



Portable temperature-controlled permeation device for the generation of formaldehyde gas standard

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ARTICLE INFO

Keywords:

Formaldehyde
Paraformaldehyde
Emission rate
Dynamic generation
Calibration source
Permeation

ABSTRACT

Formaldehyde is a major indoor air pollutant. Accurate analysis of airborne formaldehyde is essential for effective monitoring and risk assessment. For many formaldehyde analysis techniques, the accuracy of the results depends on the calibration system. Existing formaldehyde calibration methods often face limitations, such as instability over time or limited concentration range. They also lack practicality for on-field calibration either because of bulkiness or because of high gas consumption. To address these challenges, a device using a paraformaldehyde permeation tube within a custom-built, temperature-controlled system was designed and evaluated.

The device weighs less than 3 kg and operates using a nitrogen source. Its low gas consumption (30–100 mL min⁻¹) enables the use of a portable gas cylinder of pure nitrogen (<2 kg) as gas supply. Formaldehyde concentrations ranging from 8.3 to 464 µg/m⁻³ were successfully generated, demonstrating the device's versatility. A custom-built high-emission permeation tube could generate concentrations from 5 940 to 49 471 µg/m⁻³ using the same system. Additionally, the emission rate is independent of the flow rate and follows Antoine's law with respect to temperature, enabling accurate prediction of concentration in various conditions over the evaluated range and beyond. Furthermore, the study confirms the long-term stability (1 year) of the low-emission paraformaldehyde permeation tube, with emission rates remaining mostly within ± 5 % of the average value for each temperature.

The temperature-controlled permeation system approach enabled rapid stabilisation of formaldehyde generation at various concentrations and low flow rates, eliminating the need for additional dilution equipment and facilitating on-site instrument calibration at various gas concentrations. This reliable and efficient portable formaldehyde generator offers a valuable solution for field calibration, providing accurate and stable reference gas for diverse analytical needs.

1. Introduction

Among common air pollutants, formaldehyde is associated with increased risk of asthma and has been classified as carcinogen by the International Agency of Research on Cancer in 2004 [1,2]. Analytical techniques are a major tool to estimate the potential health risks associated with exposure, especially in indoor environments like homes and workplaces. A number of analytical techniques have been developed specifically for the analysis of airborne formaldehyde, such as cavity ring-down spectroscopy [3], Hantzsch fluorimetry [3,4], photoacoustic

spectroscopy [5] or differential optical absorption spectroscopy [6]. When comparing the performance of these techniques, the calibration and instrument zero settings are often identified as the primary contributors to systematic uncertainty in the results [3,6–8]. To accurately calibrate on-line analysers, a reliable source of gaseous formaldehyde is required.

The preparation of a stable and accurate formaldehyde reference gas mixture presents some challenges. Gaseous formaldehyde tends to adhere to the walls of pressured cylinders, leading to inaccurate concentrations. The concentration significantly decays over time in

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<https://doi.org/10.1016/j.microc.2024.111544>

Received 24 June 2024; Received in revised form 6 August 2024; Accepted 29 August 2024

Available online 2 September 2024

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cylinders that have not undergone any pretreatment [9–11] but some pretreatment of the inner walls of the gas cylinder (e.g., with coatings) can minimise formaldehyde adsorption so that a few manufacturers proposed gaseous formaldehyde mixture with a typical guaranteed concentration stability of only six months. Formaldehyde pressurised cylinders are bulky, and present hazards related to the handling of pressurised cylinders, as well as to the handling of concentrated formaldehyde. In addition, these 80–100 kg gas cylinders are not portable and require drastic on-road transport safety conditions. Therefore, dynamic generation methods, are commonly used to prepare formaldehyde reference gas mixtures.

Table 1 summarises the different dynamic generation devices with their main characteristics for gaseous formaldehyde generation reported in the literature [12–22]. Some methods use aqueous formaldehyde

solution to be vapourised, permeated or nebulised into a diluting carrier gas [12–15,23]. Commercially available formaldehyde stock solutions are often a mixture of water, formaldehyde (37 wt%) and methanol (10–15 %) that act as stabiliser to avoid formaldehyde polymerisation. Therefore, a formaldehyde reference gas produced from this solution also contains water, methanol and adducts such as methylene glycol and methoxymethanol, formed from the reaction of formaldehyde with methanol [24,25]. Not controlling the amount of the other individual components in the reference source is not an ideal condition to study the performance of an analyser. Worse still, it can even cause errors if the compounds mentioned are interferents with the formaldehyde instrument.

The use of paraformaldehyde permeation tubes to perform calibration and performance studies is also very frequent [3,8,26]. In this

Table 1
Dynamic formaldehyde generation techniques.

Generation mode	Primary compound	Temperature	Generation vessel	Weight (kg)	Gas flow rate ^a (mL min ⁻¹)	Stabilisation rate	Stability (month)	[HCHO] (µg m ⁻³)	Ref.
Catalytic conversion (molybdenum)	Methanol (g)	350 °C	0.95 cm OD ^b catalyst-packed stainless-steel tube	N/A ^c	1000 (N ₂)	N/A ^c	>1	N/A ^c	[19]
Catalysed depolymerisation	Trioxane (s)	35.2 °C, 160 °C (conversion)	diffusion cell with a diffusion path (7.9 cm × 4.9 mm ID ^b) + converter	N/A ^c	200 (air)	>1 week	5	62 000	[20]
Permeation	Formaldehyde (aq) (37 % wt.)	5–20 °C	microporous PTFE ^e tube in filled 250 mL glass bottle	5.6	25–100 (air)	2–3 h	0.3–1	10–1740	[13]
Vaporisation	Formaldehyde (in methanol)	40 °C	glass impinge	N/A ^c	250–1000 (N ₂)	N/A ^c	N/A ^c	12–380	[14]
Vaporisation (bubbling)	Formaldehyde (aq) (MeOH-free)	5–25 °C	microporous PTFE ^e membrane	N/A ^c	<400 (humid air)	N/A ^c	N/A ^c	4–1500	[18]
Vaporisation (bubbling)	Formaldehyde (aq) (37 % wt.)	25 °C	20 mL vial sealed with metal cap with PTFE ^e septum	N/A ^c	40	N/A ^c	N/A ^c	0.6–120	[15]
Vaporisation (nebulisation)	Acetaldehyde (aq) (applicable to formaldehyde)	RT	0.5 L evaporation chamber	N/A ^c	900 (air)	N/A ^c	N/A ^c	4 500–180 000	[12]
Vaporisation (pump motor-driven syringe)	Formaldehyde (aq) (37 % wt.)	N/A ^c	glass tee tubing	N/A ^c	315 (air)	N/A ^c	N/A ^c	980–16 000	[21]
Depolymerisation	Paraformaldehyde (s)	10–40 °C	glass column (16 mm ID ^b)	N/A ^c	500–2000 (air)	1 h	N/A ^c	1560–8940	[22]
Permeation	Paraformaldehyde (s)	10–50 °C	PE ^f tube (5 cm × 6 mm ID, 8 mm OD ^b) sealed with teflon plugs in a tube holder (20 cm × 2.8 cm ID ^d)	N/A ^c	500–6 000 (air)	40 days	8	10.1–115	[17]
Permeation	Paraformaldehyde (s)	50 °C	PE ^f tube (5 cm × 6 mm ID ^d , 8 mm OD ^b)	N/A ^c	100–600 (N ₂)	1.5 months/3h ^h	>5	293–1782	[16]
Permeation	Paraformaldehyde (s)	70 °C	AID Model 309 ⁱ	N/A ^c	12.4 (air)	<1 week	N/A ^c	6 600	[21]
Permeation	Paraformaldehyde (s) or formaldehyde (aq)	2–150 (varying)	Permeation tube ⁱ	5–33	50–20 000 (varying)	N/A ^c	N/A ^c	1–10 000 (varying)	Manufacturer ^j
Permeation	Paraformaldehyde (s)	35–65	Nut with flat membrane ⁱ	<3	30–100 (N ₂)	<1.5 h	>12	8.3–452.8	This work
		45–70	Nut with flat PDMS ^k membrane		30 (N ₂)	<1 week	>1.5	5940–49471	

^a first dilution only;

^b outer diameter;

^c not available;

^d internal diameter;

^e PTFE: polytetrafluoroethylene;

^f PE: polyethylene;

^h ageing duration/stabilisation duration when already aged.

