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Determination of gas phase peroxyacetic acid using pre-column derivatization with organic sulfide reagents and liquid chromatography

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Abstract

The first selective HPLC methods for the determination of peroxyacetic acid (PAA) in gas phase samples have been developed. PAA reacts with 2-([3-{2-[4-amino-2-(methylsulfanyl)phenyl]-1-diazenyl}phenyl]sulfonyl)-1-ethanol (ADS) to form the corresponding sulfoxide. Sampling may be performed in impingers using aqueous solutions of the reagent or by test tubes with the reagent coated on a solid sorbent. Sulfide and sulfoxide are separated by means of HPLC and detected at a wavelength of 410 nm. The method is highly selective for PAA in the presence of hydrogen peroxide when sampling in impingers. A 10 000-fold excess of hydrogen peroxide leads to the same peak area compared to PAA. Limit of detection is 10^{-8} mol PAA, thus corresponding to PAA concentration of 46 ppb when using a sampling time of 10 min with a flow-rate at 500 ml/min. Another sulfide reagent, methyl-*p*-tolyl sulfide (MTS) has been used in a similar way with impinger sampling. Major advantages of ADS towards MTS are improved UV–Vis spectroscopic properties and reduced volatility.

Keywords: Derivatization, LC; Peroxyacetic acid; Amino(methylsulfanyl)phenyldiazenylphenylsulfonylethanol; Methyltolyl sulfide; Peroxides

1. Introduction

Peroxides have found increasing use as environmentally beneficial disinfection and bleaching agents in recent years. Due to its effectiveness, peroxyacetic acid (PAA) has gained special popularity for the respective applications. For some applications, an evaporation of the peroxide cannot be avoided for technical reasons, thus possibly leading to the exposure of industrial employees. As peroxides may cause severe health problems when present in high concentrations [1], methods for workplace monitoring have to be established to control the exposure of industrial employees to PAA. Contact can irritate

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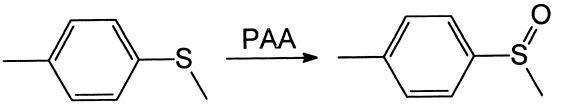
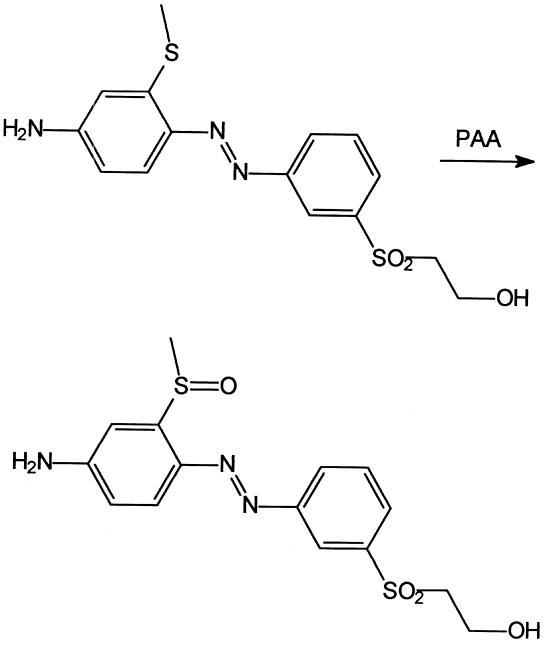
and burn the eyes, skin, nose, throat and lungs leading to permanent damage. Chronic health effects are a cancer and a reproductive hazard. At the moment, no official threshold value for PAA in gaseous phase exists. 1 ppm is used as an internal threshold value by many chemical and pharmaceutical companies.

Due to the production of PAA from hydrogen peroxide and acetic acid in the presence of a mineral acid as catalyst [2], PAA solutions always contain hydrogen peroxide in varying amounts. Therefore, the major challenge for the development of analytical methods for PAA determination consists of achieving a selectivity towards hydrogen peroxide. Titration methods are the oldest techniques used to provide the required selectivity [3,4], but the high limits of detection (LODs) are unsuitable for trace analysis in solution. Photometry [5–12] offers lower LODs, but calibration has to be performed with the relatively unstable PAA solutions. The same disadvantage applies to electrochemical sensors [13–16] which are, on the other hand, suitable for on-line analysis of the peroxides. Chromatography [17–25] offers both selectivity and low limits of detection, although more expensive instrumentation has to be used. DiFuria et al. [18] have developed a gas chromatographic method for the determination of PAA based on the selective oxidation of methyl-*p*-tolyl sulfide (MTS) by the peracid as presented in the following:



The corresponding sulfoxide (MTSO) is formed and separated from MTS by gas chromatography after liquid–liquid extraction. More conveniently, this reaction may be used in combination with liquid chromatography [21–23] without any extraction step. A recently developed, azo-dye functionalized sulfide reagent 2-([3-{2-[4-amino-2-(methylsulfanyl)phenyl]-1-diazenyl}phenyl]sulfonyl)-1-ethanol (ADS) [24] provides lower limits of detection and higher selectivity towards coloured matrix components:



Again, the respective sulfoxide (ADSO) is formed and separated by means of HPLC. Calibration is performed externally with the stable sulfoxide samples instead of the dilute peracid solutions.

