Simultaneous Sampling of Peroxyacetic Acid and Hydrogen Peroxide in Workplace Atmospheres

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The use of peroxyacetic acid (PAA) in the disinfection processes in the food industry or for medical purposes is increasing. As it is the product of the reaction of acetic acid (AA) and hydrogen peroxide (HP) and coexists with them, and given the fact that the chemical properties of these two substances are not very different from PAA, the sampling and analysis of this substance in working atmospheres is difficult. A specific sampling device was developed. It is composed of: (i) a cassette with quartz fibre filters impregnated with titanium oxysulfate hydrate for the sampling of HP followed by; (ii) a tube filled with silica gel soaked with methyl p-tolylsulfoxide for the sampling of PAA.

The analysis of this silica gel was performed by liquid chromatography with UV detection of the methyl p-sulfone generated by the sampling of PAA. The conservation of the sampling media (before and after sampling) and its efficiency were also checked. From the results of sampling campaigns performed in various workplaces, the relative contributions of PAA, AA and HP to an exposure index, taking into account the atmospheric concentrations and the threshold limit values, were established. This calculation shows that the simultaneous determination of PAA and HP, which the method presented in this paper allows, provides a fairly good estimation of the exposure.

Keywords: peracetic acid; hydrogen peroxide; simultaneous sampling

INTRODUCTION

Peroxyacetic acid (PAA) is widely used in the food industry for disinfecting buildings and equipment and for sterilizing plastic bottles, particularly those used for packaging fruit juices or sweetened drinks. It is also used for medical purposes, mainly for sterilizing the surfaces of the instruments (ECETOC, 2001). In its latter activity, at the moment in France, it is tending to replace glutaraldehyde.

PAA results from a reaction between acetic acid (AA) and hydrogen peroxide (HP):

\[ \text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O}_2 \leftrightarrow \text{CH}_3\text{CO}_3\text{H} + \text{H}_2\text{O} \]

As the vapour pressure of these products is high, workers who use PAA are likely to be exposed to all three of these irritating compounds. Consequently, industrial hygienists need a method that allows them to measure, without interference, the respiratory exposure to these three molecules. Until now, the American Conference of Governmental Industrial Hygienists (ACGIH, 2002) has proposed limit values only for HP (TLV-TWA = 1 ppm; TLV: threshold limit value and TWA: time-weighted average) and AA (TLV-TWA = 10 ppm and TLV-STEL = 15 ppm; STEL: short-term exposure limit). In a recent paper, Gagnaire et al. (2002) proposed a TLV-TWA of 0.2 ppm and a TLV-STEL of 0.5 ppm for PAA. These values are based on the decrease in the respiratory rate (RD\(_{50}\)) of mice exposed to PAA and were established in order to prevent upper airway sensory irritation. The generation of PAA (Hecht and Héry, 2002) was devised in such a way (buffering of the solution) that the quantity of HP and AA in the test atmosphere was negligible. Consequently, the proposed limit values actually correspond to the effect of pure PAA, without any interference of HP or AA.

Several collection media have been proposed for sampling AA: florisil with high performance liquid chromatography (HPLC) analysis with conductimetric detection (Simon et al., 1989), charcoal with gas liquid chromatography analysis (NIOSH...
Manual of Analytical Methods, 1994), or bubbling in an impinger containing a buffered methyl-p-tolyl-sulfide (MTS) solution (Hecht and Héry, 2002). Several methods have also been described for the sampling and analysis of HP in the atmosphere (OSHA, 1990; Hecht et al., 1999; Christensen et al., 2000). They are based on the complexation of titanium (IV). Christensen et al. used a glass frit impregnated with titanium tetrachloride. The complex is analyzed by molecular absorption photometry at 410 nm. The interference of PAA is minimized if the sampling rate is at least 1 l/min, as the reaction between PAA and titanium tetrachloride is slow and, at this flow rate, little PAA is trapped. This method was adapted as it was convenient for sampling in occupational hygiene (i.e. the use of filters, which are more suited to personal sampling than glass impingers). We used quartz fibre filters soaked with methanol, Merck ref. 1.06007.2500 as an impinger containing a buffered methyl-p-tolyl-sulfide (MTS) solution (Hecht and Héry, 2002).

