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Controlled generation of peracetic acid atmospheres for the evaluation of chemical samplers†

Amos Doepke, **Angela L. Stastny**, **Robert P. Streicher**
Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Health Effects Laboratory Division, Chemical and Biological Monitoring Branch, Cincinnati, Ohio 45213, USA

Abstract

A system for controlled generation of peracetic acid (PAA) atmospheres used to test and evaluate sampling and measurement devices was developed and characterized. Stable atmospheric conditions were maintained in a dynamic flow system for hours while multiple sensors were simultaneously exposed to equivalent atmospheres of PAA vapors. Atmospheres characterized by a range of PAA concentrations at a controlled flow rate, temperature, and humidity were generated. Presented herein is a system for vaporization of PAA solutions to generate controlled atmospheres with less than 3% relative standard deviation (RSD) of the PAA concentrations over time.

1. Introduction

Peracetic acid (PAA) is a strong oxidizer, which makes it an effective chemical disinfectant.[1] PAA is also a strong irritant, capable of producing severe chemical burns.[1–4] Determining the relationship between the magnitude of exposure to PAA and the health effects are critical to protecting worker health. Accurate measurement of PAA vapor concentrations and evaluation of measurement devices are important components of understanding PAA exposure. The goal of the experimental design and research presented herein was to produce peracetic acid (PAA) atmospheres suitable for evaluating PAA vapor sampling, measurement, and analysis methods in a controlled environment. To achieve this, generated test atmospheres must: (1) enable simultaneous exposure of multiple samplers to equivalent

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ADoepke@cdc.gov .

Author contributions
Contributions to the work herein by Amos Doepke include project conceptualization, data curation, methodology, project administration, supervision, validation, visualization and writing the original draft. Angela L. Stastny contributed to the conceptualization, data curation, formal analysis, investigation, methodology, project administration, procurement of resources, validation, writing and reviewing of this work. Robert P. Streicher contributed to the conceptualization, methodology, project administration, supervision, writing, reviewing and editing of this work.

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Conflicts of interest
There are no conflicts to declare.

atmospheres; (2) maintain a continuous stable atmosphere for a duration to exceed experimental time frames; and (3) produce a range of analyte concentrations, air velocities, temperatures and humidities.[5,6] The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) for PAA is 0.4 ppmv.[7] The goal was to generate PAA atmospheres with concentrations from one tenth of the TLV up to 100 times the TLV.

PAA is a reactive chemical, which presents some inherent challenges to generation of standard reference materials and atmospheres. PAA is a strong oxidant and PAA solutions are labile, thus it is difficult to keep reference standards or atmospheres. In solution, PAA and water are in equilibrium with acetic acid (AA) and hydrogen peroxide (HP). The equilibrium shifts as solutions of PAA evolve oxygen gas through the degradation of HP. Dynamic PAA atmospheres which are flowing and continuously refreshed are the preferred method for exposing samplers to equivalent atmospheres. Generation of static atmospheres by evaporating PAA solution into a closed container cannot be maintained for very long before needing to be refreshed. Dynamically generated atmospheres, created by a continuously renewed flow of air as a carrier and a source of PAA vapors are necessary for evaluating sensor performance over timeframes relevant to protecting worker health.

Generation of PAA vapors can be accomplished from vaporization, assisted by applying heat or using aerosolization with a nebulizer to accelerate evaporation. PAA reacts with glass to hydroxylate the silica. Henneken *et al.* used a glass syringe to deliver PAA solution to a nebulizer; however, gas bubbles formed in the syringe, leading to uncontrollable ejection of the PAA solution from the syringe.[8] To mitigate this, Christensen *et al.* used acid washed syringes to generate atmospheres of up to 2 ppm with a reported 95% recovery of theoretical delivered PAA.[9] Dugheri *et al.* also reported using a syringe system to deliver PAA.[10] Dilute solutions of PAA can help to mitigate gas evolution but require more energy to evaporate and introduce additional humidity.

An alternative is air bubbled through a PAA solution to obtain a saturated headspace which is mixed with a carrier stream. Hecht and Héry mixed PAA solution and buffer in a flow, to create the acetate salt in solution, which minimized acetic acid vapor in the headspace.[11] They swept the headspace above the mixed stream of buffered PAA solution in their generation system. For the experiments detailed in this manuscript, PAA vapors were swept directly from the headspace above an “as received” PAA solution into our generation system. For both the work of Hecht and Héry and the work presented herein, the flow rate of the air sweeping the headspace was varied to achieve the desired concentration of PAA after dilution into the carrier gas stream. When evaporating diluted PAA solutions using a nebulizer, the minimum humidity range is limited due to the water content in the dilute PAA solution. Thus, a wider humidity range on the low end is available when sweeping the headspace. The ability to maintain the concentration of PAA in the headspace above the solution is limited by the kinetics at the PAA solution–air interface. A practical solution was achieved using a PAA delivery system where air was passed through the headspace above a PAA solution in a vial.

