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A chemical potential driven micro-membrane sampler and its application for the determination of trace carbonyl compounds in air

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ABSTRACT

A chemical potential driven micro-membrane sampler for enrichment of trace gaseous carbonyl compounds has been developed. The sampler is composed of exposed parts with membrane and analysis parts with polypropylene tube. The membrane acts as a barrier, through which the analytes dynamically diffuse and transfer from absorbents present outside to extract solvent inside through the difference of chemical potential. Formaldehyde and acetic acid were selected as verification samples. Quantification is achieved through high performance liquid chromatography (HPLC) analysis. The mass of analytes determined shows a linear correlation with concentration of the gaseous analytes. The limits of detection of formaldehyde and acetic acid after 8 h sampling were 3.32 and 0.76 $\mu g\,m^{-3}$.

1. Introduction

During the last few decades, demand for the measurement of trace environment pollutants has been growing because more and more volatile toxic chemicals, particularly indoor pollutants coming from building and decorating materials, e.g., formaldehyde, sulfur compounds, acetic acid and other carbonic acid, cause harm to human health and precious cultural relics such as in museum [1–4].

Carbonylic compound is one of the gaseous pollutants receiving much attention recently. Measuring techniques based on chromatography, voltammetry, photometry, and fluorescence spectroscopy as well as chemical reactions are available [4–7]. Although various rapid and selective sensors such as electrochemical, electrical potentiometer and piezoelectric sensors are also developed to conform with World Health Organization (WHO) standards for detecting formaldehyde [8], the analytical determination of low-level concentration in ppb and sub-ppb range in air still poses challenges.

Normally, sampling processes of analytes in air are performed before measurement is taken. 2,4-Dinitrophenylhydrazine (DNPH) agent is frequently used in many improved methods for active collection of carbonylic compounds. Hong et al. [9] reported an enhanced dual coil DNPH method for the quantitative determination of carbonylic compound in ambient air. Shiraishi et al. [10] developed an integrated system for the continuous automated analysis of aldehydes at ppb level in atmosphere. The analysis involved a solid-phase extraction procedure based on the collection of aldehydes from air pumped through a silica gel cartridge coated with acidified DNPH. The limits of quantification of formaldehyde and acetaldehyde were reported to be 2.2 and 1.2 ppb, respectively.

For the determination of trace pollutants in environmental samples, active pre-concentration of the gaseous analytes pre-analysis has still been considered an effective method. The liquid membrane enrichment technique has been confirmed to be a powerful tool for extraction and separation in many fields. Earlier literature dealt with the use of membranes for separation of metals [7,11] and organic acids in aqueous solution samples [12]. The promising extraction technique has also recently been applied to complex chemicals enrichment prior to chromatographic and electrophoretic separations [13–15]. Some sampling and continuous monitoring system were also developed for detecting organic volatile compounds (VOCs) and semi-volatile compounds in environmental aqueous or atmospheric samples. A large number of chemicals, such as phenoxy acids, herbicides, organic chlorine, surfactants and anilines [16–21] were addressed. Application of membranes for collecting gaseous pollutants has also been investigated [22,4]. Zhang et al. [23] designed a membrane cell to collect and pre-concentrate carbonyl in air samples, the carbonyl was then reacted with 2,4-dinitrophenyl hydrazine to form 2,4-dinitrophenyl hydrazones and further determined by polarography. Rocha et al. [24] developed a diffusive sampling method by

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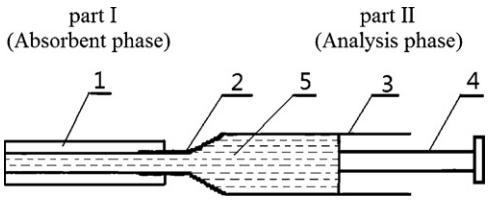

1.micro-membrane loaded absorbent
2.stainless connector
3.polypropylene tube
4.polypropylene piston
5.extractant

Fig. 1. Schematic diagram of micro-membrane sampler.

bundling polypropylene porous capillaries followed by capillary zone electrophoretic separation with 0.9 $\mu g\,m^{-3}$ detection limit obtained for formaldehyde in atmosphere. These sampling systems mentioned above are all limited structurally and spatially. Moreover, since the sampling pump continuously extracts air from the detected space, dilution effects and restricted access also bring uncertainty factors to examination of air inside sealed cabinets or drawers [4].

