

Air Monitoring and Assessment of Occupational Exposure to Peracetic Acid in a Hospital Environment

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Abstract: A new automated method based upon solid phase micro-extraction (SPME)/fast gas chromatography-mass spectrometry (GC-MS) was developed for the quantitative determination of airborne peracetic acid (PAA). The method is suitable for the quick assessment of brief acute exposure as well as for long-term environmental monitoring of PAA and can assist in improving safety and environmental quality in workplaces where disinfectants are used. During a monitoring campaign in the Regional Hospital of Florence, Italy, the 8-h average air concentration of PAA was 1/10 of the threshold limit value of time weighted average in 87% of the clinical units tested. However, the application of the new SPME method showed that short-term exposure to PAA could be relatively elevated in some hospital units with poor ventilation, allowing prompt intervention in order to reduce worker exposure to this potentially toxic compound.

Key words: Peracetic acid, Hospital environment, Solid phase microextraction, Occupational exposure, Risk assessment

Peracetic acid (PAA, CAS Number 79-21-0) was introduced as an antibacterial agent in 1955. It has a broad spectrum of activity, including bacteria, spores, molds, yeasts, algae and viruses^{1, 2)}. PAA, a possibly safe oxidizing agent, is being increasingly used recently, especially as a high-level disinfectant in hospital settings. However, if used at high concentration, it may cause skin and mucosal irritation and its vapors are extremely irritating to eyes, nose and throat³⁾.

There are a few methods to detect PAA in the gas phase described in the literature, such as photometry^{4, 5)}, spectroscopy⁶⁾ or gas-⁷⁾ and liquid-chromatography^{8–10)} with and without derivatization. But all these methods are not sufficiently sensitive and furthermore require handling of many chemicals, complicated cleaning and extraction procedures, and the use of cumbersome equipment which may interfere with job performance.

Solid phase micro-extraction (SPME), a solvent-free technique, incorporates sampling, isolation and enrichment into one step. It has been proposed since 1998 as a passive device^{11, 12)} for field and personal sampling, both as “rapid-SPME” with completely exposed fibers for short-term sampling and for determination of “time-weighted average (TWA)-SPME”. In the latter case the fiber is retracted inside the needle up to 0.1–3.5 cm.

Acceptable limits for PAA have been suggested by the Institut National de Recherche et Sécurité (INRS) and by the Subcommittee on Consequence Assessment and Protective Actions (SCAPA). INRS¹³⁾ proposed a Threshold Limit Value (TLV) as TWA for PAA of 0.62 mg/m³ (0.2 ppm) and a TLV as Short Time Exposure Limit (STEL) of 1.56 mg/m³. The PAA Acute Exposure Guidelines Level values¹⁴⁾ (AEGL 1, AEGL 2 and AEGL 3) are 0.52, 1.6 and 60 mg/m³ for 10 min of exposure.

Since PAA may have severe acute health effects at high concentrations, it seemed important to us to have a method sensitive to quick elevations of PAA in the air

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during handling and disinfecting procedures. For this reason, we developed a new, rapid, economical and automated analytical SPME fast gas chromatography-mass spectrometry (GC-MS) method for the fast quantitative determination of airborne PAA. Here we will describe the method as well as the results of a campaign of environmental monitoring in a hospital setting in Florence, Italy.

A survey carried out in the Regional Hospital of Florence, Italy, showed that Oxyster Plus Long Life PAA (Farmec, Verona, Italy), formed from hydrogen peroxide and N-acetylcaprolactam, was used in fifteen clinical units with a total per-month consumption of 803 l. To prepare the 0.2% PAA solution, a generator with peroxidic groups was used to obtain the nucleophilic attachment to the carbonyl bond of the N-acetyl in the activator.