All of the methods described above have been designed for liquid phase investigations, typically with the goal to analyze samples from disinfection or bleaching processes. Unfortunately, no dedicated methods for the gas phase determination of PAA have been published yet. In this paper, we describe the first methods for gas phase monitoring of PAA.

2. Experimental

2.1. Safety note

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

2.2. Chemicals

All organic chemicals were obtained from Aldrich (Steinheim, Germany) in the highest quality available, except those listed below. Acetic acid analytical grade was obtained from Merck (Darmstadt, Germany). Acetonitrile used for HPLC analysis was Merck LiChroSolv gradient grade. 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) are described in Ref. [24].

2.3. Photometer

The HP 8453 diode array spectrophotometer (Hewlett–Packard, Waldbronn, Germany) with software HP Chem Station 845x-biochemical UV–Vis system was used.

2.4. Conditions for spectrophotometry

UV–Vis spectra of ADS, ADSO, MTS and MTSO were recorded from 10^{-4} *M* solutions of each compound in acetonitrile–water (50:50, v/v).

2.5. Preparation of the ADS sampling tubes

A 200-mg amount of ADS was dissolved in 200 ml of ethanol. Solid-phase extraction (SPE) tubes were used as sampling tubes and were filled with Chromabond C18f ec material (500 mg) from Macherey–Nagel (Düren, Germany). This material consists of an endcapped C_{18} alkyl modified silica gel with large particle size not stated by the manufacturer. The tubes were conditioned first with 3 ml of ethanol. Afterwards, the material was coated with ADS by seeping 3 ml of the reagent solution through the tubes. Subsequently, the coated sorbent was dried in a moderate nitrogen stream. For all measurements, a collecting and a controlling tube were connected in series to identify incomplete recovery of the analyte on the collecting tube.

2.6. Preparation of the impingers using MTS and ADS

For all measurements, a collecting impinger and a controlling impinger were connected in series to identify incomplete recovery in the collecting impinger. A volume of 2 ml of a 1 m*M* MTS or ADS solution in ethanol and 3 ml of 1 *M* acetic acid was added to 35 ml of an acetonitrile–water–mixture (50:50, v/v) in each impinger.

2.7. Air sampling equipment for sampling experiments

Air sampling was performed using a personal air sampler pump model I.H. from A.P. Buck (Orlando, FL, USA) with the corresponding calibrator, also from A.P. Buck.

2.8. Sampling experiments using impingers

Air sampling with a defined amount of the analyte was performed by pipetting 100 μl of the respective peroxide solution (10^{-4}–10^{-2} *M* PAA, $5\cdot10^{-3}$–10 *M* H_2O_2) in acetonitrile on a plug of quartz wool which was placed in a tube in front of the collecting impinger. The selected evaporation and sampling time was 20 min at a flow-rate of 300 ml/min. After this time, acetonitrile–water (50:50, v/v) was added up to a total volume of 50 ml. After an additional hour, 20 μl of this solution was injected into the HPLC using the conditions stated below

2.9. Sampling experiments using sampling tubes

Air sampling with a defined amount of the analyte was performed by pipetting 100 μl of the respective peroxide solution (10^{-4}–10^{-2} *M* PAA, $5\cdot10^{-3}$–10 *M* H_2O_2) in acetonitrile on a plug of quartz wool which was placed in a tube in front of the collecting tube. The selected evaporation and sampling time was 20 min at a flow-rate of 300 ml/min. After sampling, the tubes were eluted with 25 ml ethanol. 20 μl of this solution was injected into the HPLC.

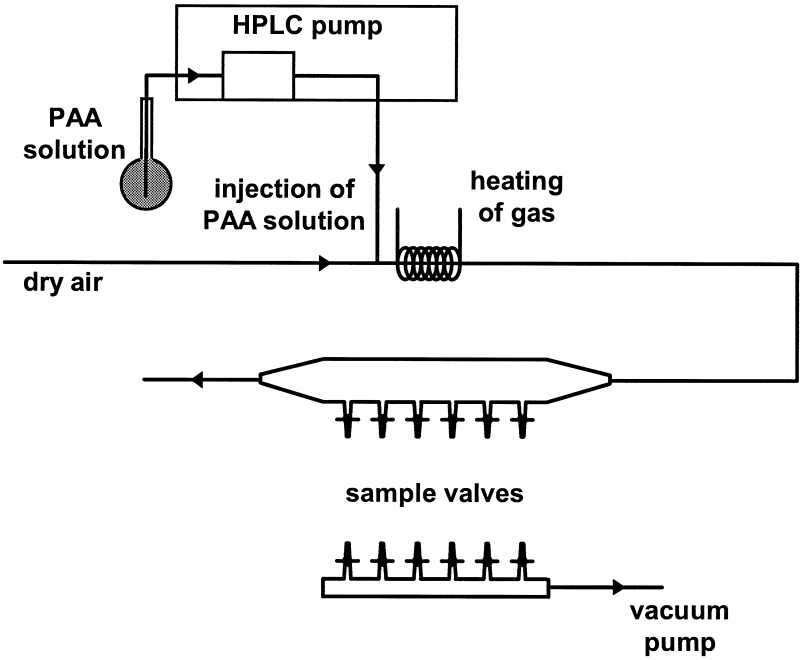


Fig. 1. Schematic assembly of the PAA gas phase generating system.