ⁱ commercially available (as opposed to custom-built);

^j combination of information collected from specifications of commercialised permeation systems: DynaCalibrator (Vici Metronics), ETG CALG 100 (ETG Risosse e Tecnologia), FlexStream (Kin-TEK), OVG-4 (Owistone Med), PermeatorPD1B/PD 1B-2 (Gastec);

^k PDMS: polydimethylsiloxane.

method, a tube is filled with paraformaldehyde powder that depolymerises into formaldehyde under the action of heat, which is, in turn, diluted by a carrier gas. Sometimes, like in this work, paraformaldehyde powder is in a metallic vessel closed by a permeable membrane on one surface. Usually, permeation tubes are certified for a 6-month duration. There are very few studies on the long-term trend in concentration generated by paraformaldehyde permeation tubes over several months [16,17]. Moreover, unlike permeation tubes of most organic compounds, paraformaldehyde is impregnated with a non-negligible mass of water (around 5 %). And since the largely used method to certify permeation tube is mass loss measurement [10,16], moisture content must be taken into account in the calculation to obtain an accurate emission rate value [10,27]. Another more elegant solution to determine the formaldehyde emission rate ($\mu\text{g h}^{-1}$) of the permeation tube is to measure the formaldehyde concentration (in $\mu\text{g m}^{-3}$) in the gas mixture at the outlet of the emission device. This can be achieved with online or offline analysis, i.e., by using either real-time formaldehyde instruments or active sampling on an adsorbent tube coupled to a chromatographic and spectroscopic measurement. The reference active DNPH/HPLC-UV method (ISO 16000-3) can advantageously be used for this current application. In addition, the dependence of the concentration generated from a paraformaldehyde permeation tube, and hence the resulting emission rate, on temperature or gas flow rate has been little studied to date. This is a real shortcoming, as establishing a relationship between emission rate or concentration as a function of experimental parameters (e.g., temperature) can enable data to be predicted under other conditions by extrapolation or interpolation.

Ideally, a generation system should be reliable, versatile, and portable. In other words, it must be able to accurately generate a stable concentration of formaldehyde over a long time, when used continuously or discontinuously. It should be capable of producing formaldehyde mixtures at a wide range of concentrations for use across diverse applications. A low range ($0\text{--}400 \mu\text{g m}^{-3}$) is well-suited for calibrating analysers used in typical indoor or outdoor environments, such as homes, offices, and public spaces. Generation at extremely low concentrations could facilitate the accurate determination of the limit of detection (LOD) for formaldehyde analysers. Targeting a higher concentration range ($>1000 \mu\text{g m}^{-3}$) would expand the applications to include calibration of analysers used in highly polluted settings, such as occupational exposure environments, industrial emissions, or smoke plumes. It could even find utility in specific applications, such as formaldehyde adsorbent studies where high concentrations are preferred to reduce the duration of the experiments. In this context, formaldehyde is introduced through the adsorbing material until it is saturated, and a breakthrough occurs [29,30].

Having a portable calibration system offers many advantages. Overall, it enables up-to-date calibrations to be carried out for measurements anytime, anywhere. First, all instruments incorporating optics can be out of adjustment during transport and often need to be recalibrated on site. Second, calibration under field conditions eliminates possible signal variations due to many experimental changes in chemical reagent, gas uptake yield, derivatization yield, gas and/or liquid flow, etc. In addition, other factors such as atmospheric pressure and temperature can also (usually slightly) influence measurements. For all these reasons, a recalibration with a few gas concentrations can be reassuring after transporting a formaldehyde analyser or sensor, and regular on-site calibration with a reliable generator significantly improves measurement accuracy. Performing occasional calibration point measurements throughout a field campaign can also help identify a dysfunction of the formaldehyde sensor or analyser. Suppose a faulty component of the formaldehyde sensor/analyser such as sensor, detector, flow regulator, or any key element, must be replaced on-site. In that case, a complete recalibration can be carried out if a reliable portable generator of gaseous formaldehyde is available.

On-site calibration for field measurement must be possible thanks to fast stabilisation of the generated concentration, low weight and easy

set-up of the device. Most dynamic calibration systems have a high gas consumption, especially when low concentrations need to be generated because of additional dilution [14,17,18]. Nitrogen generators and nitrogen cylinders are heavy and cumbersome. To minimise the bulk of the necessary nitrogen supply, the gas consumption of the calibration system must be reduced. Generating a gas mixture at a flow rate below 100 mL min^{-1} would allow the use of a small nitrogen (110 L , $\sim 1\text{--}2 \text{ kg}$), easily brought on the field.

In this work, we report for the first time to our knowledge a comprehensive long-term study spanning one year on a low-emission paraformaldehyde permeation tube within a portable custom-built temperature-controlled device enabling on-field instrument calibration. Our study is unique in its duration for the range of temperatures investigated, offering insights into the stability and performance of the low-emission permeation tube. Additionally, we extend the findings regarding temperature-to-emission rate relationship that has not been reported yet in the case of a dynamic generation setup for rather low ($<15 \text{ ng min}^{-1}$) and very high ($170\text{--}1500 \text{ ng min}^{-1}$) emission rates. We also demonstrated the simple relationship between temperature and emission rate ($\ln \text{ER}_T = f(1/T)$) for two different permeation tubes equipped with two different membranes, which allows the extrapolation of emission rate and thus gas concentration at other temperatures. Notably, our investigation demonstrates the ability to generate low concentrations with minimal gas consumption, achieved through low flow rates, an approach that has not been explored extensively in previous literature. More than the weight, the low gas consumption combined with a rapid stabilisation of the generation formaldehyde concentration are the main characteristics that enable the portability of the system. Furthermore, we have shown through measurements with a real-time monitoring technique that fast stabilisation of the target emission could be achieved in the case of dynamic generation with a permeation tube operating at low flow rates.

To our best knowledge, the formaldehyde generator developed combines three advantages that make it unique: i) the use of a low gas flow rate for, ii) the rapid stabilisation of the generated concentration ($<2\text{h}$); iii) the high stability of the generated gas concentration over time (1 year). The first two features enable the use of portable cylinders, making the device truly portable, unlike others reported in the literature [12,14–22] which must use bulky and heavy large cylinders or generators of zero air or pure nitrogen.