The synthesis of the initial reagent wasdriedat90°C for 8 h, then overnight at 140°C. After cooling, the ‘basic’ silica gel obtained was then sifted to obtain the 0.25–0.5 mm range. MTSO (154 mg) was dissolved in 50 ml of methanol; 50 g of ‘basic’ silica gel was then added to the mixture. The solvent is then evaporated at 50°C under light vacuum.

Absorption solution (for fritted-glass impingers) for the sampling of PAA. The molar MTS solution was prepared by dissolving 2.7 ml of MTS in 20 ml of ethanol; 50 μl of this solution and 50 μl of a pH 7 buffer solution (1.42 g of Na2HPO4 and 1.36 g of KH2PO4 dissolved in 100 ml of water) were then added to 10 ml of a 75/25 ethanol/water mixture.

The reaction has been described for the liquid phase, and the different derivatives of this family are unsuitable for the method we decided to apply: the use of MPS as a reference for the tests in the field would have been impossible owing to the relatively high vapour pressure of this compound.

MATERIALS AND METHODS

Chemicals

All solvents used were of HPLC grade. Ultrapure water was produced by a Millipore Milli-Q system.

- Acetonitrile, SDS ref. 0063721.
- Disodium hydrogen phosphate, Prolabo ref. 28 026.292
- Ethanol, Merck ref. 1.11727.1000
- Hydrogen peroxide (HP), Prolabo ref. 23 619.297
- Methanol, Merck ref. 1.06007.2500
- Methyl p-tolyl-sulfide (MTS), Aldrich ref. 27 595-6
- Methyl p-tolyl-sulfone (MTSOO), Fluka ref. 69422
- Methyl p-tolylsulfone (MTSOO), Acros ref. 127910050
- Peroxyacetic acid (PAA), Fluka ref. 77240
- Potassium dihydrogen phosphate, Prolabo ref. 26 936.293
- Silica gel 0.2–0.5 mm for chromatography, Merck ref. 1.07733.1000
- Sulfuric acid 95% min. Prolabo ref. 20 700.243
- Titanium oxysulfate hydrate (TiOSO4), Riedel de Haën ref. 14023

Filter coating solution for HP sampling. TiOSO4

2.1 g was dissolved in 50 ml of 0.9 M H2SO4.

Titanium oxysulfate reference solution. The coating solution 2.1 ml was dissolved in 100 ml of molar sulfuric acid.

Silica gel coating for PAA sampling. Na2CO3 106 g was dissolved in 200 ml of water. After complete dissolution, 100 g of silica gel was added. The mixture was dried at 90°C for 8 h, then overnight at 140°C. After cooling, the ‘basic’ silica gel obtained was then sifted to obtain the 0.25–0.5 mm range. MTSO (154 mg) was dissolved in 50 ml of methanol; 50 g of ‘basic’ silica gel was then added to the mixture. The solvent is then evaporated at 50°C under light vacuum.

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The aim of the study described in this paper was to develop a new sampling apparatus suitable for workplace assessment, i.e. the use of coated silica gel or filters instead of an impinger, to allow the simultaneous sampling of (at least) PAA and HP with no mutual interference. The principle is based on the following reaction:

MTSO + PAA → MTSOO + AA

The principle of this sulfoxide → sulfone reaction for the determination of PAA was originally described by Di Furia et al. (1988). It is based on

the transformation of methyl phenyl sulfoxide into methyl phenyl sulfone:

MPSO + PAA → MPSOO + AA
MTS reference solution. Molar MTS solution 0.5 ml was dissolved in 100 ml of an acetonitrile/water (57/43) mixture.

Sampling materials
Polyethylene frit 20 μm, Alltech ref. 211404
Quartz fiber filter (QM-A) 25 mm, Whatman ref. 1851 025
Sampling cassette: 25 mm, Millipore ref. M000025A0
SPE 3 ml glass tube: manufactured on request by Supelco
Teflon frit, pore size 20 μm: manufactured on request by Supelco
SPE 4 ml polypropylene tube, Alltech ref. 210104

Preparation of the cassettes for HP sampling. Two 25-mm quartz fiber filters are placed in the lower part of a cassette at 60°C. They were soaked with 210 μl of the coating solution, then dried for 1 h in a drying oven. The cassette was then closed and was ready for use.

Preparation of the tubes for PAA sampling. Coated silica gel 800 mg was packed into the glass (or polypropylene) tubes between two Teflon frits (or polyethylene frits for the polypropylene tubes).