In this paper, a chemical potential driven micro-membrane sampler was developed and applied to pre-concentrate pollutants in air. A permeable tubular micro-membrane was set as a barrier between pollutants in air and extract phase, suitable absorbents and extractant were selected to trap and enrich the analytes. The analytes-ladden extract solution was quantified for the following analysis by HPLC. Formaldehyde and acetic acid were used to validate the quality of the sampler.

2. Experimental

2.1. Reagents and standards

2,4-Dinitrophenylhydrazine (DNPH), glycerin, acetonitrile and triethanolamine were HPLC grade and purchased from Merck (Darmstadt, Germany). DNPH was recrystallized twice from acetonitrile [25], and then dried and stored in a container. Glycerin was also purified using small amounts of acetonitrile to remove tiny formaldehyde particles. 1 $g\,mL^{-1}$ formaldehyde–DNPH/acetonitrile standard solution (CAS# 1081-15-8) for calibration was purchased from AccuStandard, Inc. (New Haven, USA). HPLC-grade triethanolamine was employed without further purification. Micro-porous polyvinylidene fluoride (PVDF) tubular membrane was purchased from Siemens (Germany), polysulfone and cellulose acetate were obtained from Dalian Institute of Chemical Physics (Dalian, China). The membranes were cleaned in an ultrasonic cleaner with ultra-pure water, which was prepared on a Milli-Q/RO4 system (Millipore, Bedford, MA).

2.2. Micro-membrane sampler

Fig. 1 shows the schematics of the micro-membrane sampler. The sampler has two main parts: (I) the absorbent part is made of membrane (1 mm i.d. × 40 mm), which is permeated absorbent solution on the wall (see 1 in Fig. 1), (II) the analysis part (3, 4 and 5 in Fig. 1) was made of polypropylene (PP) tube (5 mm i.d. × 80 mm), which is filled with extractant in it. The selection of the extractant may depend on the derivatives to be analyzed, acetonitrile and 1 $mol\,L^{-1}$ sodium hydroxide solution are selected to be extractant for formaldehyde and acetic acid vapor collection, respectively, in this paper. The two parts were integrated in series by a stainless steel connector (see 2 in Fig. 1). A small amount of seal gum applied at the both end of the membrane to avoid the extractant to leak out.

DNPH-coated membranes were prepared by soaking 40 mm PVDF tubular membrane in a solution that contains 10 mg acetonitrile-recrystallized DNPH dissolved in 10 mL HPLC-grade glycerin. For acetic acid (HAC) sampling, the absorbent solution was replaced by 10 mL HPLC-grade triethanolamine agent (TEA). In order to evenly disperse absorbent on the wall of the membrane, the membrane was sonicated in absorbent solution for 30 min. After permeation, the surface of the absorbent-coated membrane was dried by tissue paper and stored in sealed glass tubes.

The micro-membrane applied in the sampler has larger permeative inner surface area, it is convenient for analytes to be trapped and to be transferred from absorbent phase to extractant phase. The inner surface area can be changed by controlling the length of the membrane. When the sampler is exposed to surrounding air, gaseous carbonyls if present will diffuse towards the surface, where it is trapped and react with special absorbents (see 1 in Fig. 1) to form a stable derivative on the surface of membrane. The derivative further diffuse from the surface to the bulk of the absorbent based on the difference of concentration, and extracted by extractant phase inside the membrane (see 5 in Fig. 1) through the difference of chemical potential.

2.3. Generation of the gaseous pollutants and the sampling by micro-membrane sampler

A 400 cm^3 cube-shaped glass was designed as exposure chamber. Dynamic dilution calibrator (model 700, USA) was applied to generate stable formaldehyde with suitable concentrations continuously, in which standard formaldehyde gas poured from a container diluted with purified air as zero air, which was obtained by passing ambient air through large beds of sorbents including activated carbon, molecular sieves and permanganate on aluminum in zero air module (model 701, USA). This zero air contains less than 0.5 ppb of NO, NO_2, SO_2, ozone, formaldehyde and other carbonyls. The mixing ratio was controlled precisely to obtain suitable concentrations of formaldehyde by mass flow controller using the state-of-the-art electronic closed-loop control.