Detection of PAA vapor concentrations has some challenges. Among published examples of vapor generation systems, there is consistency of the choice for a reference measurement. Effkemann *et al.* determined PAA recovered from generated atmosphere samples *via* an impinger containing a solution with methyl-*p*-tolyl sulfide or a solution with 2,2′-azino-bis(3-ethyl-benzothiazoline)-6-sulfonate.[12,13] Henneken *et al.*[8] and Christensen *et al.*[9] also reported impinger sampling of generated PAA concentrations (*via* methods in ref. 12 and 13) used as the independent reference for the measurements. An impinger with a *N,N*-diethyl-*p*-phenylenediamine (DPD) analysis was used as the reference measurement for the PAA concentrations in the generated atmospheres described herein.

2. Materials and methods

Water was deionized to >18 MΩ cm using an Evoqua Water Technologies (Pittsburgh, PA) water purification system. PAA solution (32% w/w of PAA, 40–45% w/w of acetic acid, and <6% w/w of H_2O_2) was purchased from Sigma Aldrich (USA). A V-2000 photometer and PAA Vacu-vials® instrumental test kits (K-7913) were purchased from Chemetrics (Midland, VA). 50 mL glass impingers were purchased from Ace Glass (Vineland, NJ). Electrochemical PAA sensor measurements were made with a SafeCide™ Portable Monitor from ChemDAQ Incorporated (Pittsburgh, PA). SAS 9.4 statistical software suite was used for PROC GLM statistical analysis.

Model 501, Miller-Nelson Instruments, Flow Temp Humidity Control System (Assay Technologies, Livermore, CA). Environmental chamber from Darwin Chambers Company (St. Louis, MO). Model 4043 Flow meter from TSI Incorporated (Shoreview, MN). Temperature and humidity sensor/recorder from Onset Corp (Bourne, MA). Custom glass mixing chamber from Kontes Kimble-Chase Glass (Vineland, NJ). Sample manifold and glass columns from Ace Glass (Vineland, NJ).

2.1. Overview of vapor generation and sampling system

A block diagram of the vapor generation system is shown in Fig. 1. An air flow, temperature and humidity control system, connected to house air and de-ionized water reservoir was used to generate conditioned air for the experiment. The air flow temperature and humidity control system was capable of air flows ranging from 0 to a maximum of 20 L min^{-1} and a temperature range from ambient ±2 °C to 35 °C. The minimum humidity of the compressed then filtered air supply was 10% relative humidity (RH). The conditioning system could condition the air up to 95% RH. An environmental chamber with an internal volume of 630 liters allowed the experiment to be contained in a temperature-controlled environment. The environmental cabinet could maintain constant temperatures in a range from 10 to 60 °C. The output air from the air conditioning control system was measured with a flowmeter, and temperature and humidity sensor/recorder inside the chamber. The conditioned air flowed into a glass column, where the headspace from the PAA delivery system was introduced. From there the headspace and carrier air passed into a 2 liter mixing chamber. A three-way valve directed the air flow to either the sampling manifold or exhaust. The sampling manifold was a 25 mm I.D. glass tube with multiple sample ports along the length. More information regarding the sampling column is shown in ESI Fig. S1.† A detailed drawing of the components inside of the environmental chamber is included as Fig. S2.†

Flow rates of the carrier air were typically in a range from 11 to 19 L min^{-1}, dependent on the desired flow rate through the sampling column. The carrier air was held at a constant flow rate during the sampling time frame. There are multiple ports to connect several samplers. A volumetric flow rate of 18.3 liters per minute passed through the 2.54 cm diameter sampling column resulted in a linear flow rate of 0.6 m s^{-1} for the atmosphere at the beginning of the sampling column. The sensors and impingers were sampled from this stream at a rate of 1 liter per minute. The volume of atmosphere consumed by each sampling method should be considered when setting a carrier flow rate. We have used sensors that consumed a combined 7 L min^{-1} from an 18 L min^{-1} total flow. A vacuum manifold with critical orifices was used to draw the atmospheres through sample media, sample tubes or impingers at controlled rates, which are independent from the atmosphere flow rate through the sampling column. The exhaust from the sampling column routed to a fume hood.

