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Passive Sampling of Airborne Peroxyacetic Acid

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The first passive sampling device for the determination of airborne peroxyacetic acid (PAA) is presented. 2-([3-{2-[4-Amino-2-(methylsulfanyl)phenyl]-1-diazenyl}phenyl]-sulfonyl)-1-ethanol (ADS) is used to impregnate glass fiber filters, and the reagent is oxidized by PAA to the corresponding sulfoxide ADSO. After elution of the filters, ADS and ADSO are separated by reversed-phase HPLC and detected by UV/visible absorbance. Limit of detection is 30 ppb, limit of quantification is 90 ppb (for 30 min sampling), and the linear range comprises 2 orders of magnitude. Thorough investigations were carried out with respect to the selectivity of the method toward hydrogen peroxide, and air samples were analyzed successfully after disinfection of a laboratory area.

Due to its oxidative properties, peroxyacetic acid (PAA) has been established in recent years as an important disinfectant, sterilant, and sanitizer in the food and beverages industries and for medical applications. Furthermore, it is frequently applied as bleaching agent or disinfectant in textile, pulp, and paper industries.[1] It has found increasing attention as a disinfectant for wastewater effluents as well. The proven effectiveness against a wide range of microorganisms and decomposition into environmentally beneficial and biodegradable compounds, such as water, oxygen, and acetic acid, are important properties. One of its major advantages compared with other sanitizers is the applicability under cold conditions, such as 5 °C, without experiencing any cold temperatures failure.[2]

Peroxyacetic acid is highly irritating to the skin, nose, throat, and lungs. Higher exposure may cause pulmonary edema, while eye contact can cause severe irritation and burns leading to permanent damage. High or repeated exposure may also cause liver and kidney damage. In many industrial and medical applications, a release of PAA cannot be fully avoided. Therefore, the airborne concentration must be monitored on a regular basis to prevent workers from being exposed to hazardous levels of PAA. In 1998, the European Parliament adopted a directive on the placing of biocidal products on the market, in which peroxyacetic acid is included.[3] So far, however, no official occupational exposure limits, such as threshold limit values (TLV) and time-weighted average (TWA), for PAA have been established. Therefore, many chemical and pharmaceutical companies use 1 ppm as an internal threshold value for the PAA workplace concentration, thus following the existing TLV for hydrogen peroxide (HP) as related compound. Recently, Gagnaire et al. published results based on bioassays and RD_{50} data, demonstrating that the irritant potency of PAA by far exceeds the one of HP, proposing a lower short-term exposure limit and TWA of 0.5 and 0.2 ppm, respectively.[4]

Under equilibrium conditions, PAA consists of a mixture of peroxyacetic acid, hydrogen peroxide, acetic acid, and water, and these substances will often coexist in workplace environments. Therefore, suitable methods must be capable of the determination of PAA in the presence of varying concentrations of H_2O_2.

Most methods published for the analysis of PAA are focusing on liquid-phase analysis, based on titrations,[5,6] photometry,[7−9] potentiometric analysis,[10,11] gas chromatography,[12−14] liquid chromatography without[15,16] and with derivatization (oxidation),[17−22] and capillary electrophoresis.[23,24] In recent years, only a few methods for gas-phase analysis of peroxyacetic acid were

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(1) Swern, D. E. *Organic Peroxides*; John Wiley & Sons: New York, 1970; Vol. 1, p 362.
(2) Jones, L. A., Jr.; Hoffman, R. K.; Phillips, C. R. *Appl. Microbiol.* **1967**, *15*, 357−362.
(3) Directive 98/8/EC of the European Parliament and of The Council, *Official J. Eur. Communities* **1998**, *41*, *L 123*, 1−63.
(4) Gagnaire, F.; Marignac, B.; Hecht G.; Héry, M. *Ann. Occup. Hyg.* **2002**, *46* (1), 97−102.
(5) D'Ans, J.; Frey, W. *Chem. Ber.* **1912**, *45*, 1845.
(6) Greenspan, F. P.; McKellar, D. G. *Anal. Chem.* **1948**, *20*, 1061−1063.
(7) Frew, J. E.; Jones, P.; Scholes, G. *Anal. Chim. Acta* **1983**, *155*, 139−150.
(8) Davies, D. M.; Deary, M. E. *Analyst* **1988**, *113*, 1477−1479.
(9) Krüssmann, H.; Bohnen, J. *Tenside Surfactants Deterg.* **1994**, *31* (4), 229−232.
(10) Awad, M. I.; Ohsaka, T. *J. Electroanal. Chem.* **2003**, *544*, 35−40.
(11) Awad, M. I.; Oritani, T.; Ohsaka, T. *Anal. Chem.* **2003**, *75* (*11*), 2688−2693.
(12) Cairns, G. T.; Ruiz Diaz, R.; Selby, K.; Waddington, D. J. *J. Chromatogr., A* **1975**, *103*, 381−384.
(13) Di Furia, F.; Prato, M.; Scorrano, G.; Stivalleno, M. *Analyst* **1988**, *113*, 793−795.
(14) Di Furia, F.; Prato, M.; Quintly, U.; Salvagno, S.; Scorrano, G. *Analyst* **1984**, *109*, 985−987.
(15) Kirk, O.; Damhus, T.; Christensen, M. W. *J. Chromatogr., A* **1992**, *606*, 49−53.
(16) Baj, S. *Fresenius J. Anal. Chem.* **1994**, *350*, 159−161.
(17) Pinkernell, U.; Karst, U.; Cammann, K. *Anal. Chem.* **1994**, *66*, 2599−2602.
(18) Pinkernell, U.; Effkemann, S.; Nitzsche, F.; Karst, U. *J. Chromatogr., A* **1996**, *730*, 203−208.
(19) Pinkernell, U.; Effkemann, S.; Karst, U. *Anal. Chem.* **1997**, *69*, 3623−3627.
(20) Effkemann, S.; Pinkernell, U.; Karst, U. *Anal. Chim. Acta* **1998**, *363*, 97−103.
(21) Effkemann, S.; Karst, U. *Analyst* **1998**,*123*, 1761−1765.
(22) Effkemann, S.; Pinkernell, U.; Neumüller, R.; Schwan, R.; Engelhardt, H.; Karst, U. *Anal. Chem.* **1998**, *70*, 3857−3862.
(23) Ruttinger, H.-H.; Radschuweit, A. *J. Chromatogr., A* **2000**, *868*, 127−134.
(24) Wang, J.; Escarpa, A.; Pumera, M.; Feldman, J. *J. Chromatogr., A* **2002**, *952*, 249−254.

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presented.[25−27] Among the air-sampling methods, only active sampling is proposed for analyte collection. So far, no diffusive sampling methods for PAA or even for HP are known in the literature, although they are known to be excellent tools for workplace monitoring of other reactive analytes[28,29] due to their easy handling and attractive analytical figures of merit.