For acetic acid gaseous standard preparation, an 11 dm^3 glass vessel was used as an environmental chamber. The desired concentrations were obtained by injecting 100 μL different concentrations of standard glacial acetic acid solution into the chamber through a half-hole septum by means of a gas tight syringe. After 30 min equilibration at room temperature, the septum of the vessel was pierced with needle to load the membrane sampler. Then the membrane was pushed into the vessel and exposed to standard mixture for 8 h. The vessel was flushed with 99.99% nitrogen at room temperature for 1 h prior to use in order to remove trace contaminants. At least one blank sample is used for analysis with each group of samples. The blank is treated identically to the samples except that no acetic acid solution injecting into the chamber. A small peak appears at the same retention time as that of acetic acid that may be from impurity of basic agents such as triethanolamine and its peak area is about 2.2 mAu s, being significantly smaller than a typical HPLC peak of acetic acid sample. If the impurity level is not satisfactory, repeat flushing with 99.99% of nitrogen until a satisfactorily low impurity level is confirmed by HPLC analysis. The influence of the blank on samples is not considered in the determination of acetic acid concentration. All standard concentration measurements were performed in triplicate at room temperature.

After sampling, all the extractant inside sampler was drawn into the analysis phase by withdrawing the piston at the end (see 4 in Fig. 1). The sampler was then sealed with polyethylene film and

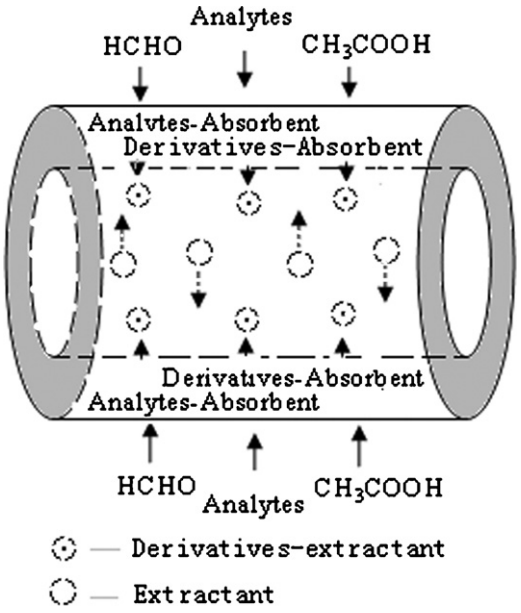

Fig. 2. The principle of sampling and collecting procedure.

placed in the dark. Before analysis, a HPLC injector replaces the stainless connector (see 2 in Fig. 1), immediately introducing the solution into the HPLC system.

2.4. Liquid chromatography analysis

An Agilent 1100 HPLC (Agilent Technology, USA) instrument equipped with an ultraviolet absorbance detector to obtain isocratic flow of the analytes-laden extract eluent at a flow rate of 1 mL min^{-1} was used. An injection valve was equipped with a 10 μL loop for formaldehyde, or 20 μL loop for acetic acid. The detection wavelength was 365 nm for formaldehyde and 214 nm for acetic acid. A 250 mm × 4.6 mm Inertsil ODS-80A analytical column (GL Sciences, Japan) was used. The mobile phase was a mixture of 65:35 (v/v) acetonitrile/water for formaldehyde derivatives and 20 mmol monopotassium-phosphate/acetonitrile (96:4, v/v) for acetate analysis, respectively.

1 g mL^{-1} formaldehyde–DNPH/acetonitrile standard solution was used to obtain standard concentrations (0.2–20 μg mL^{-1}), 10 μL of which were injected into the HPLC to provide daily calibrants corresponding to 8.57–857 ng formaldehyde–DNPH. For daily calibration graph of acetic acid, analytical grade glacial acetic acid was used to prepare a series of aqueous solutions (1.0–22.0 μg mL^{-1}).

3. Results and discussion

3.1. Designation of the chemical potential driven micro-membrane sampler

Sampling and collecting procedure of the sampler is illustrated in Fig. 2. The membrane acts as a barrier through which the analytes can be transported. Since different absorbents are sensitive to specific pollutants, the analytes in air (donor phase) could be easily trapped by reaction with sensitive chemicals in the absorbent phase. Due to the fact that the concentration of the analytes adhering to the absorbents on surface of the membrane is higher than the concentration of the analytes adhering to the absorbents on the inside of the membrane, the derivatives then continuously cross-over the absorbent phase to the inside of the membrane. In the interface between the adsorbent phase and the extractant phase, the solubility of the derivatives in the extraction phase is greater than the solubility in the adsorbent phase and the affinity of the analytes is higher for the extractant phase than for the adsorbent phase, the differences cause either the derivative or the analyte to be continuously extracted from the adsorbent phase into the extractant phase (acceptor phase), along with the derivatives continuously being removed out of the absorbent phase and entering the extractant phase inside the membrane, the concentration of the derivatives stays relatively higher on the surface than the inside, facilitating the surface derivatives to move inside. This procedure further accelerates the analytes to be trapped and the derivative reaction accordingly in the absorbent solution. This step results in the dynamic reaction and simultaneous extraction and enrichment of the low concentration analytes in air. The mass flow caused by the difference in concentration is determined by Fick's law [$Jm = -DA(dC/dx)$] [16] Which states that there is a proportionality constant that corresponds to the diffusion coefficient (D) and the area of the membrane available for diffusion (A).