2.2. Configuration of the PAA delivery system for headspace

PAA vapors were delivered to the atmosphere generation chamber by passing air through the headspace of a 40 mL glass vial, containing PAA solution, as in Fig. 2, into a carrier air stream. We chose not to bubble the air through the PAA solution in the vial, because it caused fluctuations in the generated PAA concentration coinciding with bubble frequency. Typically, a 2 to 10 mL aliquot of PAA solution was placed in the vial. The pressure regulator delivered 5 psi from a 100 psi source. The PAA concentration in the generated atmosphere was easily controlled by adjusting the needle valve which changed the flow rate of air through the vial. The PAA delivery system was kept outside of the environmental cabinet, at room temperature in the laboratory where temperatures fluctuated less than one degree Celsius. By keeping the PAA vial outside of the cabinet, the conditions of the carrier air, flow rate, temperature, and humidity could be adjusted without causing changes to the kinetics of the PAA evaporation. This delivered a constant amount of PAA, independent of environmental adjustments inside the chamber and negated any need to wait for the kinetics in the PAA vial to equilibrate at new temperatures while making adjustments to the system.

2.3. Configuration of impingers

Two glass impingers filled with 15 mL of deionized water were connected in a sampling train by Tygon® tubing. The sampling column was connected by tubing to the front impinger which was connected to the back impinger then to a critical orifice (1 L min^{-1}) followed by a vacuum. A Dry-Cal flowmeter from Mesa Labs was used to verify the flow rate of the air through the impinger inlet before and after sampling. Air samples were pulled through the impinger at 1 L min^{-1} for 15 minutes resulting in a total sample volume of 15 liters. The PAA collected in the impinger was analyzed using a Chemetrics DPD test kit. Immediately after sampling, an aliquot of the deionized water sample media was analyzed for PAA concentration using a Peracetic Acid Test Kit, K-7913 from Chemetrics. The Chemetrics test kit has an analytical range up to 5.00 ppmw (aq.) of PAA. For 15 liter

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samples of PAA atmospheres up to 1.6 ppmv of PAA vapor, the impinger solution can be analyzed directly without dilution. When sampling atmospheres with greater concentrations than 1.6 ppmv of PAA vapors, an aliquot of the impinger solution was diluted with deionized water to fall within the working range of the Chemetrics test kit before analysis. When required, 15 mL impinger samples were diluted to 500 mL in a volumetric flask.

3. Results and discussion

3.1. Range of atmospheres generated

Generated atmospheres of PAA vapor for other systems in the literature reported maximum concentrations from 4.6 to 10 ppmv.[8–13] Minimum concentrations in the literature varied from 0.02 ppmv (ref. 10) to 0.6 ppmv (ref. 11). Christensen *et al.* reported that the minimum concentration achievable was due to limitations of stability of dilute PAA solutions when using a syringe to deliver the PAA.[9]

The typical working PAA concentration range in our generated atmospheres was from 0.03 to 55 ppmv of PAA vapor. A feature of this generation system was the use of a commercial PAA solution as received and the ability to rapidly change the generated concentration of PAA vapor by adjusting the headspace sweep rate *via* a needle valve. The equilibrium time for the generated PAA concentration was approximately 5 minutes as monitored by an electrochemical sensor when changing the concentration of PAA generated *via* headspace sweep rate by adjusting the needle valve. The maximum concentration of PAA in the swept headspace is limited by the PAA vapor pressure, the PAA evaporation rate, the air-liquid surface area, and the headspace volume inside the vial. While the minimum concentrations that could be generated are generally limited by the precision of the needle valve controlling the headspace sweep rate, the verification of minimum concentrations of generated PAA vapors becomes a function of the limit of detection for the reference measurement.

The experiments shown herein were conducted at 20 ± 1 °C and 50 ± 2% RH in a total flow rate of 18.3 L min^{-1}. The volumetric flow rate of the atmosphere contributes to the linear flow rate at the sampling location, which depends on several factors, of which the largest influences are: the sample column diameter and the number of samplers and their sampling rates. Changes to temperature and humidity require approximately 30 minutes to equilibrate. Humidity change equilibrium times are due to the limitations of the Miller-Nelson. The time required for equilibration of temperature involves the change in both the temperature of the carrier air generated by the Miller-Nelson and the equilibration of the environmental chamber.

3.2. Maintain a continuous atmosphere

Fig. 3 shows multiple hours of continuously logged (a) temperature, (b) pressure and (c) flow rate from the TSI flow meter, (d) humidity and (e) temperature from the Onset sensor, and (f) PAA concentration measurements from a ChemDAQ electrochemical PAA sensor. The vertical grey bars in Fig. 3 represent the fifteen-minute intervals when impingers were actively sampling. The spikes in humidity and flow rate at regular intervals were due to the Miller-Nelson replenishing an internal water reservoir used to maintain humidity. The system generated consistent atmospheres for time frames that exceeded those of required sampling durations for sensor evaluation.