To determine airborne PAA exposure in 15 nurses in 15 different clinical units we used the SPME technique, with a 100 μm Fast Fit Assemblies (FFA)-SPME polydimethylsiloxane (PDMS) fiber (Supelco, Sigma-Aldrich, Milan, Italy). The fiber was doped for 10 s in the headspace of a PTFE-capped 4 ml amber vial containing 5 μl of methyl-*p*-tolyl-sulfide (MTS). From the reaction between PAA and MTS, methyl-*p*-tolyl sulfoxide (MTSO) was obtained. Sampling was performed both by "rapid-SPME" and by "TWA-SPME" (in this case the fiber was retracted in the needle to a distance of $Z=0.3$ cm) exposing the fiber in the air for 15 s and 8 h, respectively, under non-equilibrium conditions. After sampling, PAA was analyzed with fast GC/MS with a Shimadzu GC 2010 (Shimadzu Italia, Milan, Italy), using an SLB5-MS column by Supelco (5 m $\times$ 0.10 mm $\times$ 0.4 μm film thickness). The ionization was performed with a QP 2010 series MS detector operating in the electron impact (EI) mode. MS analysis was operated by the new fast automated scan/selective ion monitoring (SIM) technique (FASST) acquisition mode with scan range of m/z 40–200; for MTSO determination, the mass number of the target ion was $m/z=138$ and the confirming ion was $m/z=154$. Oven settings were 60°C held for 0.30 min, with a ramp of 150°C/min up to 100°C and 50°C/min up to 250°C. Inlet pressure and column flow were 348.8 KPa and 1.21 ml/min, respectively. The injector (280°C) was set in split mode 10:1. Full automation of the procedure was achieved using a Gerstel MPS2 autosampler equipped with Multi Fiber Exchange (SRA Instruments, Milan, Italy). To calibrate the fiber, PAA vapor was generated in a dynamic system by a syringe-pump Harvard Plus 11 (Harvard Apparatus, Holliston, United States), equipped with a 1 ml gas-tight syringe set to 2 $\mu\text{l}/\text{min}$. The PAA solution was set at 7.8 $\mu\text{g}/\mu\text{l}$.

The PAA air concentration ($C_{\text{PAA air}}$) was calculated according to the following formula:

$$C_{\text{PAA air}} = C_{\text{Sol}} F_{\text{syringe}} / F_{\text{air}} \quad (1)$$

where, $C_{\text{PAA air}}$ is the concentration of analyte in air ($\mu\text{g}/\text{l}$), C_{Sol} is the concentration of the solution ($\mu\text{g}/\mu\text{l}$), F_{syringe} is the syringe-pump flow ($\mu\text{l}/\text{min}$), and F_{air} is the air flow (l/min).

The experimental sampling rates (SR) of the "rapid-SPME" and "TWA-SPME" system were obtained using the equation:

$$\text{SR} = \text{uptake} / C_{\text{PAA air}} \quad (2)$$

The uptake is the slope of the line obtained by correlating the mass of PAA adsorbed on the fiber with the sampling time at calibrated air concentrations ($C_{\text{PAA air}}$). The theoretical SR of the SPME passive sampling system with "TWA-SPME" was expressed as:

$$\text{Theoretical SR} = (D_g \times A) / Z \quad (3)$$

where Z = distance between the needle opening and the fiber upper surface, A = surface of the needle opening (0.00086 cm^2), and D_g = analyte diffusion coefficient in the air (for PAA 0.149 cm^2/s by Fuller-Schettler-Giddings equation).

Table 1 describes the principal characteristics of the fifteen clinical units (dimension, type of sterilization, ventilation and aspiration systems, volumes of PAA solution used during filling operations). In two units (ns 9 and 14) lavaendoscopes (model Autoscope 2, Labcaire System Ltd, Clevedon, United Kingdom) were present, equipped with an apparatus made of an activated carbon filter for trapping disinfectant fumes. Most units had no artificial ventilation except units ns 2, 3, 4 and 5, where a mechanical ventilation system of turbulent flow type was installed and set at 15 changes/h. This system distributed the external air evenly in the room, achieving uniform air quality, temperature and air velocity. In unit n 10 an aspirating hood was installed (model G17S, PCI Medical Inc, Deep River, United States) with a face velocity of 13.7 m/min. In most units the operations were manual and cleaning devices were basins or tubes. Personnel used long-sleeved waterproof gowns, nitrile gloves, goggles and disposable charcoal-impregnated face masks.

The evaluation of airborne PAA exposure was made by means of personal sampling in the breathing zone of the workers and included the following settings (Table 1): (1) background exposure to airborne PAA in the room independently of specific manipulations; (2) disposal of the exhausted solution ("emptying"); (3) filling of basins, lavaendoscopes and tubes with activated solution ("filling"); (4) persistence of pollution in the room while the operator is busy tidying the work space ("decay"); (5) immersion of devices in the activated solution of PAA ("routine activity").