Formaldehyde vapors, if present in the surrounding air, will diffuse into the membrane ladden with DNPH–glycerin solution, where it is trapped as its hydrazone derivatives (formaldehyde–DNPH), which diffuse from the surface to the bulk of the absorbent based on the difference of concentration. At the interface of the absorbent phase (glycerin solution) and the extractant phase (acetonitrile), the derivatives will be further extracted by acetonitrile extractant inside the membrane since the bigger solubility of formaldehyde–DNPH in acetonitrile than in glycerin solution. This improves the enrichment of the formaldehyde derivatives in the extractant phase. Meanwhile, the removal of formaldehyde derivatives from the bulk of the absorbent, more and more formaldehyde in air will be dynamically trapped and simultaneous diffused into the absorbent for further enrichment and detection.

For acetic acid vapor sampling, we selected commonly used basic agent triethanolamine (TEA) as absorbent, which can permeate into the membrane. 1 mol L^{-1} sodium hydroxide solution as extractant was channeled into the membrane. When the acetic acid (HAC) is trapped by triethanolamine and produces TEA-AC, the derivative then diffuses into the bulk of the triethanolamine. Due to the concentration gradient, at the interface, when encountering more basic extractants (NaOH solution), acetate was replaced into the extractant phase, allowing TEA-AC to maintain a high concentration gradient in the adsorbent surface and the main phase, promoting surface acetic acid derivatives to dynamically and continuously proliferate inside, enriching the extractant phase. This causes the acetic acid trapped by triethanolanmine to be further transferred and extracted by sodium hydroxide solution inside the

Table 1
Membrane screening.

Micro-membranes	Surface pore size (μm)	Inner diameter (μm)	Thickness (μm)	The length (cm)	Result
Polysulfone	–	375	20	4	Break up
Polysulfone	–	200	40	4	Break up
Cellulose acetate	–	200	10	4	Fine
Polyvinylidene fluoride	0.02	500–1000	10–20	4	Fine

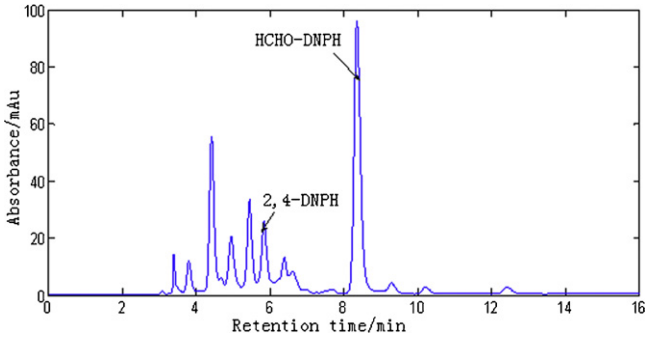

Fig. 3. Chromatogram of formaldehyde samples. Analytical column: a 250 mm × 4.6 mm Inertsil ODS-80A. Mobile phase: 65:35 (v/v) acetonitrile/water. Detection wavelength: 365 nm. Flow rate: 1 mL min^{-1}. Concentration of formaldehyde is 100 μg m^{-3}.

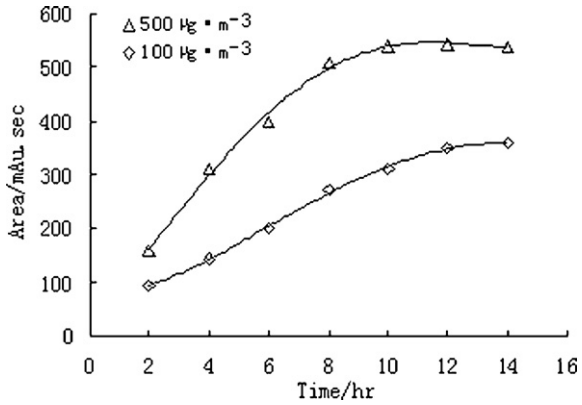

Fig. 4. Effect of exposure time on sampling.

membrane, which makes it possible for enrichment of more and more acetic acid in air.