2.10. Generation of defined PAA atmospheres

The assembly of these experiments is presented in Fig. 1. Different PAA atmospheres in the concentration range 46 ppb–4.6 ppm were generated by nebulizing PAA solutions (in water) in a concentration range from 100 to 10 000 ppm in a total synthetic air flow of 35 l/min. A HPLC pump (Gynkotec, model 330C) with a flow-rate of 50 μl/min was used for the addition of the PAA. Immediately after injection of the PAA solution, the mixture was heated (50°C) to guarantee a complete vaporisation of the PAA solution. The sampling flow-rates were generated by vacuum and regulated by valves using a volume calibrator (Top Trak Sierra, model 822S1-L-1).

2.11. Defined atmosphere experiments using impingers

Solutions for impinger sampling were prepared as described above. The selected sampling time was 10 min using a flow-rate of 500 ml/min. After sampling, acetonitrile–water (50:50, v/v) was added into each impinger up to a total volume of 50 ml. After an additional hour, 20 μl of this solution was injected into the HPLC using the conditions stated below.

2.12. Defined atmosphere experiments using test tubes

The defined atmospheres of PAA were generated as stated above. Sampling tubes were prepared as described above. The selected sampling time was 3 min at a flow-rate of 500 ml/min. After sampling, the tubes were eluted with 25 ml ethanol. 20 μl of this solution was injected into the liquid chromatograph.

2.13. HPLC instrumentation

The high-performance liquid chromatograph consisted of the following components: Two LC-10AS pumps (Shimadzu, Duisburg, Germany), SPD-10AV detector (Shimadzu), SIL-10A autosampler (Shimadzu), Class LC10 Version 1.4 software (Shimadzu), and CBM-10A controller unit

(Shimadzu). Column material was Nucleosil C_8 reversed-phase (Macherey-Nagel) in ChromCart cartridges (Macherey-Nagel): Particle size, 5 μm; pore size, 100 Å; column dimensions, 70×3 mm.

2.14. HPLC analysis

The following conditions were used for the chromatographic separation and detection of the respective sulfides and sulfoxides.

(a) MTSO and MTS

A flow-rate of 1 ml/min. was selected. The binary acetonitrile–water gradient was from 40% acetonitrile after 0.5 min up to 75% within 1 min, from 75% acetonitrile down to 40% within 0.5 min and additional 2 min isocratic at 40% acetonitrile. The detection of MTSO was performed at 230 nm.

(b) ADSO and ADS

A flow-rate of 1 ml/min. was selected. The binary acetonitrile–water gradient was from 20% acetonitrile up to 85% within 3 min, from 85% acetonitrile down to 20% within 0.1 min and additional 1.9 min isocratic at 20% acetonitrile. The detection of ADSO was performed at 410 nm.

3. Results and discussion

Besides the general requirements for a derivatizing agent, air sampling of reactive compounds demands low volatility of the reagent to prevent its evaporation from sorbents or impingers. When using this criterium to compare the two derivatizing agents for PAA liquid phase determination which are known from literature, ADS [24] may be expected to be better suited for gas phase analysis compared to MTS [21–23]. First experiments proved that the volatility of MTS is too high to use this reagent on coated solid sorbents in test tubes. We have therefore investigated the suitability of MTS and ADS using impingers and of ADS on coated test tubes.

The UV–Vis spectroscopic properties of the reagents and their respective reaction products with PAA are important, as absorption maxima located at longer wavelengths may provide improved selectivity in case of colored matrix constituents. The UV–