Table 1. Description of the fifteen clinical units monitored. The highest values and the time-weighted average environmental concentrations (mg/m³) evaluated by “rapid-SPME” and “TWA-SPME” during background exposure (1), emptying (2), filling (3), decay (4) and routine activity (5), are indicated

n.	Unit	Volume (m ³)	Emptying	Ventilation	Filling (liters)	Cleaning system	“rapid-SPME”						“TWA-SPME”			
							Background (1)	Emptying (2)	Filling (3)	Decay (4)	Avg ± SD (1)–(4)	Routine (5)	Avg ± SD (5)	N. sample	(1)–(5)	Avg ± SD (1)–(5)
1	Endoscopy	15	washbasin	natural (a)	5	basin	0.048	1.239	0.208	0.109	0.461 ± 0.356	0.154	0.101 ± 0.053	2	0.056	0.049 ± 0.008
2	Otolaryngology operating theatre	81	washbasin	mechanical (b)	0.1	tube	<0.035	0.180	0.074	0.143	0.111 ± 0.052	0.196	0.106 ± 0.081	4	0.093	0.085 ± 0.012
3	Surgical operating theatre	79	washbasin	mechanical (b)	5	basin	<0.035	0.142	0.595	0.041	0.230 ± 0.189	0.090	0.060 ± 0.025	3	<0.020	<0.020
4	Ophthalmologic operating theatre	29	washbasin	mechanical (b)	5	basin	0.045	0.249	0.357	0.056	0.179 ± 0.115	0.096	0.068 ± 0.027	2	0.039	0.030 ± 0.005
5	Radiotherapy operating theatre	97	washbasin	mechanical (b)	5	basin	<0.035	0.055	0.165	<0.035	0.095 ± 0.058	0.083	0.068 ± 0.023	2	<0.020	<0.020
6	Sport medicine ambulatory	64	washbasin	natural (a)	5	basin	0.065	0.463	0.509	0.134	0.288 ± 0.149	0.201	0.116 ± 0.077	5	0.054	0.048 ± 0.008
7	Ophthalmologic ambulatory	14	sewer system	natural (a)	5	basin	0.058	0.282	3.396	0.130	1.228 ± 1.165	0.115	0.090 ± 0.030	5	0.048	0.041 ± 0.006
8	Ophthalmologic ambulatory	16	sewer system	natural (a)	5	basin	0.066	0.228	0.414	0.212	0.239 ± 0.090	N.D.	N.D.	3	0.065	0.061 ± 0.004
9	Endoscopy	10	sewer system	aspirating hood (c)	15	lavaendosc.	<0.035	0.050	0.127	0.052	0.076 ± 0.036	0.108	0.066 ± 0.045	2	<0.020	<0.020
10	Odontologist ambulatory	62	washbasin	aspirating hood (d)	1	basin	0.107	0.134	0.325	<0.035	0.163 ± 0.095	0.135	0.112 ± 0.020	7	<0.020	<0.020
11	Otolaryngology ambulatory	14	washbasin	natural (a)	5	basin	<0.035	N.D.	0.493	0.092	0.176 ± 0.145	0.424	0.222 ± 0.192	5	0.129	0.107 ± 0.020
12	Otolaryngology ambulatory	72	washbasin	natural (a)	5	basin	0.055	N.D.	0.329	0.333	0.242 ± 0.121	0.252	0.144 ± 0.102	5	0.054	0.048 ± 0.007
13	Endoscopy	26	washbasin	natural (a)	5	basin	0.055	0.360	1.452	0.147	0.448 ± 0.396	1.218	0.736 ± 0.603	3	0.324	0.291 ± 0.036
14	Endoscopy	26	sewer system	aspirating hood (c)	15	lavaendosc.	<0.035	0.042	0.395	0.105	0.226 ± 0.108	0.206	0.129 ± 0.084	6	0.025	0.022 ± 0.003
15	Endoscopy	28	washbasin	natural (a)	5	basin	0.049	0.444	0.506	0.105	0.303 ± 0.161	0.259	0.156 ± 0.105	4	0.031	0.028 ± 0.005

(a) no artificial ventilation. (b) ventilation system as turbulent flow type set at 15 changes/h. (c) Autoscope 2 (Labcare System Ltd, Clevedon, United Kingdom). (d) G17S (PCI Medical Inc, Deep River, United States). N.D. not determined; Avg ± SD = Average ± Standard Deviation.