3.3. Generating a range of PAA concentrations in controlled atmospheres

Impingers were used to monitor (15 min time-weighted average) the PAA concentration (20 °C and 50% RH) at time intervals (dots) over several hours as shown in Fig. 4. The horizontal lines were the mean PAA vapor concentrations and dashed lines the standard deviation, which were (a) 0.228 ± 0.005, (b) 0.37 ± 0.01, (c) 0.66 ± 0.02, (d) 1.42 ± 0.03, (e) 22.4 ± 0.3, and (f) 33.2 ± 0.5 ppmv. The RSDs of mean impinger measurements were less than 3% (Fig. 4), when generating atmospheres of PAA over a range of concentrations for multiple hours.

Data from Fig. 4 was fit to a linear model with the dependent variable being ppmv and the independent variables being time and group. The groups (a through f) were labeled from 1 to 6. The linear model was run without an intercept. The results shown in Table 1 indicate that time was not significant ($p = 0.4267$) meaning that we have evidence that the magnitude of the measurements did not change over time. In addition, the 95% confidence interval for the coefficient (−0.01940) for time was quite narrow (−0.06862, 0.02982).

The confidence intervals for the least squares means (lsmean) of the six groups were quite narrow – thus providing evidence that the variability of the measurements over time was small. The statistical evidence indicates that the drift was not substantial in terms of magnitude or variability among the groups.

3.4. Simultaneous exposure of multiple samplers to equivalent atmospheres

A stable concentration of PAA was maintained in the atmosphere generator for more than 6.5 hours. Impingers were connected to 3 ports along the sampling column (ESI Fig. S1†) with impinger measurements (15 minutes at 1 L min^{-1}) initiated at 1.0, 4.5, 5.5, and 6.5 hours after generation began (Table 2). Each measurement was done using a clean impinger with fresh sampling media. The average PAA vapor concentration was 0.79 ± 0.024 ppmv. The RSD of the measurements at a port locations was 3%. The 3% RSD in the measurements from the atmosphere generation system was consistent with the inherent variability of the impinger DPD measurement method. Measurements from impingers that were simultaneously sampling from different ports along the sampling column indicated the concentration of PAA vapor in the air was stable and equivalent at the sampling port locations.

3.5. Consumption of PAA solution by evaporation

When generating atmospheres at concentrations near the AGCIH TLV of 0.4 ppmv (g), the amount of PAA solution consumed by evaporation was small compared to the 2 mL typically used in the vial (shown in Fig. 2). However, the relative amount of PAA solution evaporated when generating atmospheres of higher concentrations of PAA may be significant. The volume of PAA in the vial should be sufficient so that a relatively small portion of the PAA solution evaporates from the vial during the experimental time frame.

PAA solution consumption was calculated by starting with the ideal gas constant (R) to determine the number of moles of gas (n) in a volume (V) at a given temperature (T) and pressure (P) as shown in eqn (1).

$$n = \frac{PV}{RT} \tag{1}$$

Then, using the calculated moles of gas and a given ppmv of PAA, the moles of PAA were determined. The moles of PAA were multiplied by the molecular mass of PAA to calculate a concentration of PAA as mass per volume. At 20.7 °C and 999 mbar, an atmosphere of 1 ppmv PAA vapors contained 3.16 µg PAA vapors per liter. To calculate a consumption rate for the mass of PAA, when generating an atmosphere of a specified concentration, we multiplied the mass per volume by the total flow rate. To maintain an atmosphere of 1 ppmv PAA vapors at the flow rate of 18.3 L min^{-1} required 57.9 µg of PAA per minute.

To enable our theoretical calculations of evaporation rate, we assume for a 29% w/w PAA solution that, for every 29 grams of PAA evaporated, 100 grams of total solution was evaporated. This assumption requires that the concentration ratios of the components in solution are maintained in the headspace. A second assumption was that our solution of 29% PAA had a density of 1.04 g mL^{-1}, which was the value listed by the manufacturer for a 32% solution. For a 29% w/w PAA solution with a density of 1.04 g mL^{-1}, the solution evaporation rate would be 11.32 µL h^{-1} to create a 1 ppm PAA atmosphere at a flowrate of 18.3 L min^{-1}. If the PAA vapor concentration (ppmv) were treated as a dependent variable and the solution evaporation rate (µL h^{-1}) as the independent variable, then the relationship would have a slope of 11.32 µL h^{-1} ppmv$^{\mu 1}$. The solution evaporation rate at 45 ppmv of PAA vapors was predicted to be 509 µL h^{-1}, which can be a considerable amount of PAA solution consumed after several hours of generation.

PAA solution consumption rates were experimentally determined by directly measuring the change in the mass of the PAA vial before and after generating atmospheres. After 7.25 hours generating a 33.2 ppmv PAA atmosphere (at 18.3 liters per minute, 20.7 °C and 999 mbar), a mass change of 2.70 g (from an initial 6.51 g) was measured for the PAA solution (an evaporation of 42% of the original mass). An evaporation rate of 358 µL h^{-1} was determined, which was lower than the theoretically calculated rate of (33.2 ppmv × 11.32 µL h^{-1} ppmv^{-1} =) 376 µL h^{-1} by 5 percent. The relative agreement between the observed and theoretical rates suggests that our theoretical calculations were useful for predicting the consumption rate of PAA solution.