2. Material and method

2.1. Permeation system design

The permeation system was composed of a paraformaldehyde permeation tube, an aluminium enclosure (custom-built), a temperature monitor (custom-built), and a mass flow controller (MFC Bronkhorst, $0\text{--}500 \text{ Nml/min}$, Montigny-lès-Cormeilles, France) (see Figure SI-1). Two paraformaldehyde permeation tubes were used. The purchased low-emission permeation tube ($20 \pm 50 \text{ ng min}^{-1}$, $60 \text{ }^\circ\text{C}$, ChromatoSud, Val-de-Virvée, France) was the most extensively studied. The high-emission permeation tube was custom-built. It was made of a stainless-steel nut filled with 99.7 mg of paraformaldehyde powder (previously vacuum-dried for 1 night at room temperature) and closed with a PDMS membrane ($1.5 \times \text{Ø } 9.7 \text{ mm}$ with an effective exchange surface of $\text{Ø } 6.4 \text{ mm}$) (see Figure SI-2). The outer dimensions of the aluminium oven (Figure SI-1a) were $8.8 \times 6.2 \text{ Ø cm}$ and the inner enclosure was $6.0 \times 4.0 \text{ Ø cm}$ (69 cm^3). The thickness of the walls ensured adequate thermal inertia for a stable generation. The permeation “tube” had the size of a $1/4$ ” nut. At the bottom, the inner enclosure of the oven had a cavity into which the permeation tube was inserted (Figure SI-1b), providing optimum thermal contact for rapid stabilisation of temperature and therefore of the concentration of formaldehyde generated. This feature offers a rather unique geometry that has never been reported in the literature. The enclosure lid was put

on using 6 screws and a VITON o-ring ensured airtightness. Two heating cartridges and a temperature probe were installed in dedicated holes of the oven below the permeation tube location. They were connected to a temperature controller (CAL 9300, CAL controls, United Kingdoms) (Figure SI-1c). The gas inlet and outlet tubes were 1/8" Teflon tubes. The inlet tube was longer in the enclosure than the outlet tube to ensure homogeneity of the mixture. The oven weighed 622 g, and the full set-up also comprising the MFC and the temperature regulator weighed less than 3 kg. It was supplied in nitrogen from a cylinder (9 m³, 5.0, Linde, France).

2.2. Set-up for permeation system performance evaluation

The oven in which was placed the permeation tube was heated at 50, 55, 60 and 65 °C and supplied by nitrogen regulated at 30, 50, 70 and 100 mL min⁻¹. The experimental set-up for formaldehyde generation and monitoring is represented in Figure SI-3.

Real-time formaldehyde analysers were used to study the stabilisation dynamics of the generated formaldehyde concentration and its stability over 3–60 h, while the reference method was used to obtain an average concentration once the concentration was considered stable. Two formaldehyde analysers (MicroF, Chromatotec, France) were put in series to monitor real-time concentration (see Figure SI-3). Each was equipped with a pump and a MFC to regulate their sampling flow rate (typically set at 20 mL min⁻¹). The excess formaldehyde gas mixture generated was discharged to exhaust, enabling the resulting gas mixture to be maintained at atmospheric pressure. The sampling flow rate of the real-time analysers used to monitor generated formaldehyde was 40 mL min⁻¹ (20 mL min⁻¹ each). Depending on the flow rate applied to the permeation tube (30–100 mL min⁻¹), a make-up nitrogen flow was added to always ensure a minimum flow rate of 10 mL min⁻¹ at the exhaust. When the MFC regulating the flow to the permeation oven (MFC 1) was set at 30 mL min⁻¹, MFC 2 delivered a make-up nitrogen flow of 30 mL min⁻¹, so the total flow in the sampling line was 60 mL min⁻¹, allowing 20 mL min⁻¹ at the exhaust. A perfluoroalkoxy (PFA) Teflon tube (3 m, 6 mm OD, 4 mm ID) was used as a mixing chamber to homogenise the mixture before analysis.

For DNPH tubes, the entire flow leaving the generator, i.e., from 30 to 100 mL min⁻¹, was sampled. Both formaldehyde analysers and reference DNPH method are described below.

2.3. Real-time formaldehyde analyser

Two Hantzsch microfluidic analysers (MicroF, Chromatotec, France) were used to carry out real-time measurements of generated formaldehyde concentration. They have been described in detail elsewhere [4,31,32]. Briefly, the technique involves three consecutive steps: (1) the absorption of gaseous formaldehyde into an aqueous acetylacetone solution at ambient temperature via the formation of an annular flow; (2) the chemical reaction between formaldehyde and acetylacetone according to the Hantzsch mechanism; and (3) the fluorescence-based detection of the reaction product, namely, 3,5-diacetyl-1,4-dihydrolutidine (DDL). The concentration is proportional to the intensity of the fluorescence signal obtained after subtraction by blank measurements signal. Blank measurements were carried out every 10 h to compensate for the drift in the fluorescence signal caused by the ageing of the acetylacetone solution. The analysers were calibrated based on DNPH/HPLC measurement values of generated formaldehyde.

2.4. Sampling on DNPH tube and offline HPLC/UV analysis

Stabilised formaldehyde concentrations generated by the permeation device were determined by sampling on DNPH tubes (Sep-pack, Waters, USA) followed by HPLC analysis (UHPLC Nexera X2/XR/AR, Shimadzu, Japan) according to ISO 16000–3 standard procedure [28]. The HPLC was calibrated using a liquid formaldehyde-2,4-DNPH

standard. An average volume of 50 L (between 12 and 112 L) was collected from the device's outlet when using the low-emission permeation tube, and 0.9 or 1.8 L was collected on DNPH tubes when generating with the high-emission permeation tube. The DNPH tubes were stored at 4 °C, for up to one month (maximum) prior to their elution with about 4 mL of acetonitrile and injection into the HPLC. The parameters of the HPLC method were the following: an acetonitrile/water mobile phase at 75:25, a ProntoSIL 120–3 C18AQ column (3 μm, 250 × 3 mm) (Knauer, Berlin, Germany), a flow rate of 0.4 mL min⁻¹, a temperature of 33 °C and a UV detection at 360 nm. The uncertainty on the DNPH/HPLC-UV measurements was calculated according to Equation SI-1.

All measurements were carried out within a year for the low-emission permeation tube and within a month for the high-emission permeation tube.

3. Results and discussion

3.1. Stabilisation time

Concentrations generated by the permeation system were measured continuously with a time resolution of 10 s starting from about an hour or two at room temperature (23 °C) before regulating at the desired temperature ($t = 0$). The results for each flow rate and a temperature of 55 °C are plotted in Fig. 1 which represents the concentration–time profiles over 44–50 h depending on the studied flow rate. The plots for temperatures of 50, 60 and 65 °C over 32–35 h of analysis are available in Figure SI-4. The signal fluctuations are most likely due to the noise of the analyser.

The concentration as function of time was fitted according to a non-linear regression based on an exponential growth with a single exponent and two parameters (Equation (1)) using sigmaplot 11.0 (2008 Systat Software, Inc., CA, USA).

$$C_t = C_f(1 - e^{-kt}) \quad (1)$$

Where C_t (in μg m⁻³) and t (in h) are the concentration measured and the duration of the measurement. C_f (in μg m⁻³) is the final concentration reached once the concentration has stabilised and k (in h⁻¹) is the kinetic parameter [33].

Stabilisation time was defined as the time between the start of the heating and the emitted concentration reaching 95 % or 99 % of its final value (C_f). Stabilisation time did not significantly change depending on the temperature or the flow rate. According to microanalyser 1, it took on average 1 h to reach 95 % of the final value and 1.5 h to reach 99 % of the final value (see Table SI-1). For the same conditions, microanalyser 2 measured an average stabilisation time of 0.8 h at 95 % C_f and 1.3 h at 99 % C_f . Such fast stabilisation was probably due to the heating parameters of the generation device. The temperature increased by + 10 °C above the target temperature during the start-up, and was followed by a slow decrease to the target temperature within the next 15 min. The transfer of the heat was favoured by the contact of the stainless steel to the small cavity where the permeation tube was placed. A couple of other reasons likely influenced the fast stabilisation rate. The oven had a cylindrical shape and an inner volume of 69 mL and was large enough to allow homogenisation of the mixture before release at the outlet. Furthermore, the inlet tube was inserted in the oven, next to the permeation membrane, so that the emitted formaldehyde could be quickly swept into the rest of the oven inner enclosure. A calibration source stabilising in less than 2 h is an asset for on-site calibration applications when time is often limited.