3.2. Selection of micro-membranes

The micro-membranes obviously play a key role in sampling. In order to select a suitable membrane, four kinds of tubular membranes were tested. For each membrane, 2 h ultrasonic induced penetration of DNPH–glycerin was carried out. The results are listed in Table 1.

The results show that polysulfone membrane was broken up during ultrasonic permeation and while two other membranes of cellulose acetate and polyvinylidene fluoride were mechanically strong enough for the ultrasonic permeation. Further experiments showed that polyvinylidene fluoride (PVDF) was not only better on mechanical strength but also easier for absorbents to penetrate and coat evenly. A suitable inner diameter was selected to conveniently insert stainless connector into the membrane.

3.3. Evaluation of the sampler

3.3.1. Sampling of trace formaldehyde

3.3.1.1. Determination of collected formaldehyde with HPLC. Samplers prepared for formaldehyde were exposed to formaldehyde-containing environments with concentration of 100 μg m^{-3}. After 8 h sampling, the formaldehyde–DNPH derivative in acetonitrile phase (see 5 in Fig. 1) was analyzed by HPLC. The chromatogram is given in Fig. 3.

In comparison with standard samples, the peaks appearing at approximately 8.1 min and 5.8 min in Fig. 3 were identified as formaldehyde–DNPH and 2,4-DNPH, respectively. Other peaks are impurities of reagents used in experiment.

3.3.1.2. Effect of acidity on sampling. The formaldehyde–DNPH derivative reaction is generally acid-catalyzed [6] and requires an adjustment of the pH samples to obtain higher conversion yields and shorter reaction times [26]. However, the addition of an acid could be a possible source of contamination to environmental detection. In order to optimize the procedure and reduce contamination, absorbents with pH 3, 4.5 and 6.5 were prepared by adding different volume of phosphoric acid. The samplers with the absorbents were exposed to an experimental vessel containing 100 μg m^{-3} concentration of formaldehyde for 8 h. The derivatives (formaldehyde–DNPH) were further analyzed using HPLC. The mass of formaldehyde trapped at different pH values was also calculated and compared with standard reference. The results showed that the relative standard deviation (RSD) of the mass of formaldehyde trapped in the three samples was less than 6%, it shows that the influence of absorbent acidity was insignificant for relatively longer time sampling and reaction. Therefore, the absorbents without the addition of any acids (pH = 6.5) have been applied in experiments resulting in the simplicity of experimental procedures and reduce environmental pollution.

3.3.1.3. Effect of exposure time on sampling. Normally, increasing exposure time of the membrane sampler in air may enhance sensitivity of the method. Sampling for different exposure time (2–14 h) at two levels of concentration (100 and 500 μg m^{-3}) was carried out. The peak areas of the formaldehyde–DNPH were plotted to the exposure time in Fig. 4. The result shows that the mass of formaldehyde collected increases almost linearly with the increase of exposure time. Moreover, the mass for higher concentration increases faster than for that of lower concentrations. The results in Fig. 4 clearly show that the detected mass (peak area) is proportional to exposure time at smaller values. For the concentration of 500 μg m^{-3}, the steepness of peak area rise falls off with the exposure time after a point of 8 h, while for the concentration of 100 μg m^{-3} the point is at 10 h. This indicates that the barrier limiting mass transfer occurs in the sampling process. The derivative reaction is considered the rate-determining step of the process according to previously investigation [27]. When the concentration of formaldehyde is in excess, this chemical equilibrium of derivative reaction is occurring at equal rates in its forward and reverse directions, so that the concentrations of the products do not change with time, also known as equilibrium which will affect the yield of the formaldehyde–DNPH derivative and causes the detectible masses unproportional to their exposure time. Considering to broaden the detection range of formaldehyde (about 0–500 μg m^{-3}) and shorten the exposure time, 8 h was selected as suitable exposure time in this research.

3.3.1.4. Correlation between gaseous formaldehyde concentration and mass of the formaldehyde–DNPH derivative in extract solution. Five formaldehyde samples with concentrations of 6.7, 20.1, 40.2, 80.4 and 120.6 μg m^{-3} were generated by dynamic dilution calibrator. Gas flow rate of 100 mL min^{-1} through the vessel was controlled by a mini pump. Various sets of samplers were exposed to each level of concentration in the vessel for 8 h, the extract solution in the sampler was analyzed by HPLC. As expected the masses of the formaldehyde–DNPH derivative (collected mass) increased linearly with the concentrations of gaseous formaldehyde. When measured mean masses collected were compared with the vessel concentrations a positive linear correlation (transformation curve) was obtained, and the regression equation is $C_{HCHO} = -0.2445 + 0.1527M$, where C_{HCHO} (μg m^{-3}) is the concentration of formaldehyde in air, and M (ng) masses collected.