The weight percent of each component as specified by the manufacturer for a 32% PAA solution are listed in Table 3. The vapor pressures of the PAA and AA components are similar relative to the H_2O and HP values.

For the purposes of our experimental inquiry, we have not been able to see a practical path to a theoretically derived vapor phase concentration of the components in the headspace effluent from the PAA vial. Use of Henry's law constants would be inappropriate for concentrated solutions. Application of Raoult's law to advance our cause was also problematic given that the headspace in the vial was not at an equilibrium but was constantly diluted by flowing air through the headspace. Using the vapor pressure of PAA to calculate a rough estimate of the headspace concentration at atmospheric pressure was as follows. In an atmosphere at 999 mbar, the vapor pressure of 14.5 mm Hg is 1.9% of the headspace. 1.9% of 0.0409 moles L^{-1} of gas at 293.7 K equals 7.92×10^{-4} moles PAA per liter, or 60 μg of PAA per mL of headspace.

By measuring the atmospheric PAA concentration in the generation chamber and the flow rate of the headspace through the PAA vial (from Fig. 2), we calculated a PAA concentration in the headspace effluent from the PAA vial. We collected the effluent from the PAA vial in a Tedlar bag for 2 minutes, then measured the volume in the bag by extracting the contents into a syringe with graduation markings. From $n = 3$ measurements, a volumetric flow rate of 110 ± 2 mL min^{-1} through the PAA vial was calculated. The vial effluent combined with the carrier air, created a total flow rate of 18.3 L min^{-1} (at 20.5 °C and 1016 mbar) and generated an atmosphere of 22.44 ± 0.3 ppmv (71.0 μg L^{-1}) PAA. In this situation, a PAA solution evaporation rate was calculated to be 259 μL h^{-1}. The PAA concentration in the effluent of the PAA vial was calculated to be 11.8 μg PAA vapor per mL of headspace.

The difference in magnitude between the 60 μg of PAA per mL of headspace calculated *via* Raoult’s law and the 11.8 μg PAA per mL of headspace calculated *via* measuring the headspace volumetric flow while generating atmospheres, suggests that there are additional factors beyond atmospheric pressure that need to be considered in this situation. In the future we would like to investigate the role of PAA solution evaporation rate as a contributing factor when explaining the observed PAA concentrations in the effluent from the PAA vial. The evaporation of the PAA solution to generate PAA atmospheres produced steady atmospheric concentrations of PAA which were observed for extended periods of time.