3.2. Influence of the flow rate and temperature on the generation

When the generated concentration was stable, sampling on DNPH tubes was carried out for analysis by HPLC-UV. The average values and the standard deviation obtained for the multiple measurement for each

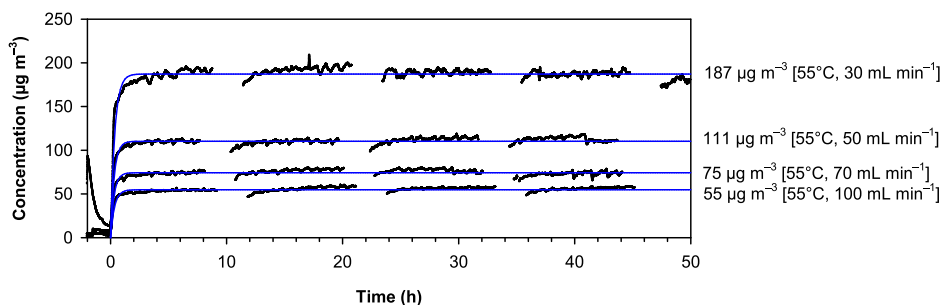


Fig. 1. Stabilisation of the generated concentration by the low emission permeation tube from the start of the heating (55 °C). Concentrations were measured by microanalyser 1. The lack of data every 10 h is due to blank periods used for drift correction. Data was fitted (blue) with equation $y = a(1 - e^{-bt})$.

condition are listed in Table SI-2. The plotted results are shown in Fig. 2, where formaldehyde concentration is plotted as function of the inverse of the flow rate supplying the permeation tube. The plots showing the direct relationship between concentration and flow rate as well as between concentration and temperature are available in Supporting materials (Figure SI-5 and SI-6).

Generated concentration (C_f in $\mu\text{g m}^{-3}$) and flow rate (Q in mL min^{-1}) are dependent according to Equation (2) where m is the mass of formaldehyde (in μg), V is the volume (in m^3), t the time (in min) and ER_T the emission rate (in ng min^{-1}).

$$C_f = \frac{m}{V} = \frac{m}{Q \times t} = \frac{ER_T \times 10^3}{Q} \quad (2)$$

The slope of the linear fit for the concentration as function of $1/Q$ corresponds to the emission rate. At temperatures of 65, 60, 55 and 50 °C they were 13.95 ± 0.18 , 8.67 ± 0.08 , 5.21 ± 0.07 , and 3.04 ± 0.05 ng min^{-1} , respectively, where the quoted errors correspond to the standard deviation of the linear fit ($\pm\sigma$). Approximately the same values were obtained when directly plotting the concentration as function of the flow rate with an inverse first-order fit (Figure SI-5).

All measurements were distributed over a year. In between each set of temperature-flow rate conditions to be measured, the oven was allowed to cool down at room temperature and the N_2 flow rate was either stopped or kept at about $10\text{--}30$ mL min^{-1} (90 % of the time) to avoid concentration build-up in the oven.

The average emission rates for all data points at all four temperatures

are summarised in Table 2. For each temperature, measurements at all four flow rates were included. The emission rate does not depend on the flow rate but only the temperature (Figure SI-7 shows the emission rate as function of the flow rate). These emission rates expressed in ng min^{-1} are in agreement with those obtained from the linear fit of Fig. 2 (values in brackets): 14.09 ± 0.66 (13.95 ± 0.18), 8.69 ± 0.39 (8.67 ± 0.08), 5.28 ± 0.24 (5.21 ± 0.07), and 3.09 ± 0.18 (3.04 ± 0.05) where the quoted errors correspond to the standard deviation based on n measurements. The standard deviation calculated from a minimum of 12 measurements of the emission rates was approximately 5 %.

Two mechanisms are involved in the emission process. First, the depolymerisation of the solid-state paraformaldehyde into gaseous formaldehyde in the headspace of the vessel. It is a single reaction process thermally driven. In its powder form, it was found to be governed by the nucleation Avrami-Erofeyev (A2) reaction model following

Table 2
Emission rate based on the average of DNPH measurements at each temperature.

Temperature (°C)	Emission rate (ng min^{-1})	σ (ng min^{-1})	RSD (%)	n^a
50	3.09	0.18	6.0 %	22
55	5.28	0.24	4.6 %	14
60	8.69	0.39	4.5 %	20
65	14.09	0.66	4.7 %	12

^a number of DNPH measurements.

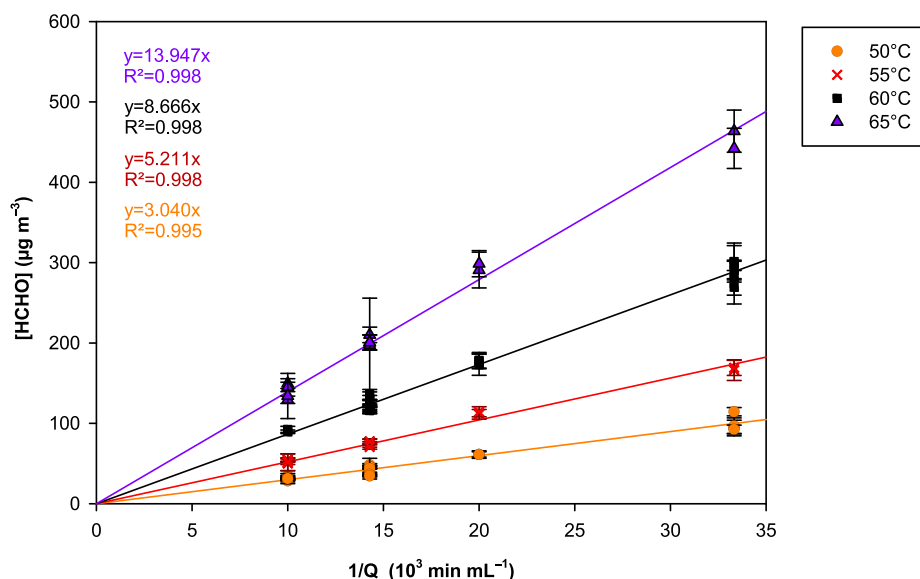


Fig. 2. Generated concentration by the low-emission permeation tube determined by the DNPH/HPLC-UV method at varying flow rate (30 to 100 mL min^{-1}) and temperature (50 to 65 °C). A linear fit was plotted on the inverse of the flow rate for each temperature. Vertical error bars correspond to the uncertainty calculated from individual errors occurring during DNPH-sampling and HPLC analysis (propagation of errors).

an Arrhenius-type behaviour [34].

In this study, the results were analysed using the empirical Antoine equation (3) that characterises the relationship of the vapour pressure as function of the temperature in Kelvin [27,35]. This equation has already been used in the literature and was found to best describe the diffusion mechanism [33].

$$\ln P_{\text{HCHO}} = A + \frac{B}{T} \quad (3)$$

Where P_{HCHO} is the vapour pressure of formaldehyde, T the temperature (in K) and A and B are constants.

The second mechanism is the transfer of the molecules to and through the membrane. The diffusion rate from the gaseous formaldehyde in equilibrium with paraformaldehyde in the headspace to the membrane is assumed to be very rapid and the associated diffusion time is supposed to be negligible in comparison with that of the diffusion process inside the membrane. The diffusion through the membrane (limiting process) is described by Fick's law of diffusion:

$$J_i = -D_i \frac{dc_i}{dx} \quad (4)$$

where J_i is the flux of species i (amount/time through the area of the membrane section) in the direction of the gradient of concentration dc_i/dx .