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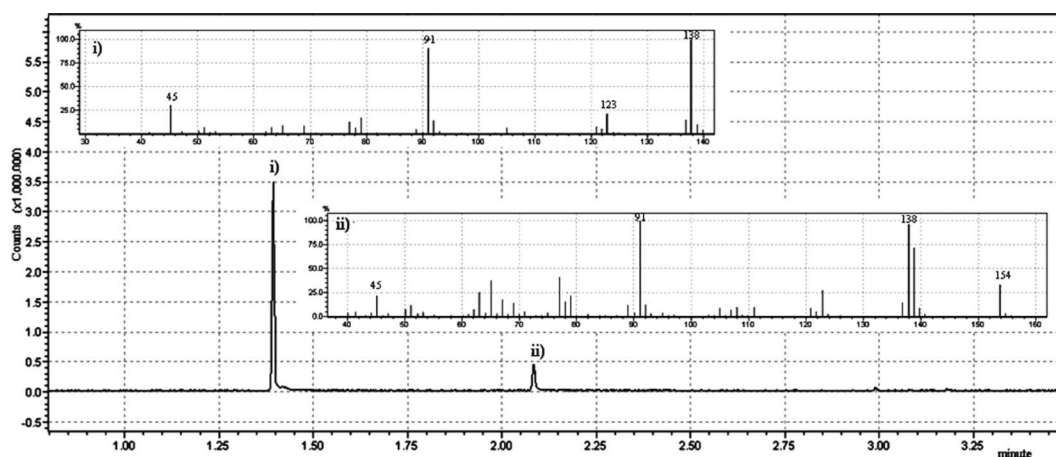


Fig. 1. Fast GC-MS chromatogram and EI mass spectrum of the i) MTS, ii) MTSO.

Short-term 10-min exposure was monitored using forty SPME fibers, each for 15 s in sequence for “rapid SPME” sampling. A multi-data logger model BABUC/A (LSI, Milan, Italy) was employed to measure microclimatic parameters during air sampling (temperature, relative humidity and air velocities).

The main goal of the work was to determine the “instantaneous” environmental concentrations of PAA using the “rapid-SPME” method and to compare the results with the long-term sampling by “TWA-SPME”. An additional goal was the minimization of GC analysis time using a narrow bore capillary column (Fig. 1). The limits of quantification (LOQ) in the SIM mode for “rapid-SPME” and “TWA-SPME” were 0.035 (for 15 s sampling) and 0.020 mg/m³ (for 8 h sampling) and were evaluated with a signal-to-noise ratio >5 and a peak area in the linear range of the calibration curve. The method for “TWA-SPME” sampling ($Z=0.3$ cm) had 8% relative standard deviation (RSD, $n=5$) at low $C_{PAA\ air}$ (0.070 mg/m³) and 9% RSD ($n=5$) at high $C_{PAA\ air}$ (3.0 mg/m³), while “rapid-SPME” sampling had 11% RSD (0.040 mg/m³) and 10% RSD (1.2 mg/m³). Figure 2a, b shows plots of the amount of absorbed PAA as a function of exposure time for both sampling methods to determine SR. The slope of the curve represents the uptake of PAA on SPME fibers as indicated in equation 2. As to “TWA-SPME” with $Z=0.3$ cm, the experimental average SR value was 0.0235 ml/min (Fig. 2b), in good agreement with theoretical SR value (0.0256 ml/min) calculated by equation 3. The experimental average SR value for “rapid-SPME” was equal to 7.7884 ml/min (Fig. 2a). The cross reactivity to hydrogen peroxide was negligible in the concentration ranges of PAA. No significant change in mass adsorbed was observed after storage (-20°C) for one week. The robustness of the fiber allowed more than 150 analyses for each fiber. The