In the 1970s, the first diffusive sampling devices were introduced for air analysis of gaseous components by Palmes et al.[30,31] The so-called Palmes tube was a precursor of most of the devices used today. Generally, the analytes reach the collector surface by diffusion down their (for a tube, linear) concentration gradient. Based on Fick's law of diffusion,[32] a certain diffusive sampler will collect one specific analyte always with the same constant sampling rate $S_R = DA/L$ at equal temperature and pressure (D, diffusion coefficient; A, cross sectional area; L, length of diffusion path). The diffusion coefficient is temperature and pressure dependent, but effects on the sampling rate are usually negligible if sampling is performed at ambient conditions.

A particular plus of diffusive sampling devices is their high acceptance by the workers, because no loud and inconvenient sampling pumps have to be transported during the work shift, but rather a very small and lightweight device, which does not limit the action of the workers. The major reason for the lack of such methods is the fact that the analytes are very instable and that no classical derivatizing agents are known, which could react with the analytes under formation of a stable and detectable product. This is combined with the very low sampling rates for passive sampling devices, which lead to a significantly decreased limit of detection for the analytes especially for short-term monitoring.

Therefore, the goal of this work was to develop the first passive sampling method for the analysis of PAA at workplaces, which should be characterized by excellent selectivity and low limits of detection below the suggested TLVs. The development and application of such a method are presented within this paper.

EXPERIMENTAL SECTION

Chemicals. All chemicals, unless specified otherwise below, were obtained from Aldrich (Steinheim, Germany) in the highest quality available. A stabilized catalase solution (ASC Super G) was obtained from Mitsubishi Gas Chemical Co., Inc. (Tokyo, Japan). Hydrochloric acid was delivered by Acros Organics (Geel, Belgium), acetic acid analytical grade and potassium permanganate Titrisol (0.02 M), as well as sodium thiosulfate Titrisol (0.1 M), sodium nitrite, and ethanol p.a. were obtained from Merck (Darmstadt, Germany). Acetonitrile used for HPLC analysis was from Biosolve (Valkenswaard, The Netherlands). Wofasteril disinfectant solution was obtained from Kesla Pharma (Wolfen, Germany). The syntheses of 2-([3-{2-[4-amino-2-(methylsulfanyl)-phenyl]-1-diazenyl}phenyl]sulfonyl)-1-ethanol (ADS) and of 2-([3-{2-[4-amino-2-(methylsulfoxy)phenyl]-1-diazenyl}phenyl]sulfonyl)-1-ethanol (ADSO) were carried out as described in the literature.[21]

Table 1. Profiles of Binary Gradients[a]

			Gradient A				
time (min)	0	0.4	0.7	1.8	2.5	(stop)	
C_A (%)	33	45	100	33	33		
			Gradient B				
time (min)	0	5	6	10	11	15	(stop)
C_A (%)	45	45	100	100	45	45	
			Gradient C				
time (min)	0	6	7	8	13	(stop)	
C_A (%)	20	60	85	20	20		
			Gradient D				
time (min)	0	4	5	6	(stop)		
C_A (%)	20	80	20	20			

[a] Conditions: flow, 1 mL/min; T, ambient; (A) acetonitrile and (B) water.

Safety Considerations. PAA and hydrogen peroxide are strong oxidizers, and their concentrated solutions should be mixed with neither reducing agents nor organic substances including solvents. Samples containing very high peroxide concentrations should therefore be diluted prior to the derivatization reaction.

Liquid Samples. Five different industrial disinfectant solutions containing PAA and H_2O_2 as well as the PAA and HP solutions delivered by Aldrich were analyzed for their PAA content. Two different derivatization methods based on oxidation of ADS[21] and methyl-*p*-tolyl sulfide (MTS)[19] were applied to all samples. For that purpose, the samples were diluted 1:1000 with 0.01 M acetic acid and subsequently derivatized as described in the literature. The analytical parameters (HPLC) are described below. The analysis was repeated three times per sample solution.

HPLC Instrumentation and Analysis. The chromatographic system for LC−UV/visible analysis was delivered by Shimadzu (Duisburg, Germany) and consisted of the following components: two LC-10AS pumps, GT-104 degasser unit, SIL-10A autosampler, sample loop with variable injection volume of up to 50 μL, SUS mixing chamber (0.5 mL), CTO-10ACvp column oven, SPD-M10Avp diode array detector, CBM-10A controller unit, and Class LC-10 software version 1.63.

For liquid chromatographic analysis, the following columns were used: column 1, Discovery RP 18 (Supelco, Deisenhofen, Germany); particle size 5 μm; pore size 120 Å; column dimensions 150 mm × 4.6 mm. Column 2, ProntoSIL 120-5-C8 (Bischoff Chromatography, Leonberg, Germany); particle size 5 μm; pore size 120 Å; column dimensions 53 mm × 3 mm. Column 3, Discovery RP18 guard column (Supelco); particle size 5 μm; pore size 120 Å; column dimensions 10 mm × 4.6 mm.

For separation, binary gradients with the profiles shown in Table 1 were chosen. For the liquid chromatographic analysis of aqueous samples containing both PAA and HP, modifications of the MTS/triphenylphosphine (TPP) method for simultaneous quantification of both analytes[19] were applied, using column 1 and gradient B (injection volume 10 μL), as well as column 3 with gradient A (injection volume 5 μL) for the development of a fast

(25) Effkemann, S.; Brødsgaard, S.; Mortensen, P.; Linde, S.-A.; Karst, U. *J. Chromatogr., A* **1999**, *855*, 551−561.
(26) Effkemann, S.; Brødsgaard, S.; Mortensen, P.; Linde, S.-A.; Karst, U. *Fresenius J. Anal. Chem.* **2000**, *366*, 361−364.
(27) Hecht, G.; Héry, M.; Hubert G.; Subra, I. *Ann. Occup. Hyg.* **2004**, *48* (*8*), 715−721.
(28) Levin, J.-O.; Lindahl, R. *Analyst* **1994**, *119* (*1*), 79−83.
(29) Namiesnik, J.; Zabiegala, B.; Kot-Wasik, A.; Partyka, M.; Wasik, A. *Anal. Bioanal. Chem.* **2005**, *381* (*2*), 279−301.
(30) Palmes, E. D.; Gunnison, A. F. *Am. Ind. Hyg. Assoc. J.* **1973**, *34*, 78−81.
(31) Palmes, E. D.; Gunnison, A. F.; DiMattio, J.; Tomczyk, C. *Am. Ind. Hyg. Assoc. J.* **1976**, *37*, 570−577.
(32) Fick, A. E. *Pogg. Ann.* **1855**, *94*, 59−86.