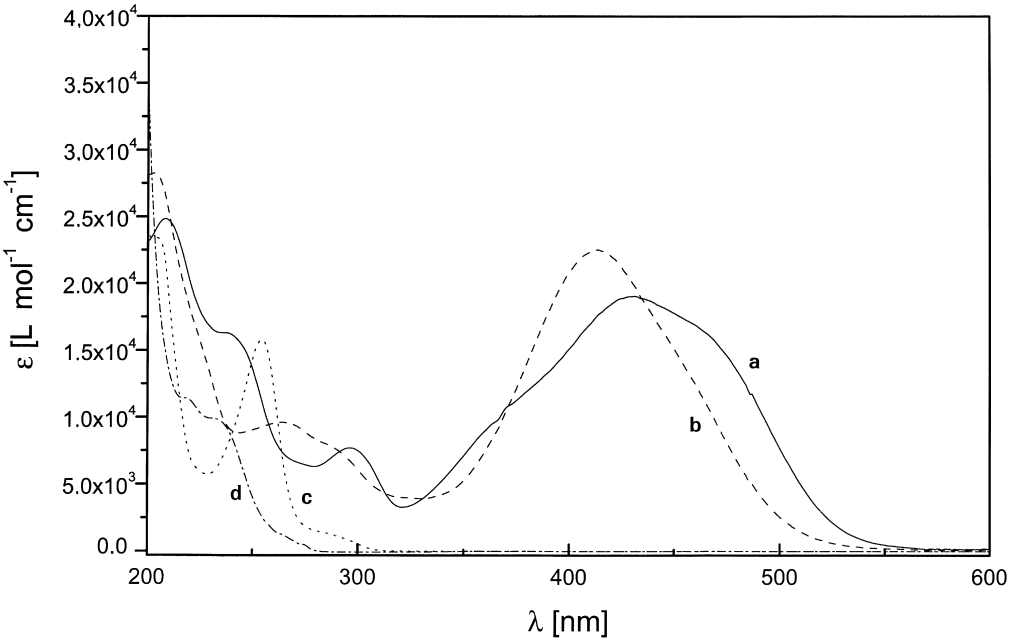


Fig. 2. UV–Vis spectra of (a) ADS, (b) ADSO, (c) MTS and (d) MTSO (for concentrations see Experimental section).

Vis spectra of ADS, ADSO, MTS, and MTSO are presented in Fig. 2.

ADS and ADSO are not only characterized by red-shifted absorption maxima but also by larger molar absorptivities at their absorption maxima compared to MTS and MTSO. This leads to the expectation of lower limits of detection in the case of ADS. In order to achieve low detection limits and to minimize interferences in HPLC, the shoulder in the UV–Vis spectrum at 230 nm for MTSO and the maximum at 410 nm for ADSO were used as detection wavelengths, respectively.

In both cases, reagent and product are easily separated by means of reversed-phase liquid chromatography under conditions as listed in the Experimental section. The respective chromatograms are presented in Fig. 3 for MTS and MTSO and in Fig. 4 for ADS and ADSO.

The large peak of acetic acid in Fig. 3 originates from the addition of this substance to the impinger solutions. Acetic acid provides a moderately acidic pH (pH 3–4) which ensures optimum reaction conditions between the sulfide reagents and PAA. As acetic acid exhibits significant absorption at 230 nm, but no absorption at 410 nm, it is interfering only under the detection conditions for MTSO. Separation of the sulfide reagents and the respective sulfoxides is achieved in less than three min in both cases.

3.1. Sampling experiments

The amounts of PAA and hydrogen peroxide given

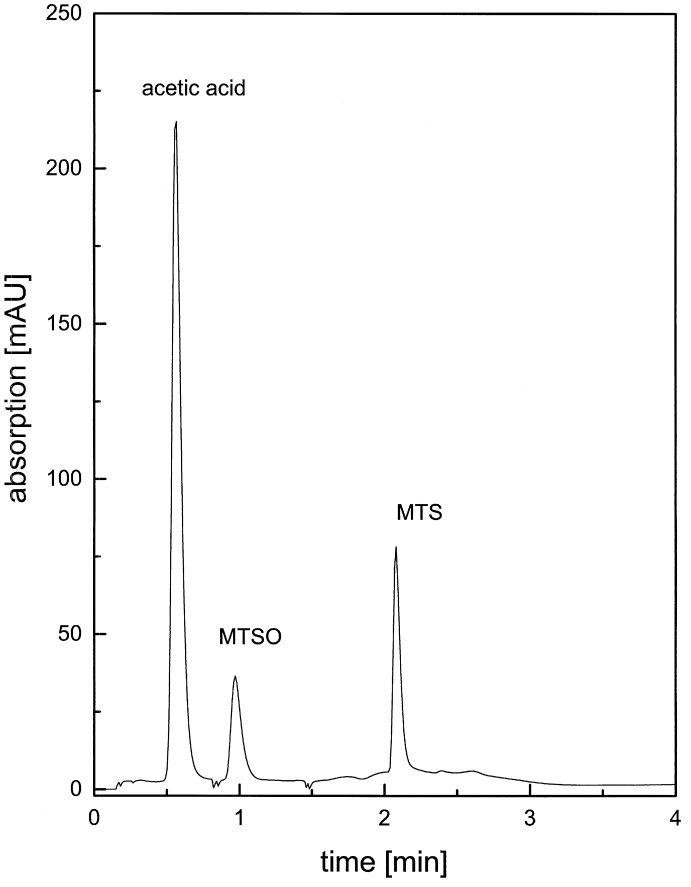


Fig. 3. Chromatogram of the separation of MTS and MTSO. Detection wavelength: 230 nm. A sample of 100 μl 10 m*M* PAA solution (10^{-6} mol PAA) was sampled using impingers and derivatized as listed in the Experimental section.