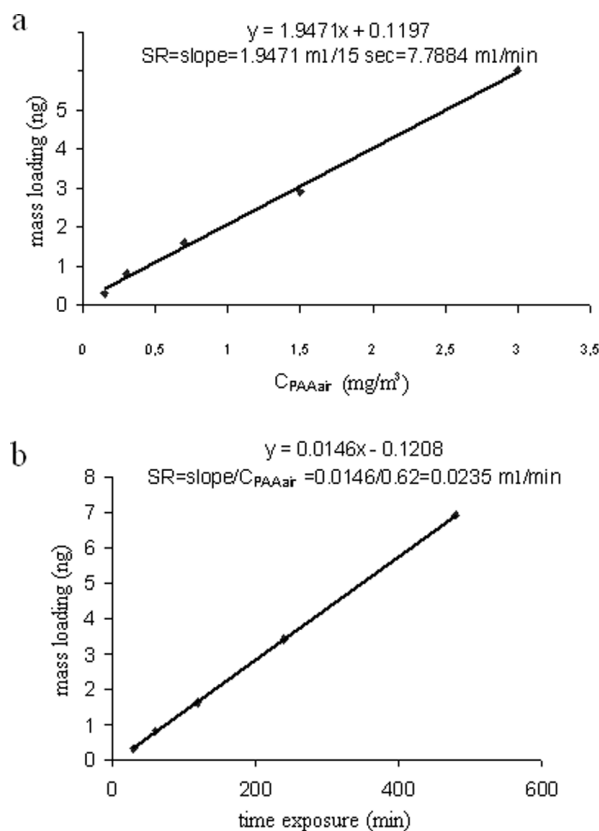


Fig. 2. a, Weight of PAA (ng) formed at 15 s exposure time as a function of various $C_{PAA\ air}$ (mg/m³) by “rapid-SPME”. b, Uptake rate (ng/s) for PAA by “TWA-SPME” with $Z=0.3$ cm ($C_{PAA\ air}=0.62$ mg/m³).

ranges in microclimatic parameters registered in the fifteen units during the PAA environmental monitoring were: air temperature ($19.1\text{--}23.7^{\circ}\text{C}$), relative humidity ($45.4\text{--}77.9\%$), air speed ($0.4\text{--}1.5$ cm/s).

With rapid SPME we measured the average environ-

mental concentrations (10 min) of PAA during step 1–4, which include all the phases of the handling of the solution. Among the fifteen units monitored, this average was higher than AEGL 1 only in unit n. 7 ($1.228 \pm 1.165 \text{ mg/m}^3$). In unit n. 13 we observed the highest average values ($0.736 \pm 0.603 \text{ mg/m}^3$) for setting 5 (defined as “routine” in Table 1). The highest instantaneous concentration levels (range $0.414\text{--}3.396 \text{ mg/m}^3$) were noticed when the filling (setting 3) was made in devices with a large evaporating surface (average diameter of the basins, 42 cm), in rooms without localized aspiration (units n. 6, 7, 8, 11, 13, 15) and in setting 2 (“emptying”), range $0.360\text{--}1.239 \text{ mg/m}^3$ (units n. 1, 6, 13, 15). In the endoscopic wards using lavaendoscopes (units n. 9, 14), the exhausted solution was discharged in closed circuits. The units using natural ventilation (n. 1, 6, 7, 8, 11, 12, 13, 15) showed a higher average level of PAA (0.423 mg/m^3) than those (n. 2, 3, 4, 5, 9, 10, 14) with assisted ventilation (0.154 mg/m^3) for short-term exposure (10 min). For long-term sampling by “TWA-SPME”, the average concentration of PAA was 1/10 lower than TLV-TWA except in units n. 2, 11 and 13.

These data are the first in the literature reporting a method for high-throughput automated analysis of airborne PAA using an MFX/SPME fast GC-MS robotic system. The high sensitivity of the method evaluates PAA concentrations with extremely short sampling periods, producing instantaneous values of PAA levels. In addition SPME reduces analytical costs, is easily applicable and uses no solvents, therefore having no environmental impact.

Evaluation of PAA exposure levels is essential to efficiently organize prevention of risks from using this potentially toxic chemical. We were able to identify high exposure steps during the handling of PAA in our hospital with this new method, which then prompted the adoption of approaches to minimize exposure such as staff training, mechanical ventilation and the use of lavaendoscopes equipped with a specific aspiration system.

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