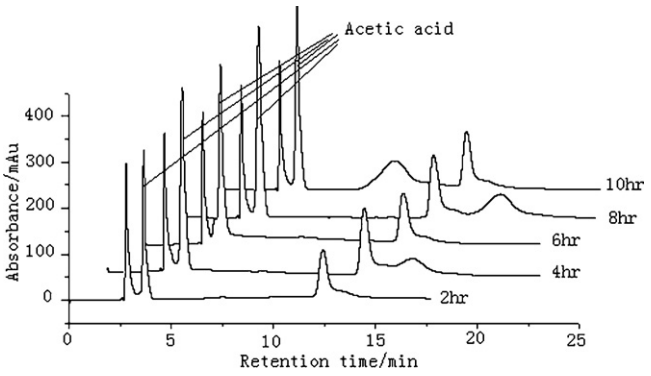

Fig. 5. Chromatograms of the acetic samples. Mobile phase: 20 mmol monopotassium-phosphate/acetonitrile (96:4, v/v). Detection wavelength: 214 nm. Injection volume: 20 μL. Flow rate: 1 mL min^{-1}. Concentration of acetic acid is 40 μg m^{-3}.

Regression analysis was performed on the data and a correlation coefficient of 0.998 was obtained. This linear correlation is very important to the quantitative analysis of formaldehyde in air, which can be obtained by using the HPLC analysis of the extract derivative and the transformation curve.

3.3.2. Sampling of trace acetic acid

In order to broaden and validate the application of the sampler, acetic acid was further investigated. Fig. 5 is the chromatogram of extract solutions from samplers after different time of exposure in acetic acid vessel with concentration of 40 μg m^{-3}. The acetic acid extracted is also easily separated and identified. The acetic acid peak was detected at approximately 3.8 min comparing it to a standard solution of acetic acid. The adjacent peak at 2.7 min and the peak at 12.3 min are not clear. These peaks probably are from the impurities of reagents such as triethanolamine reagent. We do not identify these peaks because they are separated with the peak of acetic acid completely and there is not any interference to the analyte.

In Fig. 5, the peak signal of acetic acid appears to increase with exposure time. Further exposure experiments were conducted under three concentrations (50, 100, 150 μg m^{-3}) with results shown in Fig. 6. In Fig. 6, the mass of acetic acid increases linearly with the exposure time, and the mass for higher concentration increases faster than that for lower concentration. This conclusion is similar to that of formaldehyde determination. 8 h Exposure time was selected in this study.

Sets of sampler were further investigated for four concentrations of 20, 40, 80 and 160 μg m^{-3} which is generated by standard acetic acid solution in the experimental vessel. Regression analysis

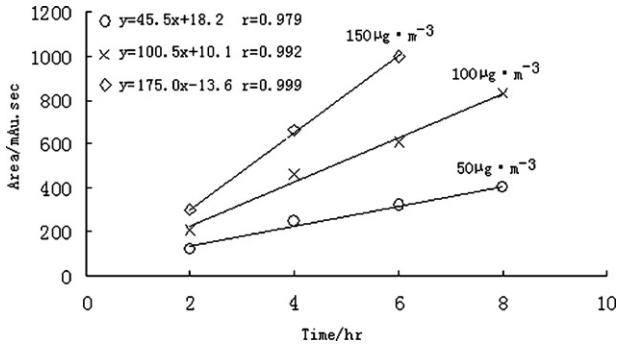

Fig. 6. Increase in mass of acetic acid collected over time: 50 μg m^{-3} (○), 100 μg m^{-3} (×), and 150 μg m^{-3} (◊).

Table 2
Error in formaldehyde determination.

Real conc. (μg m^{-3})	Mass collected (ng)	Predicted conc. (μg m^{-3})	Error (μg m^{-3})	Relative error (%)
60.3	417.4	63.5	3.2	5.31
60.3	456.3	69.4	9.1	15.1
60.3	429.2	65.2	4.9	8.13
100.5	581.8	88.5	−12.0	11.9
100.5	799.6	121.8	21.3	21.2
100.5	682.8	104.0	3.5	3.48

confirmed a good fit of the linear model between gaseous concentration and the trapped mass when adhering to the exposure time to 8 h. The regression equation is $C_{CH_3COOH} = 0.4051 + 0.0342A$, where C_{CH_3COOH} (μg m^{-3}) is the concentration of acetic acid in air, and A (mAu s) area of acetic acid peak in the HPLC chromatogram. The correlation coefficient is 0.996, indicating accurate quantitative analysis of the trace acetic acid.