Another form of this expression has been reported in the literature [36]:

$$d = \frac{\pi \times r^2 \times D \times P_{\text{HCHO}} \times M_{\text{HCHO}}}{l \times V_m \times P_A} \quad (5)$$

Where d is the diffusion rate of formaldehyde in g s^{-1} (equivalent to $\text{ER}/60 \times 10^6$ with ER in ng min^{-1}), r the radius of the permeation membrane (in m^2), l the thickness of the permeation membrane (in m), D the diffusion coefficient of formaldehyde (in $\text{m}^2 \text{s}^{-1}$), P_{HCHO} the vapour pressure of formaldehyde, M_{HCHO} the molecular mass of formaldehyde (30.03 g mol^{-1}), V_m is the molar volume of an ideal gas at standard temperature and pressure (STP) ($22.4 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$) and P_A the atmospheric pressure in Pa (101.325 Pa).

The use of equation (3) and (5) allows us to express the emission rate as function of the temperature:

$$d = \frac{\pi \times r^2 \times D \times e^{A + \frac{B}{T}} \times M_{\text{HCHO}}}{l \times V_m \times P_A} = \frac{\text{ER}_T \times 10^6}{60} \quad (6)$$

$$\ln \text{ER}_T = \ln \frac{\pi \times r^2 \times D \times M_{\text{HCHO}} \times 60.10^{-6}}{l \times V_m \times P_A} \times A + \frac{B}{T} \quad (7)$$

And considering all incorporated terms are constants, the equation can simply be written as:

$$\ln \text{ER}_T = A' + \frac{B}{T} \quad (8)$$

where A' and B are constants.

The relationship of Equation (8) was plotted in Fig. 3 using all emission rates measured by the DNPH/HPLC-UV method between 50 and 65 °C (circle, $n = 68$ measurements). In our studied temperature range, $\ln \text{ER}_T$ varies perfectly linearly as a function of $1/T$, with A' being equal to 35.45 and B equal to -11091 . In addition, the high correlation value ($R^2 = 0.993$) of the linear fit demonstrates the feasibility to predict accurately a wide range of generated formaldehyde concentrations based on measurements at a few temperatures. When using the Antoine equation, a third constant is usually introduced afterwards to adjust the experimental data such that the final equation would be $\ln \text{ER}_T = A' + B/(T+C)$. When computing it with our values, the C constant was found to be 0. This is not surprising, since our temperature range is restricted to just 15 °C amplitude, which justifies the use of Antoine's simplified equation.

To validate the model further, it was used at a temperature of 35 °C. By using the equation derived from the linear fit shown in Fig. 3 (black solid line), $\ln \text{ER}_T = -11091/T + 35.45$, the theoretical emission rate of the permeation system at 35 °C would be $0.58 \pm 0.03 \text{ ng min}^{-1}$. The quoted error corresponds to the uncertainty of the emission rate determined from the 95 % confidence band of the linear regression (Fig. 3, solid blue lines). The experimental value obtained was $0.56 \pm 0.12 \text{ ng min}^{-1}$ and is represented on the graph (orange triangle), within the 95 % confidence interval of the regression. The uncertainty of the experimental value includes the uncertainty of the N_2 flow rate to supply the permeation tube (70 mL min^{-1}), the N_2 flow rate used for additional dilution (500 mL min^{-1}), and the uncertainty of the measurement of the diluted concentration (σ based on 10 measurements). The measurement was performed by a formaldehyde analyser (airmoF, Chromatotec, France) calibrated on a formaldehyde cylinder bottle (Takachiho, Japan) DNPH-certified by our means. The device set at 35 °C was supplied by 70 mL min^{-1} and further diluted with 500 mL min^{-1} for the analyser to measure the concentration. The corresponding diluted concentration measured was $0.98 \pm 0.16 \text{ } \mu\text{g m}^{-3}$ ($\pm \sigma$ based on 10 measurements) which amounts to $8.0 \pm 1.9 \text{ } \mu\text{g m}^{-3}$ in the 70 mL min^{-1} at

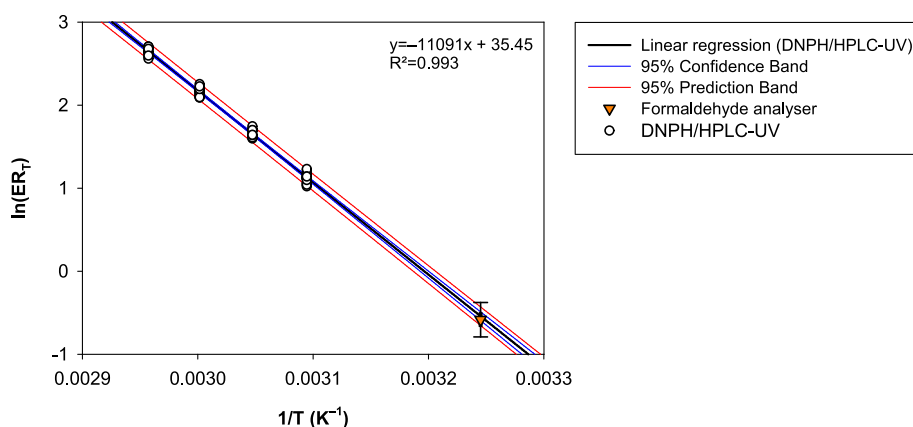


Fig. 3. Dependency of the emission rate (ER_T in ng min^{-1}) to reverse temperature between 50 and 65 °C ($n_{50^\circ\text{C}}=22$, $n_{55^\circ\text{C}}=14$, $n_{60^\circ\text{C}}=20$, $n_{65^\circ\text{C}}=12$) and its linear fit for the low emission permeation tube. The error bars for the individual DNPH points were not represented because they were too short. The linear regression corresponds to the fit of DNPH/HPLC-UV (circle) results, described by equation $\ln \text{ER}_T = -11091/T + 35.45$. The result at 35 °C (orange triangle) was measured by a separate formaldehyde analyser. The confidence (blue lines) and prediction (red lines) intervals give the range of variable values computed by sigmaplot 11.0 for the region containing the linear regression and for the region containing the population from which the observations were drawn, respectively. The level of confidence was 95 %.

the outlet of the device, before dilution (uncertainty based on the propagation of errors that includes the standard deviation on 10 measurements and the uncertainties of the dilution flow rates). For these measurements, the calculation predicted $1.02 \pm 0.09 \mu\text{g m}^{-3}$ in the 570 mL min^{-1} after dilution and $8.3 \pm 0.7 \mu\text{g m}^{-3}$ before dilution ($\pm\sigma$ based on propagation of error calculation).

These results show that this device can generate a concentration of $8.3 \pm 0.7 \mu\text{g m}^{-3}$, allowing us to easily achieve $1 \mu\text{g m}^{-3}$ with limited dilution for an accuracy of about 10–15 %. This level of concentration is low enough to enable a better assessment of the analytical performance of formaldehyde analysers, and in particular their LOD and LOQ. The literature reports that LOD and LOQ are generally determined using the instrumental noise and signal obtained from concentration between 5 and $10 \mu\text{g m}^{-3}$ [4,37,38], with aqueous formaldehyde solution instead of gaseous formaldehyde [7,39], or by large dilution of highly concentrated formaldehyde in N_2 (few ppm) [40,41]. Using a low-emitting permeation system allows minimising the need for large volumes of diluting gas, unsuitable for on-field calibration since they require a zero air generator or a bulky gas cylinder.