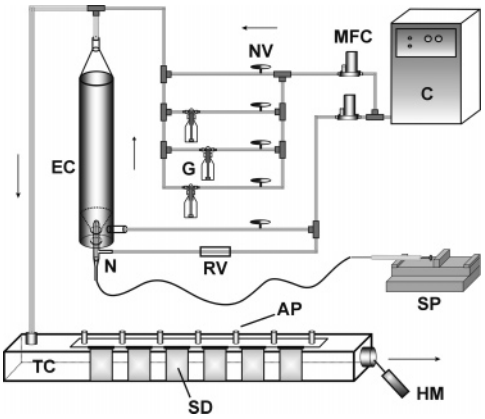

Figure 1. Assembly of the test atmosphere generation system: C, compressor; MFC, mass-flow controllers; NV, needle valves; G, gas washing bottles filled with water; RV, rotameter valve; SP, syringe pump; N, nebulizer; EC, evaporation chamber; TC, test chamber; AP, active sampling ports; SD, sliding doors for passive samplers; HM, humidity meter.

separation method. UV detection was performed at 225 nm in both cases.

For the quantification of only PAA (from liquid and air samples) using the ADS reagent, the method described by Effkemann and Karst[21] was modified using column 1 and gradient C (injection volume 10 μL), as well as column 2 with gradient D (injection volume 5 μL). The detection of the sulfide and the sulfoxide was performed at their absorption maximums at 427 nm (for the sulfide) and 410 nm (for the sulfoxide). All samples were injected in triplicate, and an external six-point standard calibration was run with each series of samples.

Titration. A two-step titration method[5,6] was used to determine the concentrations of PAA stock solutions: 1 mL of sample solution (diluted with water, if necessary) was added to 100 mL of water and 4 mL of concentrated H_2SO_4. Hydrogen peroxide was first titrated with 0.02 M $KMnO_4$ solution until the color of the solution turned pale rose. Then, an excess of solid KI was rapidly added, and the solution was again titrated with 0.01 M Na_2SO_3 until only a pale brown color remained. After addition of one drop of 1% (w/v) starch solution in water, the titration was continued until complete decolorization.

Generation of Test Atmospheres. PAA and H_2O_2 test atmospheres were dynamically generated by continuous evaporation of defined amounts of analyte standard solutions into a constant stream of humidified air. For this purpose, the following system (see Figure 1) was built according to a similar setup for other analytes described in the literature:[33,34] PAA and H_2O_2 solutions are continuously injected through a nebulizer (TR-50-C1, J. E. Meinhard, Santa Ana, CA) into a glass made evaporation chamber, using a syringe pump (KD Scientific, Holliston, MA) at flow rates between 1 and 10 μL/min with syringes from 0.5 mL up to 2.5 mL (SGE, Darmstadt, Germany). The analyte solution is nebulized at the nozzle tip by applying an air stream of 400 mL/min through the nebulizer. The produced aerosol is evaporated and carried through the evaporation chamber with 4.6 L/min air added at the bottom end of the chamber. This air/analyte mixture is then further diluted with 35 L/min humidified air and delivered into a Teflon and glass made exposure chamber with dimensions of 70 × 50 × 1000 mm, which comprises six sliding doors to introduce the passive sampler badges and seven ports for active reference sampling. At the end of the exposure chamber, the relative humidity (RH) is measured with a handheld humidity meter. Dry air is delivered by a compressor model 2xOF302-40MD2 (Jun-Air, Nørresundby, Denmark). All air flows are set and controlled with mass-flow controllers (EL-Flow series F-201C and F-201AC, Bronkhorst Hi-Tec, Ruurlo, The Netherlands), while the part flowing through the nebulizer is additionally adjusted using a rotameter valve (Cole Palmer, Vernon Hills, IL). The 35 L/min flow is split into four parallel channels, three of which are led through gas washing bottles that are filled with water and placed in a heated water bath (25 °C). These four flows are later reunited and can be adjusted individually by means of needle valves to vary the humidity conditions between 10 and 90% RH inside the test chamber. All tubing is made of Teflon, and all connections are of stainless steel (Swagelok, Waddinxveen, The Netherlands) to ensure chemical inertness.

Diffusive Sampler Setup. The passive sampling device used in this study is schematically shown in ref 35. The polypropylene housing has dimensions of 86 × 28 × 9 mm. Two ADS reagent-impregnated glass fiber filters are placed beneath a 2.9-mm-thick screen. The part of the screen covering the sample filter comprises 112 holes within a total area of 20 × 20 mm and with an entry diameter of 1.0 mm for each hole. The diameter of these diffusion channels increases slightly toward the collector surface, making a larger surface area accessible for the analytes. A sliding cover was used to seal the diffusion channels when the sampler was not in use. The second filter (control filter) was used to quantify the background signal. The sampler is commercially available as UMEx 100 (with coated filters prepared for sampling of aldehydes or amines) from SKC (Eighty Four, PA).

Preparation of Coated Filters for Diffusive Sampling. Round glass fiber filters (type A/E, diameter 37 mm, from SKC) were cut into 20 × 20 mm square pieces and placed onto a clean glass plate. Subsequently, each piece was impregnated with 200 μL of a solution of 22 mg of ADS in 25 mL of acetonitrile (2.5 mM). The plate was then transferred into a desiccator, and the filters were dried for 20 min under reduced pressure. Two filters each were placed into one diffusive sampling badge, one as sample filter and the other as control part, and the sliding cover is closed until the sampler is used.

In this work, the following other filter types were also tested and prepared the same way as described above: GF/C glass fiber filters, diameter 70 mm (Whatman, Brentford, UK); Empore SDB-XC extraction disks, diameter 90 mm (3M, St. Paul, MN); hydrophobic PTFE membranes type 11807 (Sartorius, Göttingen, Germany); Durapore hydrophobic poly(vinylidene fluoride) (PVDF) membranes, type HVHP (Millipore, Milford, MA).

Passive Sampling Experiments. To comply with internationally recognized validation procedures for diffusive samplers, six samplers were exposed to the respective test atmosphere in parallel. The common validation process usually covers a range

(33) Lindahl, R.; Levin, J.-O.; Mårtensson, M. *Analyst* **1996**, *121 (9)*, 1177−1181.
(34) Levin, J.-O.; Lindahl, R.; Andersson, K. *Environ. Sci. Technol.* **1986**, *20* (*12*), 1273−1276.
(35) Henneken, H.; Lindahl, R.; Östin, A.; Vogel, M.; Levin, J.-O.; Karst, U. *J. Environ. Monit.* **2003**, *5*, 100−105.

from 1/10 up to 3 times of the existing threshold limit value, which in the case of PAA would be from 100 ppb to 3 ppm. Due to the limited stability of diluted standard solutions (see Results and Discussion), no stable test atmospheres could be generated below 500 ppb. Therefore, experiments were carried out with test atmospheres between 0.5 and 8 ppm PAA at relative humidity conditions between 15 and 85%, mainly applying sampling periods between 15 and 30 min. To investigate the cross reactivity toward hydrogen peroxide, pure H_2O_2 atmospheres were generated as well.

