and active samplings based on DNPH with respect to the interference of ozone. One hypothesis is that in the case of passive sampling, the amount of ozone reaching the surface of the cartridge and reacting with DNPH derivatives is much less than ozone which penetrates into the sampling medium by active sampling. But, more data are needed to test this hypothesis.

Uncertainty-type on the sampling rate

From the results of the tests in the exposure chamber, an evaluation of the uncertainty-type on the sampling rate ($u_{(SR)}$) proposed by the French central laboratory for monitoring air quality (LCSQA) in the guide FD X 43-070-3 (2008) was performed based on the highest difference between the experimental sampling rates (SR_{exp} high and SR_{exp} low), the maximum standard deviation (s_{high}) and the sampling rate given by FSM (SR_{FSM}):

$$\frac{u_{(SR)}}{SR} = \sqrt{\frac{\left(\frac{SR_{exp\ high}}{SR_{FSM}} - \frac{SR_{exp\ low}}{SR_{FSM}}\right)^2}{12} + \left(\frac{s_{high}}{SR_{FSM}}\right)^2} \times 100 \quad (7)$$

Our estimation of the resulting uncertainty $u_{(SR)}$ gave a value of 11.9% consistent with those of existing passive sampler techniques considered as indicative methods.

Conclusions

The aim of the present work was to evaluate the commercial passive sampler Radiello® used for monitoring formaldehyde concentration in indoor air for a 4.5 day sampling time. The evaluation of Radiello® showed that the sampling rate for formaldehyde was dependent on the environmental conditions. It was demonstrated that temperature is the most influential factor on the sampling rate with a positive effect of 1.8% per $^{\circ}C$. It has been stated that ozone at low concentrations representative of indoor air (around 25 ppb) does not appear to interfere with the formaldehyde measurement by passive sampler Radiello®. Based on the results of the tests in the exposure chamber, an equation correcting the effects of environmental factors on the sampling rate was proposed and the uncertainty-type on the sampling rate was evaluated under the domain of tested conditions. This evaluation confirms that the passive sampler Radiello® has performance equivalent to other passive sampler techniques, considered as indicative methods.

References

- 1 E. Cartieaux, M. Rzepka and D. Cuny, Indoor air quality in schools, *Arch. Pediatr.*, 2011, 18(7), 789–796, DOI: 10.1016/j.arcped.2011.04.020.
- 2 Observatoire de la qualité de l'air intérieur (OQAI), Campagne nationale logements, Etat de la qualité de l'air dans les logements français, Rapport final, 2006.
- 3 N. Michelot, C. Mandin, O. Ramalho, *et al.*, Campagne pilote de surveillance de la qualité de l'air dans les écoles et crèches