The cassettes, the tubes and the impingers (separately or connected together) were sampled at a flow rate of 1 l/min, with MSA Escort sampling pumps. This flow rate value is usual for occupational hygiene sampling. In the particular case of our study, two reasons came out in favour of this value:
1. According to Christensen et al. (2000), under this flow rate, a reaction occurs between titanium oxysulfate and PAA, which would not allow accurate simultaneous sampling and analysis of HP and PAA.
2. At a value significantly higher (e.g., 2 l/min), the pressure drop corresponding to the sampling media (coated silica gel + soaked filter) is too high for the technical possibilities of the pump that cannot deliver a constant flow.

Moreover, all the sampling trains were tested before use. All trains with a pressure drop over 5 kPa were dismissed in order to guarantee satisfactory operation of the sampling pumps.

Sample preparation
Immediately after sampling, the cassettes were desorbed with 5–10 ml of molar sulfuric acid. The solution was then made up to 10 ml. After sampling, 5 ml of acetonitrile was percolated through tube containing the coated silica gel prepared to sample the PAA. The resulting solution was then made up to 10 ml with water. The bubbling MTS solution was transferred after sampling to a graduated 20 ml vial. The impinger was rinsed twice with 5 ml of acetonitrile each time, which was added to the graduated vial. It was then made up with an acetonitrile/water (57/43) mixture.

Analytical apparatus
The molecular absorption spectrometry for the analysis of HP was performed with a Perkin-Elmer Lambda 11 at 410 nm.

Two Shimadzu LC-10AT VP pumps were used for the HPLC analysis. The gradient and the data acquisition and processing were controlled by the Varian Star (version 5) software.

A reversed phase Kromasil C18 (Alltech, 250 × 3.2 mm, 5 μm, ref. 62625) column was used to analyze the MTSO and MTSSO. The mobile phase was a 57/43 acetonitrile/water mixture. Detection at a wavelength of 224 nm was performed with a Perkin-Elmer 785 A UV detector. For the analysis of AA a Fast Acid (Biorad 100 × 7.8 mm ref 125-0100) column was used with a 0.25 mM sulfuric acid mobile phase and a Metrohm 732 IC conductimetric detector. This system was used to analyze the solutions resulting from the desorption of coated silica gel or from the bubbling solution.

RESULTS

Laboratory Tests
The first validation test was to check the conservation of silica gel coated with MTSO, and particularly to measure the spontaneous transformation of MTSO into MTSSO. Forty samples were prepared: 20 in polypropylene tubes and 20 in glass tubes. Four series of five were constituted for each of these two types of tubes; the first to be desorbed and analyzed at day D0 (day of preparation), the second at D+4, the third at D+11 and the fourth at D+40. The series desorbed and analyzed previously was analyzed again on the next day when a new series was desorbed. The results are summarized in Tables 1 (polypropylene tubes) and 2 (glass tubes). They are expressed in the form of atmospheric concentrations: it was considered that the samples had been taken for 15 min (reference duration of a TLV-STEL).

From Tables 1 and 2, it appears that a significant quantity of MTSO is transformed into MTSSO when
the silica gel is contained in a plastic tube (0.1 ppm, i.e. a quantity corresponding to about 20% of the TLV-STEL after 40 days). As the transformation inside the glass tube is much slower, this was chosen. Also, it is worth noting that the solution does not evolve in the days following desorption. If the analysis cannot be performed immediately, the analyst has the possibility of treating the tubes and analysing them later.

In the second step, the efficiency of a device allowing the simultaneous sampling of HP and PAA was tested. This comprised a cassette containing filters soaked with titanium oxysulfate to sample the HP followed by a tube filled with silica gel soaked with MTSO to sample the PAA. The connection between the two elements was ensured by means of a silicone rubber seal. This device is shown in Fig. 1. The HP/PAA mixture was generated by depositing a known quantity of commercial PAA on a fibre filter, which was connected above the cassette/tube device. A stream was established through this assembly with a pump at a flow rate of 1 l/min to vaporize the liquid. The flow rate chosen was high enough to allow the PAA to transit the filter soaked with titanium oxysulfate with no reaction, thus taking into account the recommendations of Christensen et al. (2000). Owing to the technical characteristics of the pumps used and the pressure drop induced by the sampling media, it was not possible to perform these tests at a higher flow rate.