4. Conclusions

We have demonstrated a successful design and implementation of controlled generation of PAA atmospheres capable of covering an occupationally-relevant range of PAA concentrations, flow rates, temperatures, and humidities. Sweeping the headspace from a vial of PAA solution offers a stable delivery of PAA vapors to a carrier stream. Homogeneous atmospheres were created and continuously flowed through a sampling column where sensors were simultaneously exposed to equivalent atmospheres for hours. There were no differences between the concentration of PAA from the sampling port locations. An efficient vaporization of PAA solution and delivery of PAA vapors to sampling devices was characterized. The observed PAA concentrations and PAA consumption rates were similar to our theoretical calculations by comparison, which gave us confidence in the assumptions used to predict PAA solution consumption while generating PAA atmospheres. Theoretical and practical criteria for generation of atmospheres of PAA vapors suitable for testing and evaluating sampling devices were achieved.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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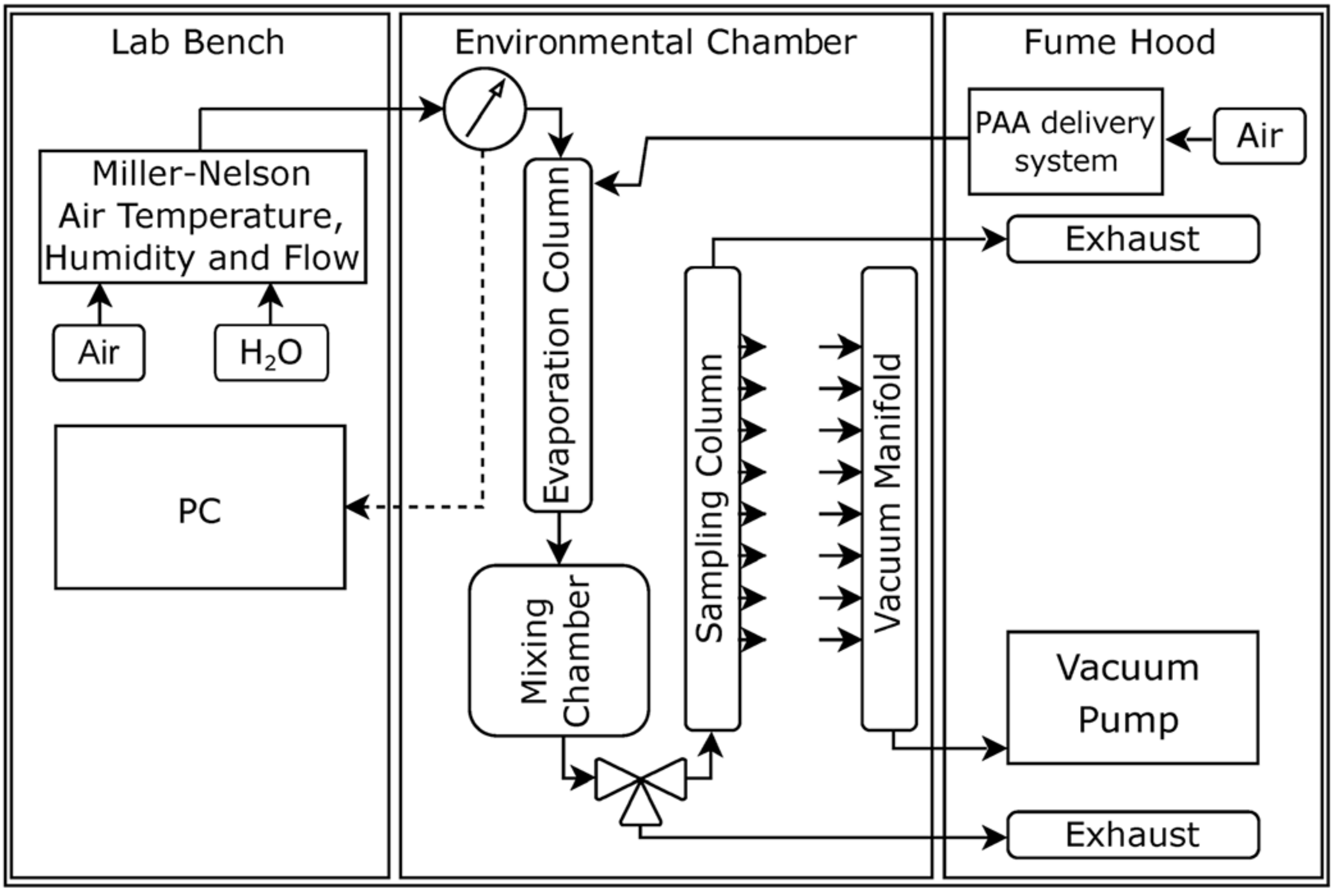

Fig. 1.

Block diagram of the atmosphere generation system used to for evaluation of samplers in atmospheres of controlled PAA concentrations, flow rates, temperatures, and humidity.

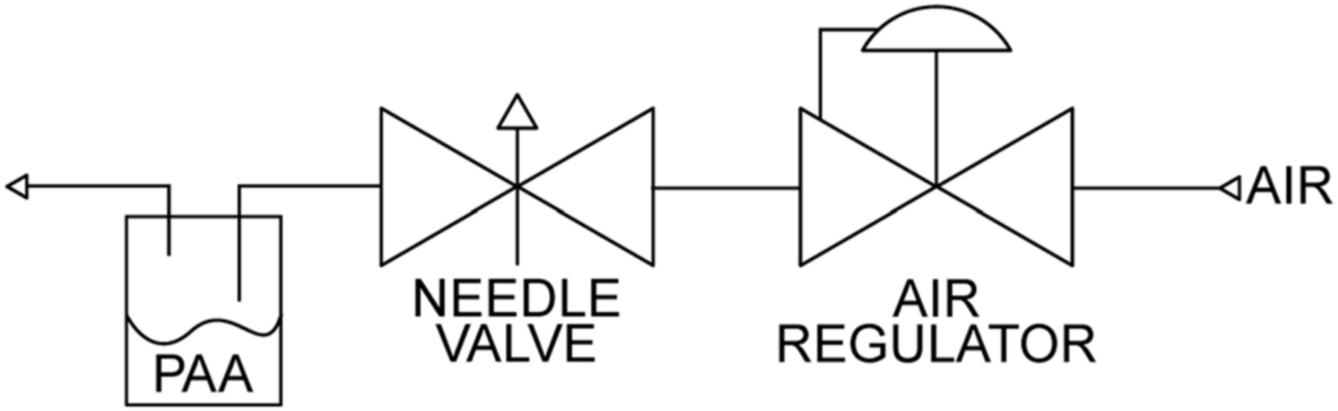

Fig. 2.

Diagram of the PAA vapor delivery system where an air pressure regulator and needle valve control the flow of air through the headspace of a vial containing PAA solution. The headspace effluent was mixed into a stream of carrier air.