- en France: Résultats de la première phase, *Pollut. Atmos.*, 2011, 267–279.
- 4 G. Poulhet, S. Dusanter, S. Crunaire, *et al.*, Investigation of formaldehyde sources in French schools using a passive flux sampler, *Build. Environ.*, 2014, **71**, 111–120, DOI: 10.1016/j.buildenv.2013.10.002.
 - 5 S. Mariano, W. Wang, G. Brunelle, Y. Bigay and T.-H. Tran-Thi, Colorimetric detection of formaldehyde: A sensor for air quality measurements and a pollution-warning kit for homes, *Procedia Eng.*, 2010, **5**, 1184–1187, DOI: 10.1016/j.proeng.2010.09.323.
 - 6 K. Kawamura, K. Kerman, M. Fujihara, N. Nagatani, T. Hashiba and E. Tamiya, Development of a novel handheld formaldehyde gas sensor for the rapid detection of sick building syndrome, *Sens. Actuators, B*, 2005, **105**(2), 495–501, DOI: 10.1016/j.snb.2004.07.010.
 - 7 C.-Y. Lee, C.-M. Chiang, Y.-H. Wang and R.-H. Ma, A self-heating gas sensor with integrated NiO thin-film for formaldehyde detection, *Sens. Actuators, B*, 2007, **122**(2), 503–510, DOI: 10.1016/j.snb.2006.06.018.
 - 8 P. A. Martos and J. Pawliszyn, Sampling and determination of formaldehyde using solid-phase microextraction with on fibre derivatization, *Anal. Chem.*, 1998, **70**(11), 2311–2320.
 - 9 D. Bourdin and V. Desauziers, Development of SPME on-fiber derivatization for the sampling of formaldehyde and other carbonyl compounds in indoor air, *Anal. Bioanal. Chem.*, 2014, **406**(1), 317–328.
 - 10 J. Zhang, L. Zhang and Z. Fan, Development of the Personal Aldehydes and Ketones Sampler Based upon DNSH Derivatization on Solid Sorbent, *Environ. Sci. Technol.*, 2000, **34**, 2601–2607.
 - 11 R. Mabilia, C. Scipioni, F. Vegliò and M. C. Tomasi Scianò, Fractional factorial experiments using a test atmosphere to assess the accuracy and precision of a new passive sampler for the determination of formaldehyde in the atmosphere, *Atmos. Environ.*, 2010, **44**(32), 3942–3951, DOI: 10.1016/j.atmosenv.2010.07.013.
 - 12 M. Pires and L. R. F. Carvalho, An artifact in air carbonyls sampling using C 18 DNPH-coated cartridge, *Anal. Chim. Acta*, 1998, **367**, 223–231.
 - 13 D. F. Smith, T. E. Kleindienst and E. E. Hudgens, Improved high-performance liquid chromatographic method for artifact-free measurements of aldehydes in the presence of ozone using 2,4-dinitrophenylhydrazine, *J. Chromatogr. A*, 1989, **483**, 431–436.
 - 14 S. Achatz, G. Lörinci, N. Hertkorn, I. Gebefügi and A. Kettrup, Disturbance of the determination of aldehydes and ketones: Structural elucidation of degradation products derived from the reaction of 2,4-dinitrophenylhydrazine (DNPH) with ozone, *Fresenius' J. Anal. Chem.*, 1999, **364**(1–2), 141–146.
 - 15 R. Arnts and S. Tejada, 2,4-Dinitrophenylhydrazine-coated silica gel cartridge method for determination of formaldehyde in air: identification of an ozone interference, *Environ. Sci. Technol.*, 1989, **23**(11), 1428–1430.
 - 16 M. S. Bates, N. Gonzalez-Flesca, R. Sokhi and V. Cocheo, Atmospheric Volatile Organic Compound Monitoring. Ozone Induced Artefact Formation, *Environ. Monit. Assess.*, 2000, **65**(1–2), 88–97.
 - 17 N. a. Mullen, M. L. Russell, M. M. Lunden and B. C. Singer, Investigation of formaldehyde and acetaldehyde sampling rate and ozone interference for passive deployment of Waters Sep-Pak XPoSure samplers, *Atmos. Environ.*, 2013, **80**, 184–189, DOI: 10.1016/j.atmosenv.2013.07.074.
 - 18 F. Villanueva, I. Colmenar, R. Mabilia, C. Scipioni and B. Cabañas, Field evaluation of the Analyst® passive sampler for the determination of formaldehyde and acetaldehyde in indoor and outdoor ambient air, *Anal. Methods*, 2013, **5**(2), 516–524, DOI: 10.1039/c2ay25978h.
 - 19 S. Uchiyama and Y. Otsubo, Simultaneous Determination of Ozone and Carbonyls Using *trans*-1,2-Bis(4-pyridyl) ethylene as an Ozone Scrubber for Cartridge, *Anal. Chem.*, 2008, **80**(9), 3285–3290.
 - 20 B. Pavilonis, P. O'Shaughnessy, R. Altmaier, N. Metwali and P. Thorne, Passive monitors to measure hydrogen sulfide near concentrated animal feeding operations, *Environ. Sci.: Processes Impacts*, 2013, **15**(6), 1271–1278.
 - 21 http://www.radiello.com/english/ald_en.htm.
 - 22 V. Cocheo, C. Boaretto, L. Cocheo and P. Sacco, Radial Pathin Diffusion: The Idea to Improve the Passive Sampler Performances, *Int Conf Air Qual Eur Challenges 2000's*, ed. V. Cocheo, E. Saeger and D. Kotzias, Venice, Italy, 1999.
 - 23 S. Uchiyama, S. Naito, M. Matsumoto, Y. Inaba and N. Kunugita, Improved Measurement of Ozone and Carbonyls Using a Dual-Bed Sampling Cartridge Containing *trans*-1,2-Bis(2-pyridyl) ethylene and 2,4-Dinitrophenylhydrazine-Impregnated Silica, *Anal. Chem.*, 2009, **81**(15), 6552–6557.
 - 24 J. Roukos, N. Locoge, P. Sacco and H. Plaisance, Radial diffusive samplers for determination of 8-h concentration of BTEX, acetone, ethanol and ozone in ambient air during a sea breeze event, *Atmos. Environ.*, 2011, **45**(3), 755–763, DOI: 10.1016/j.atmosenv.2010.09.012.
 - 25 R. H. Brown, Monitoring the ambient environment with diffusive samplers: theory and practical considerations, *J. Environ. Monit.*, 2000, **2**(1), 1–9.