Active Reference Method. To verify the PAA concentration in the exposure chamber, an active impinger method described by Effkemann et al.[25] was chosen to serve as independent reference. Two impingers were filled with acidified aqueous solutions of ADS and connected in series to the exposure chamber. Air samples were pumped through these solutions at flow rates between 200 and 300 mL/min for 15 min. Two model 1067 dual channel ambient air sampler pumps from Supelco (Bellefonte, PA) were used, allowing for four parallel samples.

Active reference samples were taken directly before or after the diffusive sampling experiments, and the pump flow through the impingers was calibrated prior to and after the sampling using a DryCal DC-Lite flow calibrator (Bios, Butler, NJ).

Active Filter Method. An active filter method was also tested for suitability to serve as reference. In these tests, two ADS-impregnated filters (round GF/B glass fiber filters, diameter 25 mm, from Whatman) were placed on top of each other in a Swinnex 25 filter cassette from Millipore. Two cassettes were connected in series to check for a possible breakthrough. PAA air samples were drawn through these cartridges at a rate of ~400 mL/min for 15 min.

Sample Workup for Analysis. The control and sample filters from exposed diffusive samplers were transferred into separate 4-mL vials and covered with 3 mL of acetonitrile each. After 30-min elution time, the vials were centrifuged for 10 min at 5000 rpm to settle loose material from the filter and the supernatant was analyzed by means of HPLC−UV/visible. The active reference samples taken with filter cartridges were treated the same way, except that 4 mL of acetonitrile was used for elution. The impinger samples did not require any pretreatment and were ready for HPLC analysis after transferring aliquots into appropriate vials.

RESULTS AND DISCUSSION

Selection of the Reagents. According to experience of our and other groups[35−38] on the analysis of other reactive organics in air samples, the use of reagent-impregnated glass fiber filters for collection of PAA with the UMEx diffusive sampling badge was considered first. For HPLC analysis, two reagents are known from the literature, MTS[17] and ADS,[21] both of which contain a sulfide group that is selectively oxidized by PAA to yield the respective sulfoxide. TPP can be added to the reaction mixture after completed reaction of PAA to either remove the HP or even for its determination by quantifying the formed triphenylphosphine oxide (TPPO).[19] Because of more favorable spectroscopic properties and a lower vapor pressure, ADS appears to be better suited to be used on filters in a diffusive sampling device. Moreover, the ADS method offers a slightly lower limit of detection, which is beneficial due to the inherently very small sample volumes that come along with passive sampling methods.

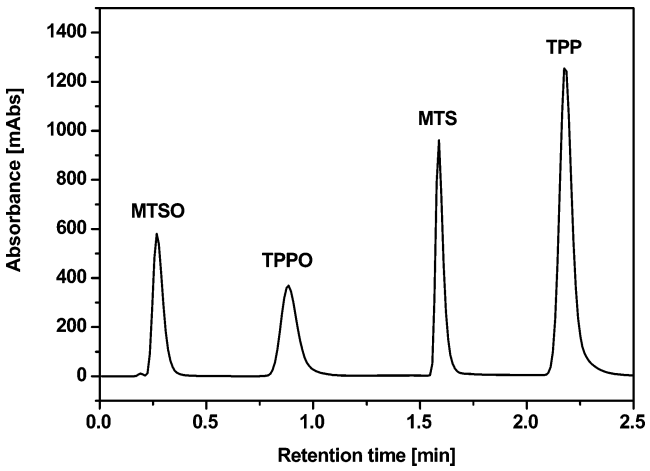

Figure 2. Fast LC separation of a derivatized PAA and HP solution. Peaks: MTSO (1), TPPO (2), MTS (3), and TPP (4).

HPLC Analysis and Method Validation. The ADS method was tested in comparison with a procedure based on MTS oxidation and with the titration method for the analysis of a series of liquid samples. The goal was to investigate the reliability and applicability for this specific application. The MTS−TPP method for simultaneous PAA and H_2O_2 determination was carried out on a C18 column with dimensions of 150 mm × 4.6 mm. As indicated by a chromatographic resolution far better than required, the used column appeared to be by far too large and the separation system was scaled down to achieve shorter retention times. Pinkernell et al.[19] used a C8 column with dimensions of 70 mm × 3 mm for this separation problem, allowing for an analysis time of 5 min per chromatographic run. We could perform the analysis in half of this time by using a 10 mm × 4.6 mm guard column with excellent separation of all four components (Figure 2).

For the ADS/ADSO separation, it was not possible to scale the column down to the same extent, because baseline separation could not be achieved on the 10-mm column. The column used during first tests and method evaluation contains a C18 material and has dimensions of 150 mm × 4.6 mm, resulting in a total analysis time of 13 min including reequilibration. The column used later for most series of experiments contains a C8 material and has dimensions of 53 mm × 3.0 mm, thus allowing for a higher throughput due to reduced analysis times of 6 min per run.

The results of all three methods correlated very well with each other (Table 2, Figure 3). The main difference between the two HPLC methods was the higher standard deviation of the results obtained when using the MTS method. The improved limit of detection of the ADS method known from the literature could be confirmed from external calibration data (not shown), allowing quantification down to concentrations of 1.7×10^{-7} mol/L, with a linear concentration range of more than 3 orders of magnitude. These results showed that the ADS method is well suited for accurate and robust quantification of PAA samples using the equipment available in our laboratory.

(36) Lindahl, R.; Levin, J.-O.; Andersson, K. *J. Chromatogr., A* **1993**, *643*, 34−41.
(37) Büldt, A.; Lindahl, R.; Levin, J.-O.; Karst, U. *J. Environ. Monit.* **1999**, *1*, 39−43.
(38) von Zweigbergk, P.; Lindahl, R.; Östin, A.; Ekman, J.; Levin, J.-O. *J. Environ. Monit.* **2002**, *4*, 663−666.

Table 2. PAA Content of Six Different Disinfectant Solutions Determined with Both HPLC Methods (Based on ADS and MTS Oxidation)[a]

sample	MTS method c(PAA) (mass %)	RSD (%)	ADS method c(PAA) (mass %)	RSD (%)	label (mass %)	density (g/mL)
1	15.3	5.2	15.2	1.3	16.0	1.129 36
2	8.2	8.3	8.4	1.9	8.5	1.105 12
3	4.2	16.2	4.5	3.7	5.0	1.081 09
4	4.5	13.1	4.9	3.5	5.0	1.114 21
5	15.8	4.6	15.8	1.2	16.0	1.132 10
6	43.0	2.4	42.4	1.2	32.0	1.147 03

[a] RSD, relative standard deviation ($N = 3$).