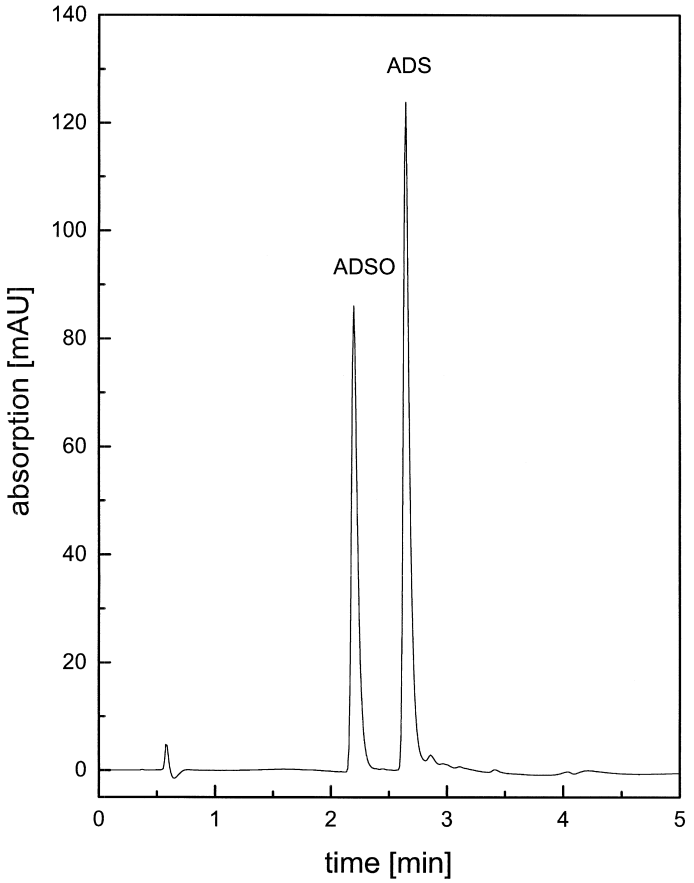


Fig. 4. Chromatogram of the separation of ADS and ADSO. Detection wavelength: 410 nm. A sample of 100 μl 10 m*M* PAA solution (10^{-6} mol PAA) was sampled using impingers and derivatized as listed in the Experimental section.

in this chapter are absolute numbers, and collected with impingers or test tubes, respectively. The calibration curve for the ADS sampling experiment with impinger sampling and the cross selectivity towards hydrogen peroxide is presented in Fig. 5. The method is highly selective for PAA, with a 10^4-fold higher concentration of hydrogen peroxide required to give the same peak area as PAA. The 10^4-fold differences of the peak area between PAA and hydrogen is due to different oxidation kinetics of both peroxides. In contrast to PAA, the reaction of organic sulfides with hydrogen peroxide is kinetically inhibited. The linear range of the calibration curve extends over a factor of 20 from 50 nmol to 1 μmol ($r>0.999$). The LOD ($S/N=3$) is 10 nmol, the limit of quantification 50 nmol. The error bars indicate the standard deviation ($n=3$). The detailed recovery rates and relative standard deviations for PAA using ADS and impingers are given in Table 1.

The respective data for the MTS sampling experiment in impingers are provided in Fig. 6. This method is highly selective for PAA as well, with a 10^3 fold larger signal for PAA compared to equal hydrogen peroxide amounts. The linear range of the calibration curve extends over a factor of 10 from 0.1 μmol to 1 μmol ($r>0.999$). The LOD ($S/N=3$) is 25 nmol, the limit of quantification 100 nmol. The error bars indicate the standard deviation ($n=3$). The detailed recovery rates and relative standard deviations for PAA using MTS and impingers are presented in Table 2.