A temperature variation would cause an unstable generation. At a temperature of $50 \text{ }^\circ\text{C}$, a variation by $\pm 0.1 \text{ }^\circ\text{C}$ translates into an uncertainty of $\pm 0.03 \text{ ng min}^{-1}$ for the emission rate value of 3.09 ng min^{-1} . With $\pm 0.5 \text{ }^\circ\text{C}$, the emission rate would be $3.09 \pm 0.16 \text{ ng min}^{-1}$. At more extreme temperatures, the emission rate and its uncertainty would be equal to 0.58 ± 0.01 at $35 \pm 0.1 \text{ }^\circ\text{C}$, 0.58 ± 0.03 at $35 \pm 0.5 \text{ }^\circ\text{C}$, 14.20 ± 0.14 at $65 \pm 0.1 \text{ }^\circ\text{C}$ and 14.20 ± 0.69 at $65 \pm 0.5 \text{ }^\circ\text{C}$. The temperature being the variable with the greatest impact on the concentration generated, its stability is thus crucial. Although it does not appear evident in Fig. 1 because of the visible noise of the analyser, the strong thermal inertia of the device described here kept the temperature variations at the precision level of the temperature regulator ($0.1 \text{ }^\circ\text{C}$).

To complete our study, a high-emission permeation tube was designed and evaluated. Generating at high concentrations can be advantageous for specific applications such as formaldehyde adsorption studies. In those experiments, adsorbent materials to be tested are exposed to the pollutant until they saturate. Using higher concentrations allows faster saturation, thus reducing the duration of the experiment which can last weeks [29,30]. The custom-built permeation tube was made by filling a stainless-steel nut with 0.1 g of paraformaldehyde powder and closed with PDMS membrane ($1.5 \times \text{Ø } 6.4 \text{ mm}$) (see Figure SI-2). Similarly to experiments performed with the low emission permeation tube, DNPH/HPLC-UV measurements were carried out to determine the generated gaseous formaldehyde concentration and then the emission rate of the custom-built permeation tube at temperatures between 45 and $70 \text{ }^\circ\text{C}$ according to Equation (2). For a flow rate of 30 mL min^{-1} , the concentration measured were $5940 \pm 218 \mu\text{g m}^{-3}$ at $45 \text{ }^\circ\text{C}$, and $49471 \pm 1814 \mu\text{g m}^{-3}$ at $70 \text{ }^\circ\text{C}$ where the quoted errors represent the uncertainty calculated from individual errors from the DNPH measurements (propagation of error). The corresponding emission rates were then $178 \pm 13 \text{ ng min}^{-1}$ and $1484 \pm 108 \text{ ng min}^{-1}$ (Table SI-3) where the quoted errors represent uncertainty calculated from individual errors from the DNPH measurements and dilution flow rates (propagation of error). The relationship between the emission rate and the temperature was plotted in Figure SI-8 according to Equation (8). In this case, the constant A' was found to be 34.58 and $B -9354$. Compared to the purchased low-emission permeation tube where the generated concentration at 30 mL min^{-1} and $45\text{--}65 \text{ }^\circ\text{C}$ was in the range of $19.6\text{--}452.8 \mu\text{g m}^{-3}$, the custom-built high emission permeation tube allowed us to generate formaldehyde at concentrations 70 to 300 times higher for the same conditions, i.e., ranging between 5940 and $33\ 044 \mu\text{g m}^{-3}$. A very high correlation coefficient was obtained in the range studied ($R^2 = 0.999$). The fact that a linear relationship was observed for both low-emission and high-emission tubes between 35 and $70 \text{ }^\circ\text{C}$ suggests that the same linear behaviour can be expected for permeation tubes of all ranges of emission. To obtain lower emission rates, the thickness of the PDMS membrane can be increased or less permeable

materials, like PTFE, could be used [42,43].

3.3. Long-term stability (1 year)

The device was used almost continuously (approximately 75 % of the time) throughout a year at the 4 temperatures. The DNPH results of the samplings are represented in Fig. 4 as function of time. The emission rate was stable over the 12 months of measurements as no significant decreasing trend was observed. 65 % of the individual values are within $\pm 5 \%$ of the average emission for a set temperature and 97 % are within $\pm 10 \%$. Such stability makes the system fit for punctual on-field measurements as well as regular analyser calibration control.

For continuous use at $60 \text{ }^\circ\text{C}$ ($\text{ER}_{60^\circ\text{C}}=8.7 \text{ ng min}^{-1}$), the permeation tube would lose about 4.6 mg of paraformaldehyde per year. Assuming the low-emission permeation tube contained 0.1 g of paraformaldehyde, this represents a 4.6 % mass loss per year.

Under the same conditions ($60 \text{ }^\circ\text{C}$), the high-emission permeation tube ($\text{ER}_{60^\circ\text{C}}=678 \text{ ng min}^{-1}$) would lose about 30 % of its mass per month. Nevertheless, the emission rate was stable over a month of use. In Figure SI-8, the measurements were carried out in a random chronology and still shows perfect linearity. These results suggest that it does not depend on the mass of the bulk, but more on the solid-gas exchange surface (top of the bulk flat area) which remains the same while paraformaldehyde is consumed.

From previous experience, the certification by mass often overestimated the amount of generated gaseous formaldehyde from permeation tubes. For an accurate determination of emission rate using mass loss, the presence of about 5 % of water must be considered in the calculation [10,27]. Here, the concentration and emission rates have been determined by DNPH/HPLC-UV. It is a technique that must be calibrated using liquid standard of formaldehyde-2,4-DNPH derivative. It is a standard method that is quite reliable for the determination of formaldehyde concentration. The standard gas generated is therefore a secondary standard. However, having demonstrated that the emission is stable as long as the permeation "tube" is filled with paraformaldehyde, only 3 to 5 measurements are enough to calibrate the gas generation system and plot the emission rate-to-reverse temperature linear relationship over the target range of use.

3.4. Comparison with the literature

To summarise the experimental results obtained in section 3, the main advantages of the formaldehyde gas generator developed in this work are thus: i) the use of low gas flow rate to reach ($30\text{--}100 \text{ mL min}^{-1}$) to obtain a wide range of formaldehyde gas concentrations varying between low values ($8.3 \mu\text{g m}^{-3}$) and high levels ($464 \mu\text{g m}^{-3}$), combined with a rapid stabilisation of the gas generation ($<2 \text{ h}$), enables the use of a small portable gas cylinder on the field. Indeed, in this type of generation system, weight and size are mainly related to the pure gas cylinder or generator. The weight of the generator itself is thus quite often negligible; ii) the high stability of the generated gas concentration over time (12 months) within 10 % of the target generated gas concentration.

Formaldehyde reference gas is produced using different means. The methods used for dynamic generation of formaldehyde in the literature are listed in Table 1.

The purely technical differences are difficult to identify because the precise geometries that characterise generation devices using paraformaldehyde permeation tubes are rarely described in the literature. Nevertheless, two major differences seem to contribute to the improvement of the temperature stability at the permeation tube level and the rapid stabilisation of gas concentration generation: (i) the cavity at the bottom of the oven allowing direct contact between the oven and the permeation tube; (ii) the thickness of the oven walls providing better thermal inertia.

Most either involve an aqueous formaldehyde solution, or formaldehyde in one of its polymerised forms (trioxane or paraformaldehyde).