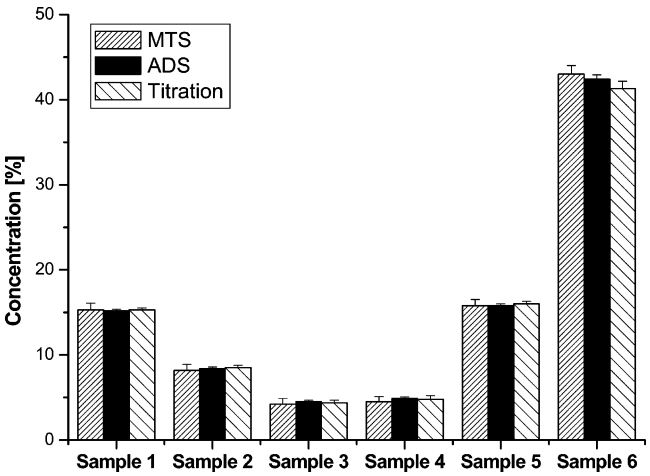

Figure 3. Comparison of the PAA analysis results of six different industrial PAA solutions determined by applying the ADS and MTS HPLC methods, as well as the titration method.

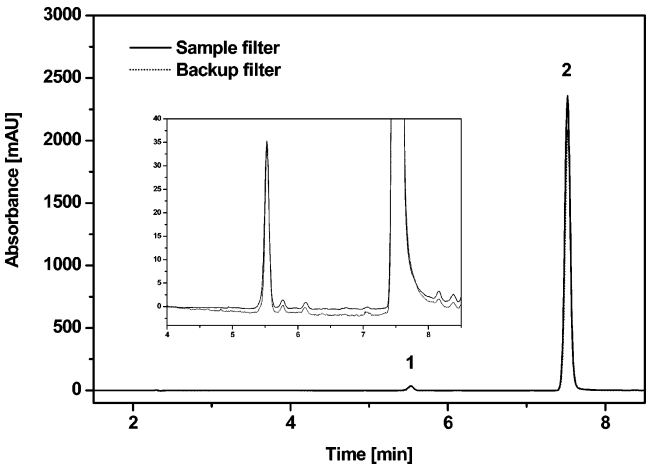

Figure 4. HPLC analysis of an active PAA air sample drawn through ADS-impregnated filters. The chromatograms shown are from the eluted filters taken out of the sample and backup cartridges. Peaks: ADSO (1) and ADS (2).

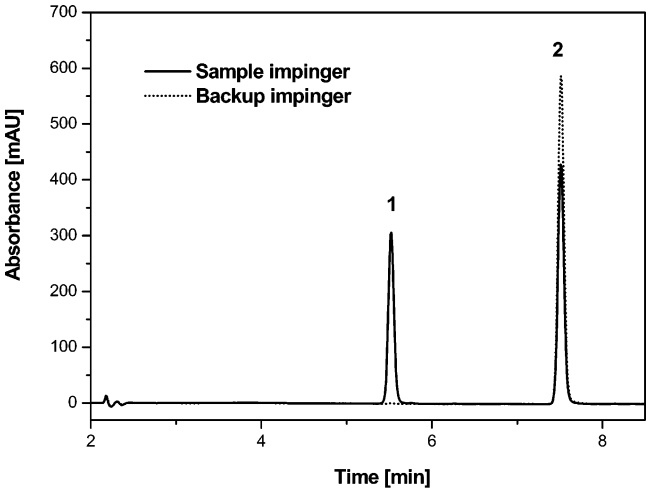

Figure 5. LC separation of sample and backup solutions obtained from active impinger sampling of a PAA test atmosphere. Peaks: ADSO (1) and ADS (2).

Active Reference. To verify the PAA concentration inside the exposure chamber during the diffusive sampling experiments, an independent reference method had to be applied. First tests showed that an active method with air samples drawn through cartridges loaded with ADS-impregnated glass fiber filters is not suitable for this purpose. The collection efficiency was poor, as the amount of ADSO found on the backup filters was equal to the one on the sample filters (Figure 4). Presumably, the contact time between analyte and derivatizing agent was too short for a quantitative reaction yield. Therefore, the active impinger method was chosen to serve as independent reference. Applying this method, no significant breakthrough of PAA into the backup impinger was detected (Figure 5) and the recovery was in the range of 95% of the expected concentration. This also proved that the generation system works well for PAA as the analyte is effectively evaporated and delivered into the exposure chamber.

Owing to the complex and time-consuming setup of four parallel impingers mounted to the chamber, it was not possible to perform the reference and diffusive sampling experiments simultaneously.

Stability of Standard Solutions for Test Atmosphere Generation. A challenge for the generation of PAA atmospheres is the instability of PAA standard solutions. If the original highly concentrated PAA solution is diluted with water or acetic acid, decomposition may take place at least partly due to the dilution of stabilizers in the sample. This is observed by the formation of gas bubbles in the syringe (Figure 1), sometimes amounting to up to half of the syringe volume within 1 h. The most critical issue in this procedure is not the loss in PAA concentration itself, but the large volume effect of the yielded gas in the syringe, which leads to an uncontrollable injection through the nebulizer. Generally, the standards should always be freshly diluted from stable stock solutions.

Regardless of all measures taken, it was not possible to generate sufficiently stable PAA test atmospheres below a

concentration of 500 ppb in air. However, this is not surprising, as to the best knowledge of the authors there are no methods described in the literature in which stable test atmospheres at such low concentrations can be achieved. Hecht and Héry recently described a generation system for controlled PAA atmospheres where the lowest reported PAA concentration was 1.9 ppm.[39]

To perform reproducible diffusive sampling experiments with exposure times of 30 min, it is crucial to generate test atmospheres that are stable for at least 90 min, due to the facts that the reference method cannot be applied simultaneously and that the system should be allowed at least 30 min for equilibration before the experiments are started. On one hand, the syringe speed (analyte standard flow through the nebulizer) should be set as high as possible in order to minimize the effects of gas bubbles yielded inside the syringe. On the other hand, the concentration of the standard solution should be as high as possible (ideally nondiluted) for maximum stability. Both cases are tending toward high concentrations in the exposure chamber, which is not desired. To achieve lower concentrations, a compromise must be found. Very often, even the same procedure yielded different stable atmospheres at different days, as obviously catalytic effects of impurities in the syringe or the solvents used for dilution did accelerate the degradation process. However, this effect was easily observed by watching the formation of gas bubbles in the syringe. In such cases, the experiment was aborted and restarted with new standards and syringes.

Diffusive Sampling. The PAA passive sampling rate (S_R) needs to be determined experimentally during the validation process. It can be calculated from the amount of ADSO found on the filters and from exposure times and known concentrations of the test atmospheres. During field application, the unknown concentration can then be determined from the ADSO analysis result, exposure time, and the sampling rate now known from validation.

As stated earlier, a temperature and pressure dependency of the sampling rate is related to the diffusion coefficient, but the effect on the sampling rate is usually negligible if sampling is performed at ambient conditions. For example, the sampling rate for PAA is expected to increase or decrease ~6% if the temperature during sampling is changed from 20 to 30 or 10 °C, respectively (determined from the calculated diffusion coefficient according to the Fuller–Schettler–Giddings (FSG) equation described further below).