Fig. 7 contains the data for ADS when sampling

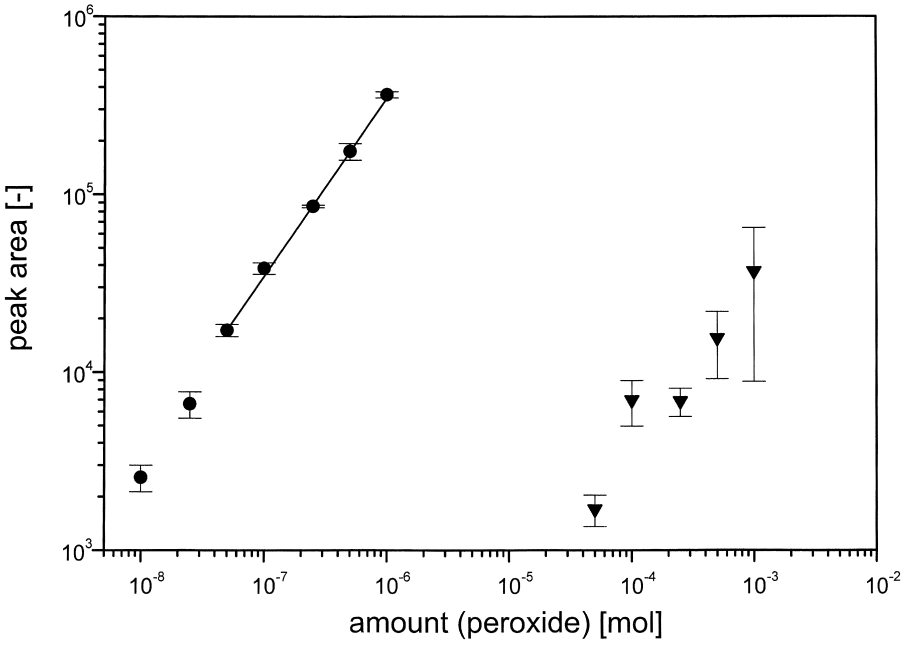


Fig. 5. Calibration curve for PAA in gaseous phase (sampling experiment) using the ADS/impinger method, including the cross selectivity towards hydrogen peroxide (●: PAA, ▼: hydrogen peroxide).

on test tubes. This method is still very selective for PAA as well, with a 10^2-fold larger signal for PAA compared to equal hydrogen peroxide amounts. The linear range of the calibration function extends over a factor of 10 from 50 nmol to 0.5 μmol ($r>0.999$). The LOD ($S/N=3$) is 10 nmol, the limit of quantification 50 nmol. The error bars indicate the standard deviation ($n=3$). The recovery rates for PAA and the respective standard deviations are shown in Table 3.

Table 1
Recovery rates and standard deviations (sampling experiments) using the ADS/impinger method

Amount (PAA) (mol)	Recovery rate (%)	Relative standard deviation ($n=3$) (%)
5×10^{-8}	80.0	6.5
1×10^{-7}	89.2	6.5
2.5×10^{-7}	80.0	1.3
5×10^{-7}	81.3	8.2
1×10^{-6}	84.6	3.4

3.2. Sampling of defined atmospheres

The concentrations used in this chapter describe the PAA concentration of the sampled atmosphere. The calibration data for all three PAA methods when sampling in defined atmospheres are presented in Fig. 8. All concentration data are given for a sampling time of 10 min (impingers) and 3 min (tubes) at a sampling rate of 0.5 l/min. For ADS with impinger sampling, a linear range from 115 ppb to 4.6 ppm ($r>0.999$) was obtained. The LOD ($S/N=3$) is 46 ppb, the limit of quantification 115 ppb. The error bars indicate the standard deviation ($n=3$). The recovery for PAA ranges from 81% to 90%, with an average of 86% and a relative standard deviation ($n=3$) between 0.1% and 10.6%. For MTS with impinger sampling, a linear range from 460 ppb to 4.6 ppm was obtained ($r=0.998$). The LOD ($S/N=3$) is 115 ppb, the limit of quantification 460 ppb. The recovery for PAA ranges from 88% to 95%, with an average of 94% and a relative standard deviation ($n=3$) between 7.8% and 12.1%. For ADS

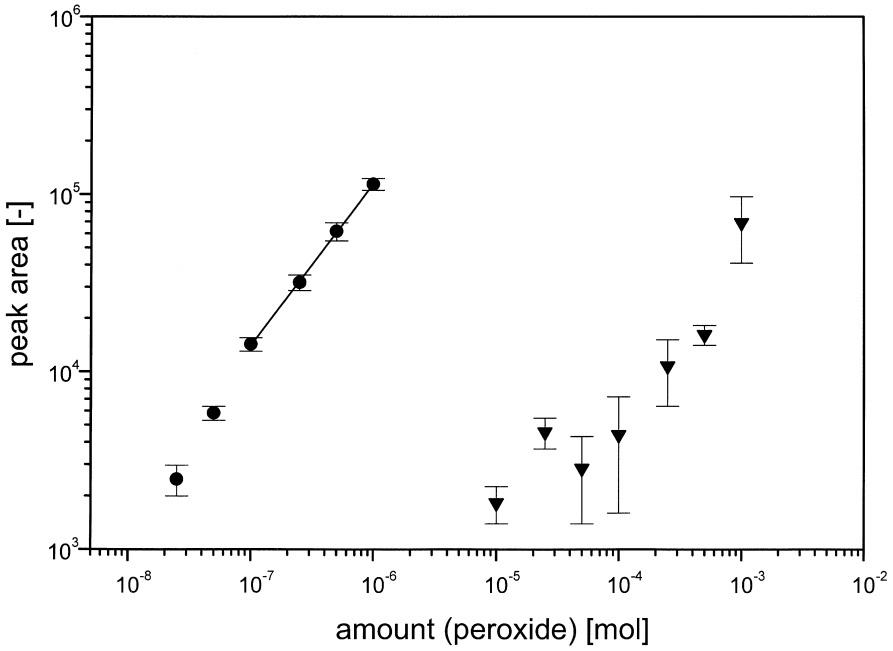


Fig. 6. Calibration curve for PAA in gaseous phase (sampling experiment) using the MTS/impinger method, including the cross selectivity towards hydrogen peroxide (●: PAA, ▼: hydrogen peroxide).

with sampling on test tubes, a linear range from 460 ppb to 4.6 ppm was obtained ($r=0.994$). The LOD ($S/N=3$) is 46 ppb, the limit of quantification 460 ppb. The recovery for PAA ranges from 85% to 95%, with an average of 89% and a relative standard deviation ($n=3$) between 1.4% and 8.4%.