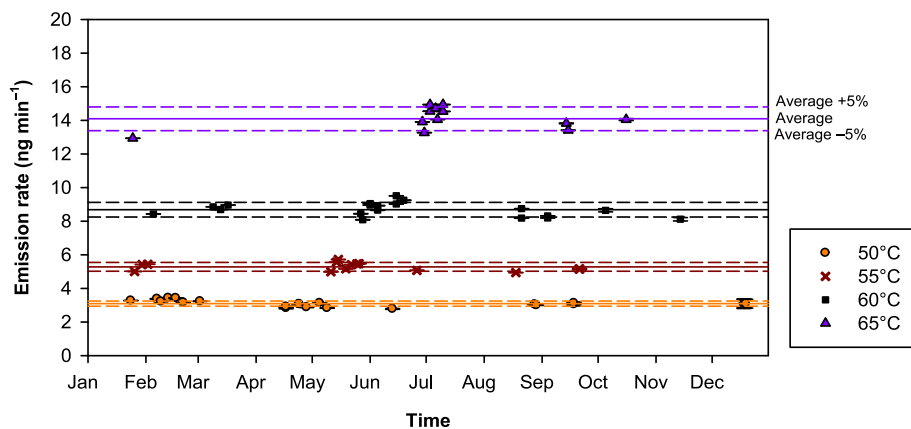


Fig. 4. Discontinuous use of the permeation system over a year (~75 % of the time, turned off between each measurement) and resulting emission rate at 50 °C (orange circle), 55 °C (red cross), 60 °C (black square) and 65 °C (purple triangle). Flow rates varied from 30 to 100 mL min⁻¹ (undifferentiated in the graph). Full lines correspond to the average emission for a temperature and dashed line to $\pm 5\%$ the average value. Vertical error bars correspond to the uncertainty calculated from individual errors occurring during DNPH-sampling and HPLC analysis (propagation of errors).

Only one makes use of methanol to carry out a catalytic conversion to gaseous formaldehyde. They studied the performance of several metal oxide catalysts to convert methanol into formaldehyde and obtained the highest conversion efficiency ($97 \pm 4\%$) with a molybdenum catalyst [19]. Catalytic conversion of methanol is the industrial way of producing aqueous methanol [44] but is rarely if not never, used in laboratory settings because simpler methods are available.

One of them is the direct vaporisation of aqueous formaldehyde into the gas phase. Aqueous formaldehyde can be injected continuously into a flow of pure gas [12,14,21] or the opposite can be executed by injecting the pure gas into the formaldehyde solution [15,18]. Commercially available formaldehyde solutions typically contain 37 % wt. of formaldehyde, water and 10–15 % of methanol that prevent formaldehyde polymerisation. A mixture of pure gas (air or nitrogen), formaldehyde, and most often water and methanol is then formed. Such systems are relatively easy to implement but the presence of water and methanol can be unwanted.

Paraformaldehyde, on the other hand, produces relatively dry formaldehyde when depolymerised. The commercially available powder contains about 5 % of impurities, being mainly water. Paraformaldehyde depolymerisation is activated simply by heating ($E_a = 31.7 \text{ kJ mol}^{-1}$ [34]). Hori and Arashidani packed glass columns with paraformaldehyde and injected dry air through the column [22]. For formaldehyde generation in a test chamber, Salthammer et al. pressed paraformaldehyde into a pill and placed it in a hollow cylinder, letting depolymerised formaldehyde diffuse through the hole [33].

Paraformaldehyde is the linear polymer of formaldehyde. Trioxane is another stable polymer of formaldehyde. It is a cyclic molecule that releases three formaldehyde molecules when depolymerised. Like with methanol, trioxane must be passed onto a catalytic bed to produce formaldehyde. With methanol dehydrogenation, it is the only method that can generate completely dry formaldehyde [20].

Often, gas-permeable membranes are used to limit and control the diffusion or vaporisation process. Becker et al. used a PTFE microporous tube immersed in an aqueous formaldehyde solution. The vapour formed at the inner surface of the tube was swept by the flow of pure air injected. For generation of formaldehyde in a test chamber, Wei et al. filled a vessel with an aqueous formaldehyde solution and sealed it with a PDMS membrane, allowing formaldehyde to passively permeate through the membrane [13,35,45]. In the literature, calibration and performance studies of analysers are most often carried out with paraformaldehyde permeation tubes [3,8,26], though they have not been extensively studied. To our knowledge, only two studies have addressed the dynamic generation of formaldehyde using paraformaldehyde permeation tubes [16,17]. In this work, compensation for this lack of

knowledge was attempted.

Ultimately, a wide range of concentrations has been generated by above-mentioned methods. The lowest range measured was 0.6–120 $\mu\text{g m}^{-3}$ by vaporisation by bubbling method (black triangle down in Fig. 5). Concentration was changed by using aqueous solutions of various concentrations [15]. The highest value (62 000 $\mu\text{g m}^{-3}$, black square) was obtained by trioxane depolymerisation [20]. When focusing on paraformaldehyde permeation only (green circles), our work measured concentrations in the lowest (8.3–452.8 $\mu\text{g m}^{-3}$) and highest (5940–49 471 $\mu\text{g m}^{-3}$) range (green circle) reported. Presumably, concentrations in the range of 1–10 000 $\mu\text{g m}^{-3}$ can be generated, as stated by permeation tube manufacturers. In practice, they are certified for one temperature only, limiting the control of concentration to only one parameter: the gas flow rate. The lowest concentrations reached in other works were measured when applied flow rates were above 100 mL min⁻¹ (see Fig. 5).

By injecting gas directly through the paraformaldehyde-packed column, Hori and Arashidani noted a rise in the generation rate with increased gas flow rates [22]. For paraformaldehyde permeation tubes, on the other hand, the emission rate remains unaffected by the gas flow rate at fixed temperatures, as observed by Aoyagi and Matsunobu and the current study [17]. It indicates that the gas flow rate exerts no influence on the solid–gas equilibrium established beneath the membrane, making temperature the only parameter that must be empirically studied for concentration control.

The linear dependence between the logarithm of the emission rate and the reverse temperature has been observed for permeation of VOCs such as acetone [46]. In such cases, the primary compound is the target gas in its liquid state, while the emission of formaldehyde is based on a depolymerisation reaction. Aoyagi and Matsunobu showed that the linear relationship was also observed for a paraformaldehyde permeation tube made of polyethylene filled with 1 g of formaldehyde and for temperatures between 10 and 50 °C [17]. Salthammer et al. did not use a permeation membrane but a hole to limit the emission process from paraformaldehyde. Yet, the logarithm of the concentration generated in test chamber conditions between 23 and 33 °C also decreased linearly with the reverse temperature [33]. In our study, the emission rate-to-temperature relationship was observed from 35 to 70 °C, extending the observation to a higher temperature range and for different membrane materials (PDMS for the high-emission permeation tube). The solid–gas equilibrium of formaldehyde formed beneath the membrane can be assimilated with a liquid–gas equilibrium, allowing us to describe the temperature dependence with the Antoine equation. We showed that only a few measurements were required to plot this equation that could then be used for a year with good confidence.

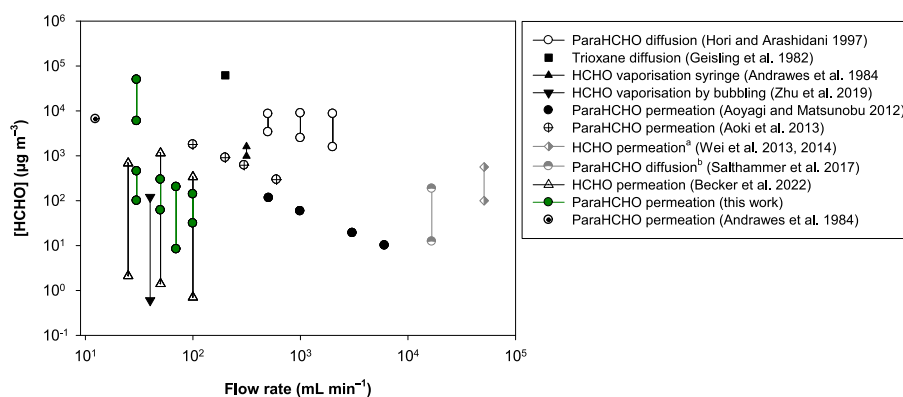


Fig. 5. Concentrations of formaldehyde generated by various techniques reported in the literature as function of the flow rate of the diluting gas used. ^a generation in a 51 L test chamber at 1 h^{-1b} generation in a 1 m³ test chamber at 1 h⁻¹.