In parallel, the same quantity of PAA was injected directly into:

1. a solution of titanium oxysulfate, the analysis of which gave the total concentration of peroxides (HP and PAA) in the deposited sample; and
2. a solution of MTS in which the MTSO was analyzed and which yielded the concentration of PAA in the deposited sample. This MTS → MTSO reaction was preferred as a reference to the MTSO → MTSOO reaction because the latter does not work properly in the liquid phase.

The concentration of HP was determined by calculating the difference between the results of the concentration of the total peroxides and the concentration of PAA.

Five concentrations were tested. For each concentration, four cassette/tube devices, four titanium oxysulfate references and four MTS references were taken or prepared.

The results are summarized in Table 3. The results of the reference analysis are expressed in concentrations (ppm) corresponding to a 15-min sampling (same convention as in Tables 1 and 2). The results of the cassette and tube are expressed in percentage of the corresponding reference (difference between total peroxide concentration obtained from the titanium oxysulfate reference and the MTS reference for the cassette [HP], and the MTS reference for the tube

Table 2. Conservation of the coated silica gel contained in glass tubes

<table>
<thead>
<tr>
<th>Analysis</th>
<th>D₀</th>
<th>D₄</th>
<th>D₄₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₀</td>
<td>0.01 (20.4)</td>
<td>0.01 (7.9)</td>
<td>0.01 (12.0)</td>
</tr>
<tr>
<td>D₄</td>
<td>0.02 (19.1)</td>
<td>0.01 (20.2)</td>
<td>0.01 (19.2)</td>
</tr>
<tr>
<td>D₄₀</td>
<td>0.02 (35.3)</td>
<td>0.02 (35.9)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Efficiency of the device for simultaneous sampling of PA and HP

<table>
<thead>
<tr>
<th>Series</th>
<th>Reference concentration (ppm (RSD %))</th>
<th>Recovery % (RSD %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiO</td>
<td>MTS</td>
</tr>
<tr>
<td>I</td>
<td>2.09 (1.0)</td>
<td>1.61 (1.8)</td>
</tr>
<tr>
<td>II</td>
<td>3.75 (0.5)</td>
<td>2.99 (5.4)</td>
</tr>
<tr>
<td>III</td>
<td>0.42 (4.4)</td>
<td>0.23 (1.0)</td>
</tr>
<tr>
<td>IV</td>
<td>0.32 (3.2)</td>
<td>0.23 (1.1)</td>
</tr>
<tr>
<td>V</td>
<td>0.59 (1.9)</td>
<td>0.47 (0.7)</td>
</tr>
<tr>
<td>Mean</td>
<td>2.07 (2.4)</td>
<td>1.58 (1.8)</td>
</tr>
<tr>
<td>RSD%</td>
<td>6.2</td>
<td>3.4</td>
</tr>
</tbody>
</table>
For the sampling of HP, the efficiency of the cassette is \(~92\% (87–95\%)\), which is consistent with the previous results of Hecht et al. (1999) obtained for sampling on silica gel coated with titanium oxysulfate. For the sampling of PAA, the efficiency of the tube is \(~96\% (94–97\%)\).

The conservation of the PAA sampled on the tubes was also checked. Twenty-five were sampled according to the same method as in the previous experiment. The quantity was chosen to correspond to an atmospheric concentration close to the TLV-STEL sampled for 15 min. In parallel, five reference samples (MTS solution into which the same quantity of PAA was directly injected) were also prepared and analyzed on day $D_0$. The 25 tubes were then separated randomly into five series of five and desorbed and analyzed on $D_0$, $D_{+3}$, $D_{+8}$, $D_{+21}$ and $D_{+35}$. The series desorbed and analyzed previously were again analyzed the next day when a new series was being desorbed.

The results are summarized in Table 4. Despite the quantity of PAA remaining constant in the desorbed solutions, the recovery rate does, however, decrease slowly but regularly from $D_0$ to $D_{+35}$. It was therefore considered that it would be better to treat the tubes in the few days after the sampling. This method was adopted in the field study described below.