The recovery has been calculated as the amount of PAA found by gas phase measurements divided by an expected value obtained from nebulized amount and air flow-rate. Analysis for PAA in stock solution was performed by the same method as used for the gas phase measurements. It is observed that the recovery is significantly below 100% in all cases, thus indicating that the instable PAA decomposes slightly during the nebulization process. As all sampling techniques and testing schemes used in this work indicate similar recoveries, it is not likely that the loss of analyte may be associated to reaction or sampling problems. However, as there is no other reliable method available to determine the gas phase concentration of PAA, it cannot finally be proven that sampling using the methods described within this work is almost quantitative, although the data indicate a loss of the peroxide during evaporation.

The general limitations of the techniques described herein are based on blanks of the sulfoxides in the reagents or which are formed during sample preparation and elution steps. This limits the lower end of

Table 2
Recovery rates and standard deviations (sampling experiments) using the MTS/impinger method

Amount (PAA) (mol)	Recovery rate (%)	Relative standard deviation ($n=3$) (%)
1×10^{-7}	84.4	8.2
2.5×10^{-7}	75.2	8.3
5×10^{-7}	73.1	9.4
1×10^{-6}	77.4	4.7

Table 3
Recovery rates and standard deviations (sampling experiments) using the ADS/test tubes method

Amount (PAA) (mol)	Recovery rate (%)	Relative standard deviation ($n=3$) (%)
5×10^{-8}	94.1	10.1
1×10^{-7}	87.7	4.7
2.5×10^{-7}	79.9	0.8
5×10^{-7}	86.9	4.5

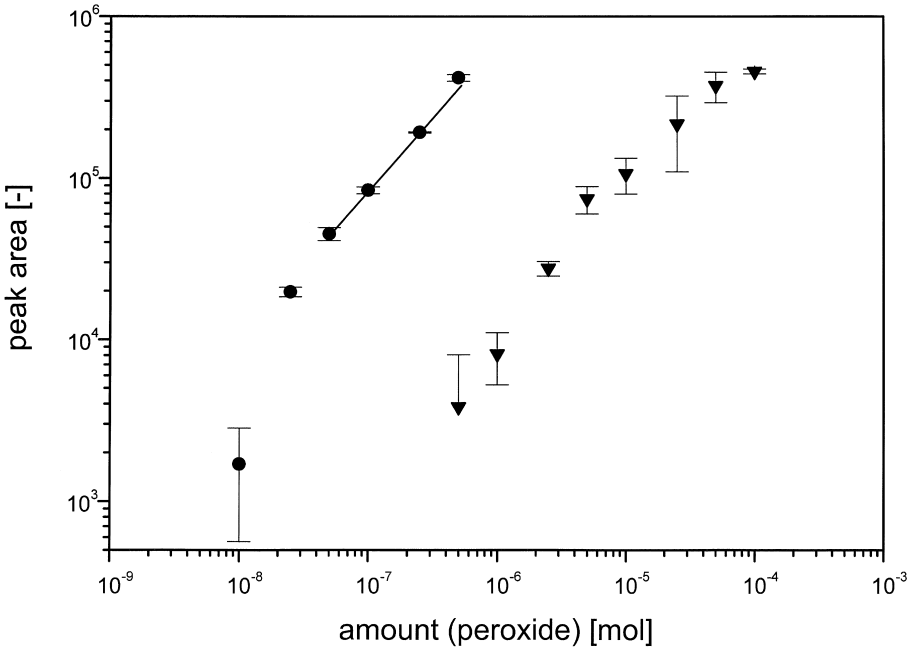


Fig. 7. Calibration curve for PAA in gaseous phase (sampling experiment) using the ADS/test tubes method, including the cross selectivity for hydrogen peroxide (●: PAA, ▼: hydrogen peroxide).