Initial Diffusive Sampling Experiments. First diffusive sampling tests proved the general applicability of ADS-impregnated glass fiber filters for diffusive sampling of PAA. Figure 6 shows a chromatogram of eluted control and sample filters from a diffusive sampler exposed for 2 h to a test atmosphere of 5 ppm (16 mg m^{-3}) PAA. The chromatogram of the control filter showed an ADSO peak (T_R = 5.5 min) that represented ~10% of the sample filters peak area. This is not only a background signal but also caused by a literature-known[35,38] leakage into the diffusive sampler, which cannot be avoided, as the sampler is not completely tight at the two outside corners. However, this is not crucial, as the control filter value is subtracted from the sample filter value and the sampling rate is always calculated under these conditions. The evaluation of this first test resulted in a preliminary sampling rate of 9.1 mL/min.

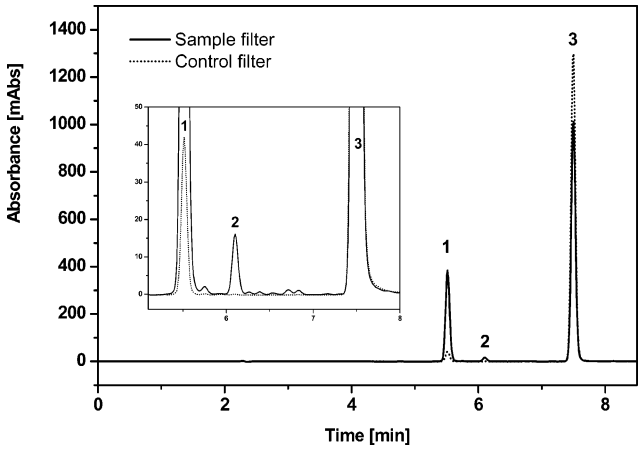

Figure 6. HPLC analysis of a passive PAA air sample. The chromatograms show the separation of eluted control and sample filters from a diffusive sampler exposed to 5 ppm PAA for 2 h. Peaks: ADSO (1), $ADSO_2$ (2), and ADS (3).

The ADS sulfide reagent always contains, due to oxidation during the synthesis, a small contamination of ~0.2% of the sulfoxide. Moreover, it was found that the background signal increased during the impregnation procedure, possibly due to catalytic effects of the larger surface. Therefore, it was important that the control and sample filters for one badge were always prepared simultaneously and treated in the same way before use.

The sample filter chromatograms sometimes also revealed a third distinct peak (T_R = 6.2 min; Figure 6) that was related to the sulfone ($ADSO_2$) as a further oxidation product from ADSO. This was confirmed by means of mass spectrometry, as mass traces could be assigned to each peak that differed by a mass-to-charge ratio (m/z) of 16, thus representing one additional oxygen atom each (ADSO ($[M + H]^+$) m/z = 368; $ADSO_2$ ($[M + H]^+$) m/z = 384; ADS ($[M + H]^+$) m/z = 352).

In theory, the sampling rate could also be calculated using the Fick law of diffusion (see above) and the FSG correlation (eq 1) for estimation of binary diffusion coefficients.[40] However, in

$$D_{BA} = \frac{0.001T^{1.75}\cdot\sqrt{M_r}}{p(V_A^{1/3} + V_B^{1/3})^2} \quad (1)$$

practice, these theoretical values may differ from the experimentally determined sampling rates.

The FSG method is based on the regression formula where D_{BA} is the diffusion coefficient of compound B in compound A (in cm^2/s), T is the temperature (in K), p is the pressure (in atm), M_r a function of the molecular weights M_A and M_B of compounds A and B, and V_A and V_B are the molar volumes of air (A) and the gas (B) in question. M_r is equal to $(M_A + M_B)/M_AM_B$. V_B can be estimated from volume increments associated with each element in the compound. These increments give the volume (cm^3) per mole of atom present.

If the preliminary result of S_R(PAA) = 9.1 mL/min was compared to a theoretically calculated value for PAA using the

(39) Hecht, G.; Héry, M. *Ann. Occup. Hyg.* **2002**, *46* (*1*), 89–96.

(40) Fuller, B. N.; Schettler, P. D.; Giddings, J. C. *Ind. Eng. Chem.* **1966**, *58* (*5*), 19–27.

Table 3. Examination of the Effect of the Sampling Time (*t*) on the Determined Sampling Rate (SR), on the Amount of $ADSO_2$ Yielded, and on the Percentage of ADSO Found on the Control Filter (CF) Compared to the Sample Filter (SF) (Control Filter Percentage, CFP)

c(PAA) (ppm)	*t* (min)	SF peak area $ADSO_2$	*N*	SR (mL/min)	RSD (of SR) (%)	CF peak area ADSO	CFP (%)	SR (for CFP = 7%)
3	60	*x*	4	14.2	1.1	16 000	7.0	14
3	120	7300	4	8.3	12.5	26 000	9.9	13
3	180	13400	3	5.2	18.3	45 000	17.0	14

FSG correlation, it was found to be far less than the calculated value of 19.4 mL/min. Based on own and other groups' experiences with other analytes and the same diffusive sampling device,[35,38] the experimentally determined sampling rate was expected to be only slightly lower than the calculated one, e.g., 92% for formaldehyde,[34] or 73% for methyl isocyanate.[38] The relatively high control filter value raised suspicion that the selected reagent excess was too small. Another experiment was then performed to examine the effect of the reagent excess, this time at a PAA concentration of 3 ppm. Three series of samplers were exposed to this test atmosphere for 1, 2, and 3 h, respectively, in order to find out if there is a saturation effect.

The results are shown in Table 3: The determined sampling rates were continuously decreasing with longer sampling periods, while the $ADSO_2$ peak increased in that order. During the 1-h experiment, no sulfone was formed. This clearly indicated that, as long as the ADS excess was sufficient, only ADSO was formed. If the ratios between the ADSO peak areas of the control filters and their corresponding sample filters were considered, it could be seen that the control filter fraction increased from 7 to 17%. If the measured control values for all three experiments were set to be 7% and the respective sample amounts were extrapolated on that basis, the resulting sampling rates corresponded well with each other and were all in the range of 14 mL/min for this set of experiments, which is in the expected range. These are further indications that the amount of reagent on the filter was not sufficient for longer sampling periods than 60 min, especially in combination with high PAA concentrations.

However, if the reagent excess would be increased, the background signal would interfere stronger with the determination of lower concentrated atmospheres. Therefore, the sampler was mainly tested with respect to short-term sampling (15−30 min), to cover the required concentration range around the target concentration of 1 ppm. As discussed earlier, this has the advantage that the generation of stable atmospheres is the easier the shorter the required period is.