3.4. Application of the sampler for the determination of formaldehyde and acetic acid

The sampler was placed in unidirectional formaldehyde flow at concentrations of 60.3 and 100.5 μg m^{-3} with rate of 100 mL min^{-1} for 8 h. Quantitative analysis was repeated three times to measure the concentration of gaseous formaldehyde for each sample according to the HPLC result and the transformation curve, the results are listed in Table 2.

In Table 2, one can find that absolute values of the determination error are from 3.2 to 21.3 μg m^{-3}, most of them are below 10.0 μg m^{-3}, and the relative errors (|detected concentration − real concentration|/real concentration × 100%) are from 3.48% to 21.2%. Mean of the relative error values are 9.51% and 12.2% for concentrations of 60.3 and 100.5 μg m^{-3}, respectively. The precision of the measurements was also calculated. Standard deviation values of the predicted concentrations are 3.04 and 16.7 μg m^{-3} corresponding to RSD of 4.6% and 15.9% for concentrations of 60.3 and 100.5 μg m^{-3}, respectively. Although few error values and RSD are not small, the results are satisfactory to formaldehyde detection in the low concentrations between 6.7 and 120.6 μg m^{-3} after comparing with the reported value [1,28]. The reported values are 50–60% lower than the real concentrations between 81 and 2978 ppb (ca. 101–3723 μg m^{-3}), and RSD of 1.3–25.4% for detection of formaldehyde ranged from 16 to 156 ppb (ca. 20–195 μg m^{-3}).

According to the suggestion of *Analytical Methods Committee* [29], the limit of detection (LOD) was estimated. LOD of formaldehyde determination was 3.32 μg m^{-3} by collecting 12 blank samples using zero air, and the LOD for the determination of acetic acid was 0.76 μg m^{-3} based on five gaseous samplers prepared as blank samples by passing through nitrogen air into the vessel for 8 h. The corresponding absolute detectable quantity estimated is 23.4 ng for formaldehyde and 19.8 ng for acetic acid, respectively. The LOD's of 3.32 and 0.76 μg m^{-3} reveal the potential application of the developed sampler to the determination of trace gaseous analytes.

Comparison of performance including detection limit, precision and accuracy of the proposed method to some relative ones recently developed was listed in Table 3.

Although sensitive sampling and analysis methods for formaldehyde have merits at different aspects, data in Table 3 shows that the proposed method based on passive sampling provides equivalent LOD value relative to the DNPH allied active methods, and significantly lower than those of solid-phase microextraction method. Moreover, the precision was established to be 4.6% and 15.9% the detection of low concentrations formaldehyde in the

Table 3
Comparison of performances between the proposed method and some preexisting methods for formaldehyde detection.

Methods	Principle	Linear range	Limit of detection (LOD)	Precision (RSD)	Accuracy
(The proposed method) Derivatization on DNPH-ladden PVDF micro-membrane	Room temperature on-line derivatization, HPLC-UV detection	0–120.6 ($\mu g\,m^{-3}$)	3.32 $\mu g\,m^{-3}$ (or 2.48 ppbv) (23.4 ng)	4.6% (60.3 $\mu g\,m^{-3}$) 15.9% (100.5 $\mu g\,m^{-3}$)	9.51% (60.3 $\mu g\,m^{-3}$) 12.2% (100.5 $\mu g\,m^{-3}$)
Derivatization with dinitrophenylhydrazine (DNPH) and analogs [5]	HPLC separation visible absorbance detection. Electrochemical detection	–	2.68 $\mu g\,m^{-3}$ (or 2 ppb)	–	–
Derivatization with Fluoral-P reagent [30]	80 °C for reaction, fluorimetric detection	–	0.55 ng mL^{-1} (0.55 $\mu g\,L^{-1}$)	8.6% (5 $\mu g\,L^{-1}$)	0.48% (5 $\mu g\,L^{-1}$)
	Gaseous samples, GC-flame ionization detection	15–3200 ppbv	40 ppbv (10 s) 4.6 ppbv (300 s)	12% (15 ppbv, 300 s) 2% (3200 ppbv, 10 s)	–
Derivatization with PFBHA[a] on SPME fibers [31,27]	Liquid samples, HS-SPME, GC-flame ionization detection	25–250 ($\mu g\,L^{-1}$)	25 $\mu g\,L^{-1}$ (liquid sample)	10.5% (100 $\mu g\,L^{-1}$)	–
Derivatization with PFPH[b] on SPME fibers [27]	HS-SPME, GC-flame ionization detection	65–250 ($\mu g\,L^{-1}$)	65 $\mu g\,L^{-1}$	10.7% (100 $\mu g\,L^{-1}$)	–
Derivatization with PFBHA/PDMS/DVB[c] fiber [32]	Time-Weighted Average Sampling GC–flame ionization detection	–	23.8 ng (1007 min for exposure to 636 ppbv)	–	6.8% (679 ppbv)