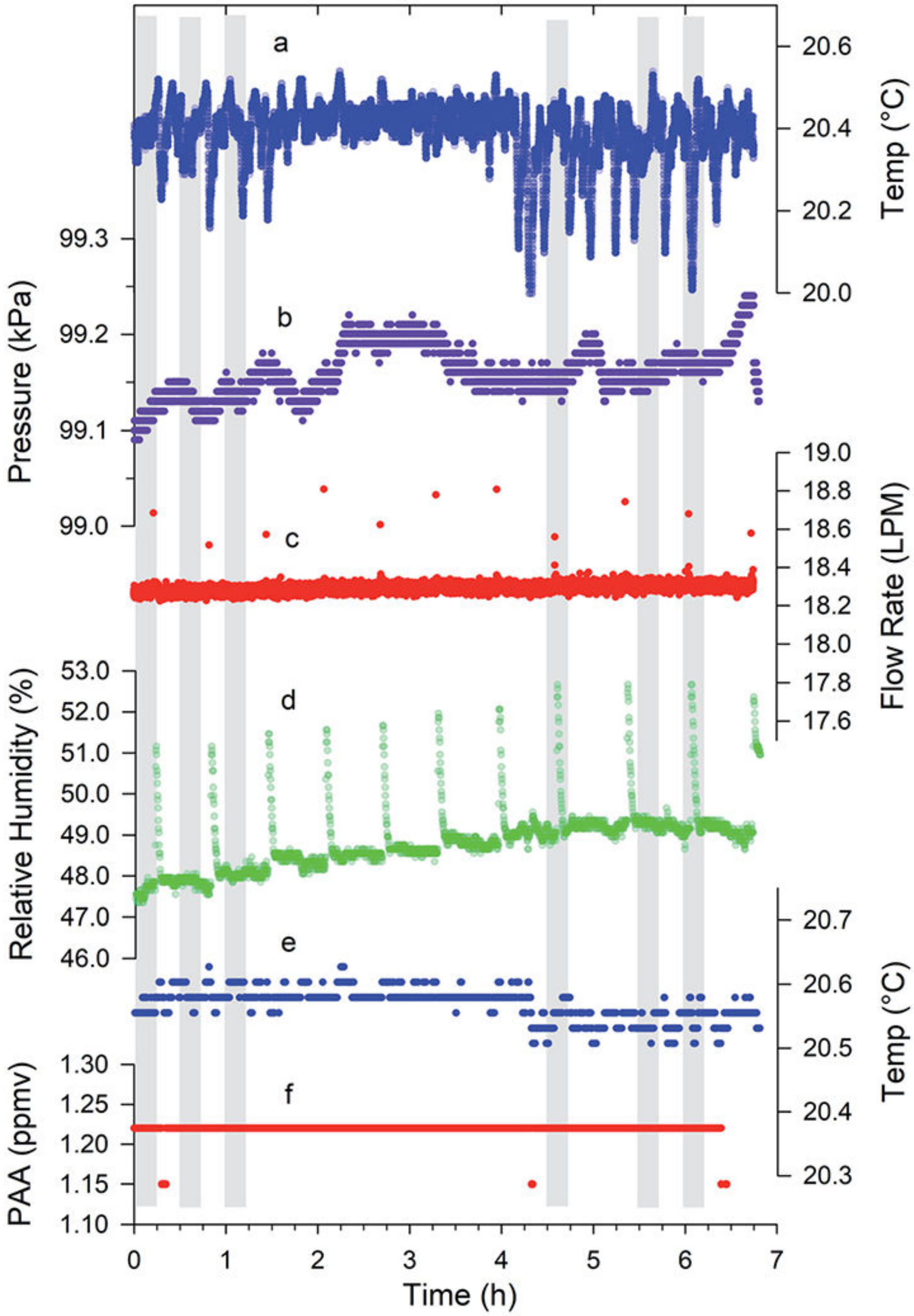

Fig. 3.

Simultaneously recorded (a) temperature, (b) pressure, (c) flow rate, (d) relative humidity, (e) temperature and (f) PAA vapor concentration as measured by electrochemical sensor plotted *versus* time.