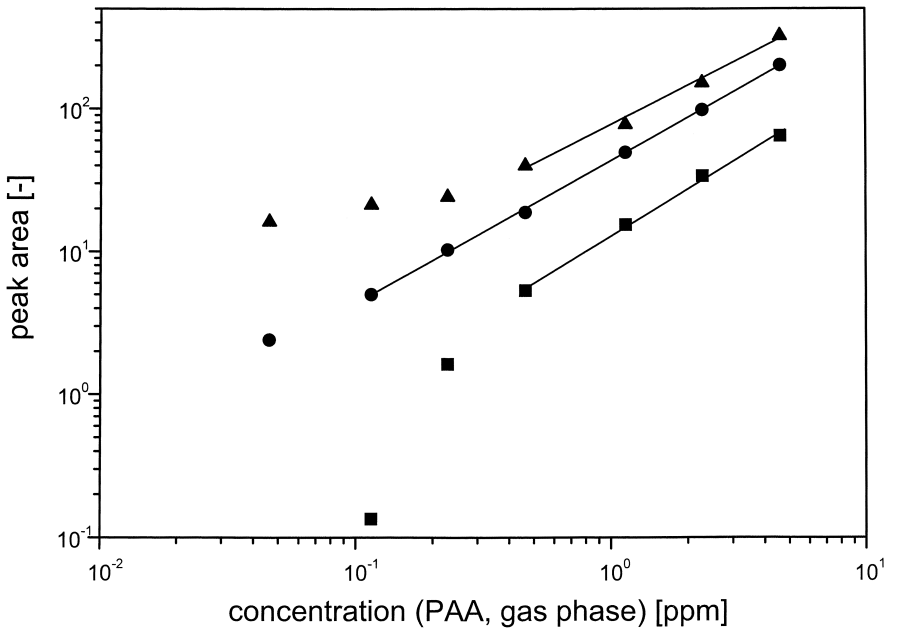


Fig. 8. : Calibration functions for PAA in defined atmospheres using all three methods (■: MTS/impinger, ●: ADS/impinger, ▲: ADS/tubes).

the calibration function, while its upper end is limited by the demand for a sufficient excess of the reagent. In conclusion, the ADS method with impinger sampling may be considered to be the most valuable method for PAA gas phase determination, as its linear range is larger and its LOD is lower compared to the other methods. It should be noted that all methods described in this work are suitable to determine concentrations in the range of 1 ppm PAA when using the sampling conditions stated above.

Acknowledgements

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References

[1] Berufsgenossenschaft Chemie, Merkblatt Organische Peroxide, Verlag Chemie, Weinheim, 1980.
[2] G. Boullion, C. Lick, K. Schank, in: S. Patai (Ed.), The Chemistry of Functional Groups, Peroxides, Wiley, London, 1983, p. 287.
[3] J. D'Ans, W. Frey, Chem. Ber. 45 (1912) 1845.
[4] F.P. Greenspan, D.G. McKellar, Anal. Chem. 20 (1948) 1061.
[5] J.E. Frew, P. Jones, G. Scholes, Anal. Chim. Acta 155 (1983) 139.
[6] D.M. Davies, M.E. Deary, Analyst 113 (1988) 1477.
[7] J.E. Christner, L.J. Lucchese (Serim Research Corp.), WO 92/22806 (1992).
[8] H. Krüßmann, J. Bohnen, Tenside Surfact. Deterg. 31 (4) (1994) 229.
[9] J. Mallard de la Varende, P. Crisinel, L'Air Liquide S.A., US Pat., 5 438 002 (1995).
[10] J. Williams, Interox Chemicals Ltd., EP 0 150 123 (1985).
[11] W. Fischer, E. Arlt, B. Brabänder, Merck Patent, DE 37 43 224 (1987); EP 322 631 (1988); US Pat., 4 900 682 (1988).
[12] U. Pinkernell, H.-J. Lüke, U. Karst, Analyst 122 (1997) 567.
[13] B.J Birch, C.E Marshman, Unilever, EP 0 333 246 (1989).
[14] A. Pinkowski, ProMinent Dosiertechnik, US Pat., 5 395 493 (1995).
[15] G. Teske, Dr. Thiedig & Co., US Pat., 5 503 720 (1996).
[16] H. Kaden, S. Herrmann, Forschungsinstitut Kurt Schwabe Meinsberg, DE 43 19 002 (1995).
[17] G.T. Cairns, R. Ruiz Diaz, K. Selby, D.J. Waddington, J. Chromatogr. 103 (1975) 381.
[18] F. Di Furia, M. Prato, U. Quintly, S. Salvagno, G. Scorrano, Analyst 109 (1984) 985.
[19] O. Kirk, T. Damhus, M.W. Christensen, J. Chromatogr. 606 (1992) 49.
[20] S. Baj, Fresenius J. Anal. Chem. 350 (1994) 159.
[21] U. Pinkernell, U. Karst, K. Cammann, Anal. Chem. 66 (1994) 2599.
[22] U. Pinkernell, S. Effkemann, F. Nitzsche, U. Karst, J. Chromatogr. A 730 (1996) 203.
[23] U. Pinkernell, S. Effkemann, U. Karst, Anal. Chem. 69 (1997) 3623.
[24] S. Effkemann, U. Karst, Analyst 123 (1998) 1761.
[25] S. Effkemann, U. Pinkernell, R. Neumüller, F. Schwan, H. Engelhardt, U. Karst, Anal. Chem. 70 (1998) 3857.