To perform on-site calibration, the stabilisation rate of the generated concentration is important. Fast stabilisation is preferred when time is limited. Becker et al. mention that it took a few hours for their aqueous formaldehyde permeation system to stabilise [13]. After storing at room temperature, the paraformaldehyde permeation tube of Aoyagi and Matsunobu only generated a stable concentration after 40 days of use at 50 °C and 200 mL min⁻¹ of dry fresh air [17]. The same research team later used two permeation tubes of the same size and material (polyethylene). One contained untreated paraformaldehyde; the other paraformaldehyde dried in a vacuum at 95 °C for 14 h (vacuum-dried). They both were aged for 2–3 months at 50 °C before use. After another one-month storage, concentration in both tubes became stable within 3 h upon introduction into the apparatus flushed with nitrogen [16]. In our work, the paraformaldehyde powder for the high-emission permeation tube was vacuum-dried at room temperature for one night before making the “tube”. The first DNPH measurement was carried out after 4 days after placing it in the heating device, but stable generation was directly observed from then and over the whole month of measurement. The difference might lay in the type of membrane used i.e. PDMS for us and polyethylene for them. Regarding the low-emission permeation tube, the use of a real-time formaldehyde analyser allowed us to observe it took on average 1–1.5 h for the generated concentration to stabilise for all temperatures and flow rates tested. It is faster than all the other dynamic generation systems mentioned above (see Table 1), and it is combined with a lower gas flow rate inducing a faster gas calibration on the field with a lower pure gas consumption. The systems designed by Wei et al. (aqueous formaldehyde permeation) and Salthammer et al. (paraformaldehyde diffusion) were made to generate controlled atmosphere formaldehyde in test chambers. The former could generate stable concentrations within 5 to 24 h, and the latter in about 4 h [33,35,45]. Hori and Arashidani indicated that the gas concentration generated by injection through paraformaldehyde-packed glass column becomes constant within 1 h.

Few data are available in the literature about the long-term use and stability of formaldehyde generation systems. When it was studied (see Table 1), the stability is short, from a few weeks [13,19] to a few months [16,17,20]. Paraformaldehyde permeation tubes seems to be the most promising ones for long-term stability: Aoyagi and Matsunobu observed that their polyethylene paraformaldehyde permeation tube maintained a stable generation for more than 8 months after having aged the tube. Permeation tubes prepared identically by Aoki et al. were used to continuously generate a formaldehyde mixture in nitrogen for six months [16,17]. In our study, the low-emission permeation tube was used discontinuously about 75 % of the time over a whole year and did not show any variation in concentration for a set temperature and flow rate condition. Being used to generate low concentrations, the mass loss is minimal and does not seem to significantly impact the emission rate. The high-emission permeation tube was used continuously over 1–2

months and the generated concentration was stable. Although it was not tested for longer, the fact that 30 % of paraformaldehyde has been used in the first month of use obviously indicates that it cannot be used for more than 2 or 3 months.

Except Becker et al.’s device that weighs 5.6 kg, none was explicitly made to be portable. The weight of commercialised external calibration system designed to generate via aqueous formaldehyde or paraformaldehyde permeation varies between 5 kg and 33 kg [13]. Our system weighs less than 3 kg without the nitrogen supply. In fact, the gas supply may pose a greater limitation for transportation compared to the heating module itself. As illustrated in Fig. 5, most studies generate formaldehyde at high flow rates. Here, a reduced amount of gas was required to operate our system. Therefore, it can be brought on the field with a disposable nitrogen cylinder (110 L, 1–2 kg) as gas supply. By generating at 30 mL min⁻¹ for 8 h a day, the autonomy of the system is approximately 7.6 days (61 h in total). It can be used to calibrate portable formaldehyde analysers that samples at low flow rates, like the microfluidic analyser used in this study (microF, Chromatotec, France).

4. Conclusion

A portable formaldehyde generation device was designed based on a paraformaldehyde permeation “tube” to dynamically generate low formaldehyde concentrations for calibration and analytical performance evaluation of analysers. The complete device including the oven, regulator, and circuit board weighed less than 3 kg and needs nitrogen supply that can be fulfilled with a small nitrogen cylinder (1–2 kg). Its small size also offers the possibility to integrate it into formaldehyde analysers to use as internal calibration system, and to bring it along as an independent system with portable analysers to field campaigns.

Using a low-emission permeation tube, concentrations between 8.3 and 464 µg m⁻³ were generated at temperatures varying from 35 to 65 °C and reduced flow rates (from 30 to 100 mL min⁻¹). At all sets of temperature-flow rates, a rapid stabilisation of the generated concentration (<1.5 h) was observed, which is an asset for on-field calibration when time is limited.

The emission rate was independent of the flow rate and followed the Antoine law regarding temperature, allowing for the prediction of concentrations under new conditions. While the initial assessment was performed between 50 and 65 °C, a concentration of 8.3 µg m⁻³ was generated at 35 °C for a flow rate of 70 mL min⁻¹ as predicted by the model. After a second dilution, 1 µg m⁻³ was obtained in 570 mL min⁻¹ with an accuracy of around 10–15 %. It would require dilution with 12 L min⁻¹ of zero air to generate the same amount using 10 mL min⁻¹ of a typical 1 ppm formaldehyde cylinder.

The dependence of the emission rate with the temperature when generating with a high-emission permeation tube was also verified. This custom-built tube was used to generate gaseous formaldehyde

concentration from 5 940 to 49 471 $\mu\text{g m}^{-3}$ at 30 mL min^{-1} for temperatures ranging between 45 and 70 °C.

The low-emission permeation tube showed stable emission rates over a year, with most values within $\pm 5\%$ of the average value for each temperature.

This developed portable formaldehyde generator offers a reliable and efficient solution for field calibration of portable analysers, providing an accurate and stable reference gas at a wide range of concentrations based on a limited number of measurements. Generating at a very high range of concentrations with low flow rates may also be useful for specific applications such as adsorption studies.

Future work could explore the use of zero air instead of nitrogen to assess its impact on tube stability. If no significant effect is observed, the miniaturisation and autonomy of the portable system developed here could be further improved. By incorporating a pump and a formaldehyde adsorbent, the system could draw in and purify surrounding air to supply the oven. Aoyagi and Matsunobu prepared a permeation tube supplied by zero air. No change was mentioned when Aoki and al. used identically prepared permeation tubes supplied with nitrogen [16,17].

Credit authorship contribution statement

Audrey Grandjean: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Anais Becker:** Writing – review & editing, Visualization, Methodology. **Coralie Kustner:** Formal analysis, Data curation. **Michel Wolf:** Methodology, Conceptualization. **Christophe Sutter:** Methodology, Conceptualization. **Romain Severac:** Resources, Funding acquisition. **Jean-Philippe Amiet:** Resources, Project administration, Funding acquisition. **Damien Bazin:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Conceptualization. **Stéphane Le Calvé:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This study was supported by the CIFRE programme between SME Chromatotec (Saint-André-de-Cubzac, France) and the French National Association of Research and Technology (ANRT, grant number 2020/0977). This study was also funded by the CIFRE programme between Advancion Company (Argenteuil, France) and the French National Association of Research and Technology (ANRT, grant number 2021/0617).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2024.111544>.

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