[a] PFBHA: o-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine hydrochloride.
[b] PFPH: Pentafluorophenylhydrazine.
[c] PDMS/DVB: Poly(dimethylsiloxane)/divinylbenzene.

range of 60.3 and 100.5 $\mu g\,m^{-3}$, which is acceptable comparing with the 8.6% for 5 $\mu g\,L^{-1}$ (equivalent to 5 $mg\,m^{-3}$) and 2% for 3200 ppbv (ca. 4000 $\mu g\,m^{-3}$) formaldehyde given by fluorimetric determination and SPME method, although the latter two methods have advantages in relative shorten exposure time and wider linear range. The development of such a low cost and easily operated sampler will certainly enhance the conservator's ability to describe art objects exposure to airborne pollutants in enclosed microenvironment.

To further evaluate reliability of the developed sampler, the micro-membrane sampler was field-tested against a well known EPA standard method, i.e., Compendium Method TO-11A (EPA/625/R-96/010b, 1999) in which formaldehyde is collected in SKC formaldehyde sampling tube (Cat. No. 226-119) containing 2,4-dinitrophenylhydrazine.

The compatibility of two approaches is discussed based on the concurrent measurements of the identical environment in an 100 m^2 room. There is a 25 m long wooden table and 40 wooden chairs in the room. The table and chairs are painted. Although they have been used for about 10 years, small amount of formaldehyde is still being released. In order to adjust concentration of formaldehyde pieces of particleboard were put into the room keeping at least 24 h before sampling. When sampling, three developed samplers hung in scattered locations in the room for 8 h exposure, meanwhile active sampling for Compendium Method TO-11A was also made with 20 min sampling time at 0.5 L min^{-1}. Average result of the three samplers for the developed method was compared with the EPA method. The measurements using the proposed method and the EPA method were carried out three times for concentrations of formaldehyde. The results of the three measurements were presented in Table 4.

For three concentrations of 43.1, 73.7 and 80.3 $\mu g\,m^{-3}$, results of the micro-membrane method were quite close to those of the EPA method (Standard DNPH-HPLC method). The errors between them are −0.7, 4.6 and 2.6 $\mu g\,m^{-3}$, and the relative errors are −1.60%, 6.66% and 3.35% for the three concentrations, respectively. These results reveal the reliability of the proposed method in formaldehyde measurements comparing with standard DNPH-HPLC method.

Table 4
A comparison study between the proposed method and standard DNPH-HPLC method in formaldehyde detection.

Order	The proposed method ($\mu g\,m^{-3}$) (8 h)	Standard DNPH-HPLC method ($\mu g\,m^{-3}$)	Error ($\mu g\,m^{-3}$)	Relative error %
1	43.1	43.8	−0.7	−1.60
2	73.7	69.1	4.6	6.66
3	80.3	77.7	2.6	3.35
|Aver|	–	–	2.6	3.87

4. Conclusions

A chemical potential driven micro-membrane sampler based on dynamic reaction and on-line extraction has been designed. A corresponding improved method for collecting trace airborne carbonyl has also been developed for sampling and enrichment of trace gaseous analytes following HPLC analyses of the extracted derivatives.

The mass of analytes collected by the sampler and detected by HPLC shows a linear correlation to the concentration of gaseous analytes. This indicates that it can be used in the quantitative analysis of the pollutant gases. Mean relative error of the detection of formaldehyde concentration is around 10.0%, and the RSD values of three detections are about 9.8%. The limit of detection has been estimated as 3.32 and 0.76 $\mu g\,m^{-3}$ for formaldehyde and acetic acid, respectively.

The sampler developed in this study provides a simple method for determining accurate concentrations of airborne carbonyl compounds. As the sampling system is easy to assemble and operate, it can be potentially applicable to trace pollutant monitoring, particularly in small spaces, such as museum showrooms to monitor and assess the possible risks to collections.

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