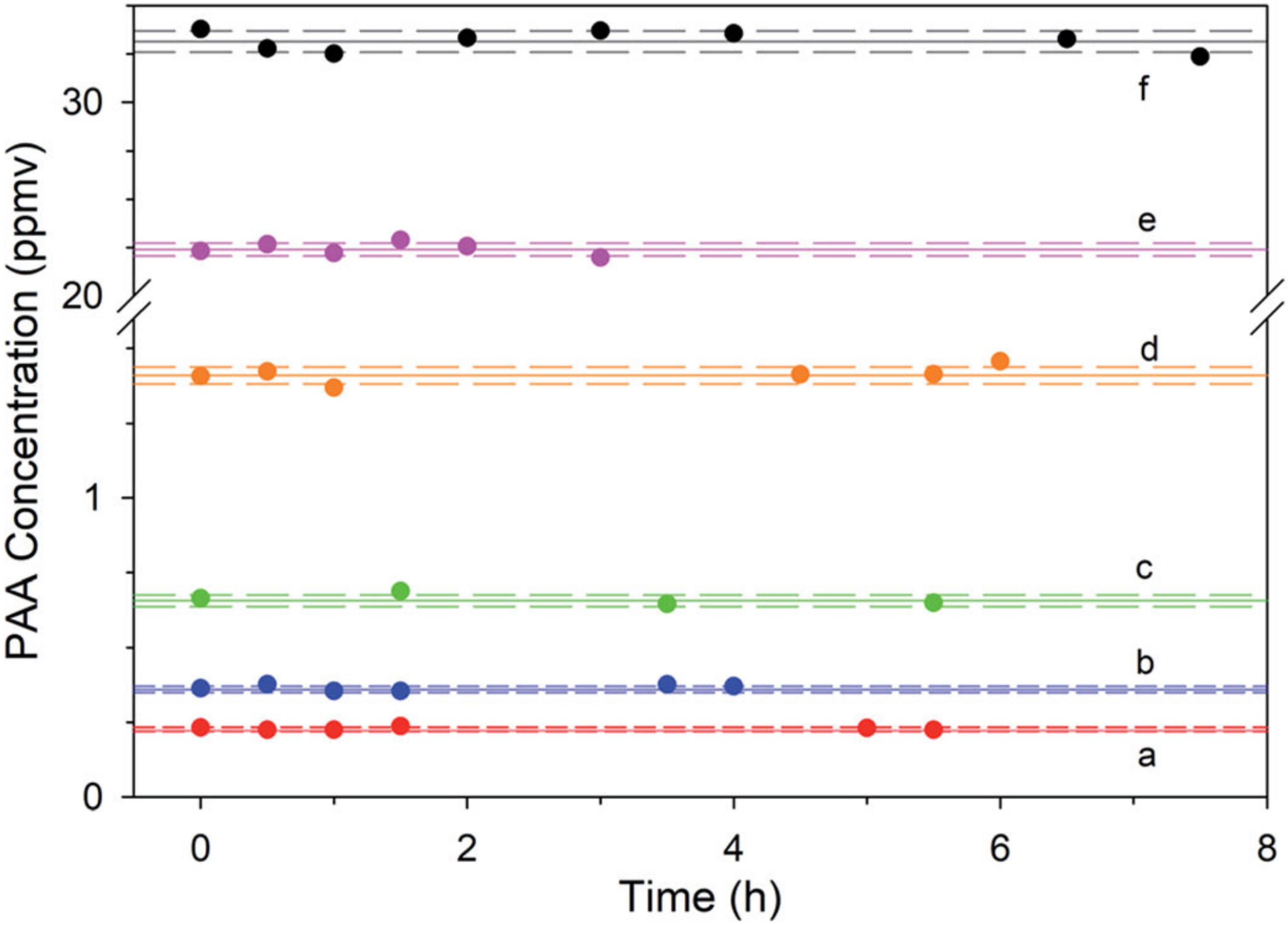

Fig. 4.

Concentrations (a)–(f) of PAA vapors (ppmv) determined at intervals (dots) by impinger collection then DPD analysis while generating PAA atmospheres maintained for several hours. The mean (solid lines) ± the standard deviation (dashed lines) are shown.

Table 1

Results of a linear model with dependent variable ppmv and independent variables time and group

Source	**DF**	**Type III SS**	**Mean square**	***F* value**	***p*-value**
Time	1	0.0584	0.0584	0.65	0.4267
Group	6	8964	1494	16 623	<0.0001

Table 2

Atmosphere concentrations of PAA vapors determined by impinger 15 minute measurements at different positions (ports) on the sampling column over 6.5 hours, demonstrating the equivalency of PAA concentration along the sampling column

		1.0 h	**4.5 h**	**5.5 h**	**6.5 h**	**Average ± S.D. (ppmv)**
PAA concentration (mg L^{-1})	Port 2	0.76	0.80	0.80	0.80	0.79 ± 0.02
	Port 8	0.76	0.74	0.81	0.81	0.78 ± 0.04
	Port 10	0.76	0.78	0.80	0.79	0.78 ± 0.02

Table 3

PAA solution component composition and vapor pressures

	PAA	**H_2O**	**AA**	**HP**
Percent weight[a]	32%	17–25%	40–45%	<6%
Molarity	4.8	13.8	7.5	1.9
Vapor pressure[b] (mm Hg@25 °C)	14.5	23.6	15.7	1.97

[a] Millipore-Sigma.[14]

[b] PubChem.[2]