Tests of Different Filter Materials. Prior to a more extensive validation, it was tested to determine whether the choice of another filter material had an influence on the sampling rate. For this purpose, filters were cut from poly(styrene−divinyl benzene) (SDB), PVDF, and Teflon disks. Also, comparable GF filters from a different manufacturer were examined. The Teflon membranes could not be impregnated at all, as the reagent solution refused to wet the material. The SDB filters were impregnated the same way as the glass fiber filters, but the HPLC analysis revealed an almost complete conversion of the ADS into ADSO, even without exposure to any peroxides. This was probably due to traces of peroxides that were left as impurities on the SDB material from its production process. For the other filter types, however, the diffusive sampling experiments showed no difference compared with the original glass fiber filters.

Table 4. PAA Sampling Rates (SR) of the Diffusive Sampler, Determined at Different PAA Concentrations, for Different Sampling Periods (*t*), at Different RH Conditions[a]

c(PAA) (ppm)	t (min)	RH (%)	N	recovery (%)	SR (mL/min)	SD (mL/min)	RSD (%)
0.5	30	15	5	102.2	15.95	0.52	3.3
0.7	45	15	6	98.4	15.36	0.60	3.9
1.0	30	15	6	103.3	16.12	1.56	9.7
1.0	30	85	6	99.3	15.50	0.95	6.1
2.0	30	15	6	94.4	14.74	0.71	4.8
2.0	30	15	6	120.2	18.77	0.70	3.7
2.8	60	15	4	90.8	14.18	0.16	1.1
5.0	30	15	5	96.1	15.00	1.40	9.3
5.0	15	15	6	107.8	16.82	0.92	5.5
5.0	15	15	8	110.8	17.30	1.10	6.4
5.3	15	85	4	96.8	15.11	0.10	0.7
5.4	30	15	5	92.2	14.39	0.78	5.4
6.4	30	15	5	94.1	14.69	0.36	2.5
6.4	30	85	4	95.5	14.91	0.23	1.5
6.4	15	15	6	101.9	15.90	1.10	6.9
8.0	15	15	6	96.6	15.08	0.59	3.9
av of mean values					15.61	0.74	4.7
av of all individual samplers ($N = 88$)					15.73	1.45	9.2

[a] SD, standard deviation; RSD, relative standard deviation; recovery based on mean sampling rate and expected concentration.

Diffusive Sampling Results. The results for all PAA passive sampling experiments performed at concentrations between 0.5 and 8 ppm are summarized in Table 4. The sampling rate was determined to be 15.6 mL/min with a relative standard deviation of 4.7% (based on the mean results of the different experiments). If all analysis results of each single diffusive sampler were averaged, the mean sampling rate was found to be 15.7 mL/min with a slightly higher standard deviation of 9.2% ($N = 88$). This standard deviation incorporates all instrumental and experimental errors that were accumulated during sampling and analysis, including the preparation and cutting of filters and the generation of test atmospheres. The relative humidity conditions were varied between 15 and 85% and did not show a significant influence on the diffusive sampler's performance. If a recovery was calculated based on the determined mean sampling rate, most results were within 10% of the expected value.

Applicable Concentration Range. As stated earlier, the sampler could not be tested with test atmospheres below 500 ppb, meaning that test atmospheres in the range of the detection limit could not be experimentally reached in the laboratory. Limiting factors are the limit of detection (LOD) and the background signal from the reagent excess. In this case, the background signal is always present above the analytical LOD, thus being the effective limiting factor. To estimate the sampler's experimental LOD, the ADSO peak areas of all HPLC injections from all control filters of the 500 ppb experiment were taken ($N = 15$) and their standard deviation was determined. The mean uptake rate of 15.7 mL/min and three times this standard deviation as hypothetical peak area value were used to calculate back to a PAA concentration in air, which would represent the LOD. The same calculation was accomplished with 10 times the standard deviation to determine the limit of quantitation (LOQ). According to these results, the detection limit of the ADS diffusive sampler is 30 ppb, while the quantification limit was determined to be 90 ppb (based on 30-min sampling). Therefore, this diffusive sampling device is capable of fully covering the required concentration range down to 0.1 ppm. However, it would be advantageous to reduce the reagent excess if such low concentrations are expected, thus minimizing the negative effect of the background signal. The analytical method would allow an LOQ of 25 ppb under these conditions, or even lower, if the filter elution volume was reduced from 3 to, for example, 2 mL.

Storage Stability. ADS and its oxidation product ADSO are known to be stable compounds. A bulk amount of ADS was used for more than half a year without significantly increasing ADSO content. For the investigations described in this paper, filters were impregnated and stored mostly one week prior to sampling, while analysis was usually performed within 24 h after sampling, in some cases after a few days. Filters and exposed samplers were always stored in the refrigerator (in the dark) in sealed vessels. Every diffusive sampler contains a sealed control filter for blank subtraction; thus, the contribution of any slowly proceeding oxidation that is not caused by the sampling procedure will be eliminated during the evaluation process.

Cross Reactivity toward H_2O_2. First, semiquantitative experiments revealed that there was a significant cross reactivity toward hydrogen peroxide. This stood in contradiction to our experience with liquid-phase reactions, where a 10 000-fold excess of H_2O_2 over PAA was needed to give the same response. However, it was not totally unexpected, as Effkemann et al. reported a decrease in selectivity on coated sorbent cartridges: In that case, a 100-fold excess of HP gave the same signal as that from PAA, which was already by a factor of 100 lower compared to reactions in aqueous solutions.[25] Interferences resulting from other oxidants, e.g., ozone or methyl hydroperoxide (MHP), which are mainly associated with atmospheric chemistry, are not expected in the case of PAA sampling. Usually, ozone concentrations are in the low-ppb range, while MHP is normally found in the sub-ppb range. Thus, even if these compounds were present at relevant indoor workplaces, their contribution to ADS oxidation would be neglectable.

A full series of experiments was then performed to evaluate the extent of the HP cross reactivity. During these experiments, six identical samplers were exposed to pure H_2O_2 atmospheres between 1 and 11 ppm. To verify the HP concentration inside the test chamber, "online gas titrations" were performed in some cases: Gas washing bottles filled with dilute acidic permanganate solutions were connected to the exposure chamber, and continuous air samples were drawn through at known flow rates until the pale pink color disappeared. If this point was difficult to visualize, it could be verified by titrating this solution back to the first pale pink color with a permanganate solution.