### Test in the field

The method was validated during an exposure assessment campaign in four factories manufacturing aromatized mineral waters and in three hospital dispensaries where solutions for injection were prepared under insulators. A total of 144 comparative samplings was carried out. The principle of these comparative samplings is described in Fig. 2. Each sampling point is composed of a tube containing silica gel impregnated with MTSO and an impinger containing the MTS solution in parallel. The inlets of these two sampling apparatuses are connected to the outlet of a cassette for the sampling of HP via a T-shaped joint. Each of the two sampling apparatuses placed in parallel is connected to a sampling pump at a flow rate of 1 l/min. For technical reasons, all these samples were taken statically at fixed locations.

The relationship between the 144 pairs of values is shown in Fig. 3:

$$C_{\text{tube}} = 0.98027 \times C_{\text{impinger}} + 0.00452$$

A similar relationship was established with the 144 pairs of samples for the determination of HP. They were both taken with the same method but the close correlation between the results proved that the experimental atmospheres were homogeneous. The relationship is shown in Fig. 4.

The reaction between PAA and MTS produces AA:

$$\text{PAA} + \text{MTS} \rightarrow \text{AA} + \text{MTSO}$$

It is possible however, to determine the concentration of AA in the atmosphere since the total AA in the bubbling MTS solution comes from the atmospheric AA and from the reaction between

<table>
<thead>
<tr>
<th>Description</th>
<th>$D_0$</th>
<th>$D_{+3}$</th>
<th>$D_{+8}$</th>
<th>$D_{+21}$</th>
<th>$D_{+35}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_0$</td>
<td>96</td>
<td>95</td>
<td>97</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>$D_{+3}$</td>
<td>95</td>
<td>94</td>
<td>94</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td>$D_{+8}$</td>
<td>95</td>
<td>94</td>
<td>92</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td>$D_{+21}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{+35}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>96</td>
<td>94</td>
<td>93</td>
<td>92</td>
<td>90</td>
</tr>
</tbody>
</table>
PAA and MTS. As the concentration of PAA is known, it is therefore possible to obtain the atmospheric concentration of AA by determining the difference between them. This was done in 101 of the 144 samples. On the basis of these results and the concentrations of HP and PAA, an exposure index (EI) was calculated using the conventional formula:

\[
EI = \frac{C_{HP}}{LV_{HP}} + \frac{C_{PAA}}{LV_{PAA}} + \frac{C_{AA}}{LV_{AA}}
\]

with \( C \) being the atmospheric concentration of the pollutant and \( LV \), the limit value of the pollutant.

INRS has proposed limit values for PAA. These values, used in association with the values for HP and AA proposed by the HSE (2002) to calculate two different EIs, were:

1. established with \( LV_{HP} = 1 \) ppm (HSE TWA LV), \( LV_{PAA} = 0.2 \) ppm (LV TWA proposed by INRS) and \( LV_{AA} = 10 \) ppm (HSE TWA LV);
2. established with \( LV_{HP} = 2 \) ppm (HSE STE LV), \( LV_{PAA} = 0.5 \) ppm (STE LV proposed by INRS) and \( LV_{AA} = 15 \) ppm (HSE STE LV).

As the sampling duration of the filters and the impingers considered in this study ranged generally from 1 to 2 h, neither of these two indices is directly relevant to these samplings. In fact, the use of these indices is merely a way of showing the respective influence of the three pollutants on the overall exposure.

From Figs 5 and 6, it can be seen that the contribution of AA to the global indices is low and tends to decrease as the exposure level increases (from 9 to 2% for the long-term index, and from 8 to 3% for the short-term index). In such conditions, the device proposed in the present study, which only allows the simultaneous measurement of PAA and HP exposure, can be considered as sufficient at around the limit value to provide a fairly good estimation of exposure. Nevertheless, given the limited contribution of AA to the EI, such an estimation can probably be considered as sufficient in most cases. This relative imprecision is, however, to a large extent offset by the convenience of use of the method.

The method is easy to use. No special protection of the sampling pumps against the corrosive vapours due to the impregnation of the filters used for sampling HP with sulfuric acid is necessary. These potential vapours would be neutralized by the highly basic properties of the coated silica gel used for the sampling of PAA. The attention of industrial hygienists using this method should be drawn to the fact that although the PAA sampling tube stores well, the HP filters should be desorbed immediately after sampling because the complex formed is stable only in solution. This drawback is minor as this desorption is easy to perform. This method has been described in detail in the paper devoted to its development (Hecht et al., 1999).

REFERENCES