Table 5. HP Sampling Rates (SR), Determined for Different Sampling Periods (t) and at Different HP Concentrations

c(HP) (ppm)	t (min)	SR (mL/min) ($N = 6$)
1.0	240	2.73 ± 0.32
1.1	15	2.26 ± 0.38
2.5	60	3.47 ± 0.66
3.4	15	2.94 ± 0.45
5.7	15	2.26 ± 0.18
6.8	15	3.46 ± 0.42
6.8	15	1.27 ± 0.44
10.2	15	1.97 ± 0.20
10.3	15	2.25 ± 0.22
11.4	15	1.92 ± 0.39
average		2.45 ± 0.70

The average sampling rate determined for H_2O_2 was found to be 2.45 mL/min with a standard deviation of 29% (see Table 5). This relatively high standard deviation could be due to the fact that the absolute amount of ADSO formed is very small. Also, the requirement of immediate reaction ($c_0 = 0$) at the collector surface might not be fulfilled in this case, which means that the diffusion theory might also be overlaid by kinetic effects and back diffusion might occur. The experimental series at 1.1, 5.7, and 10.3 ppm were performed directly after each other, setting up the test atmosphere just by increasing the syringe flow. In that series, the formation of gas bubbles inside the syringe was negligible. The excellent correlation within that series indicated that the mean value of all experiments is a good description of the real cross reactivity.

If the FSG correlation is used to calculate an uptake rate for HP, a value of 36.2 mL/min is found. This is a factor of ~15 higher than the experimentally determined sampling rate, which proves that there still is a significant difference in selectivity for ADS oxidation by PAA and H_2O_2, but that this difference is too small to allow for an unrestricted application in an environment of fully unknown composition. However, it must be stated that, because of the Henry's law constants (K_h), the cross reactivity toward HP might be insignificant if gaseous PAA shall be determined from evaporation out of diluted aqueous solutions that contain both PAA and HP: O'Sullivan et al.[41] measured K_h(PAA) = 837 M/atm and K_h(HP) = 8.33×10^4 M/atm, which means, according to Henry's law ($C_{perox} = K_h p_{perox}$) that at equal concentrations PAA has a partial pressure (p) that is 100 times higher than the one of HP.

Tests To Overcome Cross Reactivity. A large number of experiments were performed attempting to minimize this cross reactivity. One approach was impregnating the filters with manganese dioxide in addition to the ADS reagent in order to

(41) O'Sullivan, D. W.; Lee, M. Y.; Noone, B. C.; Heikes, B. G. J. *Phys. Chem.* **1996**, *100* (8), 3241−3247.

Table 6. ADSO Peak Areas from HPLC Analyses of ADS Diffusive Samplers Simultaneously Exposed to the Same Pure HP Atmosphere[a]

filter impregnated with	ADSO peak area
ADS only	62000
catalase + ADS	700
manganese dioxide + ADS	300

[a] The filters were additionally impregnated with manganese dioxide or catalase in order to decompose the HP.

Table 7. ADSO Peak Areas from HPLC Analyses of ADS Diffusive Samplers Simultaneously Exposed to the Same PAA Atmosphere[a]

filter impregnated with	ADSO peak area ($N = 3$)
ADS	180000 ± 10%
catalase + ADS	75000 ± 12%
manganese dioxide + ADS	60000 ± 60%

[a] The filters were additionally impregnated with manganese dioxide or catalase in order to decompose the HP fraction present in the test atmosphere.

use its ability of catalytical HP decomposition without affecting the PAA. For this purpose, permanganate and sodium hydroxide solutions were applied to the filters. By doing so, the yielded MnO_2 was strongly attached to the glass fiber material of the filters. Several steps of this procedure were varied, such as the concentrations of the permanganate or the NaOH solutions. Different washing steps with water, acetic acid, acetonitrile, or acetone (and combinations thereof) were used in order to control the pH value on the filter. As a second approach, different attempts were made to impregnate the filters with catalase, which is also known for selective HP decomposition. First tests in pure HP atmospheres were promising, as no oxidation of ADS was observed on both catalase- and MnO_2-modified filters (Table 6), which was exactly the goal of this experiment.

However, when such modified samplers were exposed to PAA atmospheres, a strong effect on the PAA sampling performance was observed as well. Although some PAA exposure experiments looked promising, the reproducibility was not sufficient and the deviations within single experiments were extremely high (sometimes amounting up to 300%). In some cases, the oxidation of ADS by means of PAA was completely inhibited on MnO_2- or catalase-treated filters, while other tests indeed revealed a significant reaction with PAA (Table 7), but with a reaction yield that was lower than expected compared with the original method on pure ADS-impregnated filters. Because of these uncertainties, it seems preferable to keep the original procedure without filter modification.

Field Application. The ADS diffusive sampler was tested in a field application. For this purpose, a commercially available PAA-based disinfectant solution was used for area (floor and shelf) disinfection in a well-ventilated room of ~20 m^2. Approximately one-third of the floor was treated. The disinfectant was diluted and used strictly according to the instructions that were provided by the manufacturer. The concentrated disinfectant solution contained 40.3% PAA (label 40 ± 2%) and 11.5% H_2O_2. A 0.25% dilution was used, and the residence time was 30 min.

Three sets of three diffusive samplers each were placed at three different positions in the room. The samplers were positioned close to the floor and on top of the shelf. The diffusive samplers were analyzed and gave the following results, provided as average concentration and its standard deviation: The samplers on the floor indicated a PAA concentration of 2.30 ± 0.34 and 1.69 ± 0.14 ppm, while the result obtained from the shelf series was 1.36 ± 0.18 ppm. Concentration data obtained by passive sampling experiments were compared with a pumped reference method, in which the PAA concentration was determined to ~1 ppm. However, it is important to state that the sampling positions of active and diffusive samplers had to be different in order not to remove the analyte from the air by the reference. These results cannot be compared directly, as the sampling positions were different, and in contrast to the validation experiments, the PAA concentration in the room was certainly not homogeneous due to ventilation. As expected, the concentration close to the floor is higher than on the shelf, which was positioned at the best-ventilated position in the room. The standard deviations within one set of samplers were relatively small, indicating the good reproducibility of the measurements.

CONCLUSIONS

A passive sampling method has been developed for the determination of gas-phase peroxyacetic acid. It is based on diffusion-controlled collection of PAA on ADS-impregnated glass fiber filters. Even though similar procedures are known for a wide variety of analytes, this was the first time that a passive method was proposed for the sampling and analysis of airborne peroxides. The mean uptake rate for peroxyacetic acid was determined to 15.7 mL/min ± 9.2% ($N = 89$), and no significant deviation was observed at relative humidity conditions between 15 and 85%. However, a cross reactivity toward hydrogen peroxide was observed and found to be 2.45 mL/min, which means a certain limitation in terms of applicability, as the approximate concentration of airborne hydrogen peroxide must be estimated. This assessment is simplified by the fact that PAA has a strong penetrative and characteristic odor, which can be easily recognized above concentrations of 1 ppm. However, if a signal was falsely interpreted as PAA-caused (instead of HP), this would from the workplace safety point of view reveal an even more serious issue, as that would mean an exposure to much higher hydrogen peroxide concentrations than expected. As diffusive sampling methods are, because of their ease of handling, generally best suited for screening purposes, a positive result should be in any case reaffirmed by other independent methods before measures are taken. The general applicability of the new method has been demonstrated by performing a determination of PAA during a room disinfection process with a commonly used and commercially available disinfectant solution.

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