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Rapid high-performance liquid chromatographic method for the determination of peroxyacetic acid

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Abstract

The selective oxidation of methyl *p*-tolyl sulfide (MTS) to the corresponding sulfoxide (MTSO) by peroxyacetic acid and the subsequent rapid separation of the sulfide and sulfoxide are the basis for a fast and reliable HPLC method for the determination of this oxidizing agent in the presence of hydrogen peroxide. The time required for chromatographic separation was reduced to less than 1 min. To improve the long-term stability of the sulfoxide solution, hydrogen peroxide was decomposed catalytically by manganese dioxide. Even in the presence of a tenfold molar excess of hydrogen peroxide, a storability of at least 20 h without a significant increase in MTSO concentration was achieved. External calibration can be performed using the stable and commercially available MTSO. Real samples from a brewery cleaning-in-place disinfection process were analysed and the results were compared with those of the classical two-step titration.

Keywords: Peroxyacetic acid; Methyl-*p*-tolyl sulfide/sulfoxide

1. Introduction

Owing to its increasing use as a disinfectant in the food and beverage industries and as a bleaching agent for textile and paper, peroxyacetic acid (PAA) has to be determined using reliable and accurate methods. As PAA is a strong oxidizer, most analytical techniques for PAA are based on the redox properties of the acid.

Because of the acid-catalysed equilibrium (Fig. 1) hydrogen peroxide is always present in PAA solutions. PAA is technically synthesized by mixing concentrated solutions of acetic acid and hydrogen peroxide in the presence of sulfuric acid as catalyst. H_2O_2 is characterized by similar oxidizing properties as PAA. Therefore, a general problem in PAA determination is to obtain a sufficient selectivity towards hydrogen peroxide.

An early approach to PAA determination [1] involves a two-step titration. As H_2O_2 may act as an oxidizing or as a reducing agent, D'Ans and Frey [1] oxidized hydrogen peroxide with $KMnO_4$ in the first step. After addition of excess

Fig. 1. Acid-catalysed equilibrium.

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iodide and the oxidative formation of iodine by PAA, a thiosulfate titration gives indirect information on the PAA content in solution. Problems arise from the decomposition of PAA catalysed by Mn(II) [2], which is the reaction product of the first titration step. Although devised in 1912, this method is still the most popular technique for PAA determination owing to the low cost and the lack of efficient and reliable alternatives.

More recent methods include photometric methods for PAA determination [3–6]. However, these methods require calibration using PAA standards. Because of the low stability of dilute PAA solutions, they have to be recalibrated frequently using titration or other absolute determination methods. The same calibration problems arise when applying electrochemical (amperometric) sensors, which have been described recently [7] and are now commercially available from several manufacturers. This applies also to automated photometric systems [8].

Direct chromatographic approaches for the determination of peroxycarboxylic acids have been described recently [9,10], but the accuracy of the methods is limited by the low stability of the analytes and the requirement for calibration with peroxide standards as described above.

In contrast, indirect chromatographic methods for PAA determination require more expensive instrumentation but are in general suitable for reliable external calibration procedures if they are based on precolumn derivatization to stable and well defined products. DiFuria and co-workers [11,12] described a gas chromatographic (GC) approach based on the selective oxidation of methyl *p*-sulfide (MTS) by PAA to the corresponding sulfoxide (MTSO) (Fig. 2).

To avoid the extraction step which is necessary to transfer the sulfoxide into an organic phase for GC, Pinkernell et al. [13] recently developed a liquid chromatographic method based on the oxidation of MTS, which requires no further sample pretreatment after sampling.

Fig. 2. Selective oxidation of MTS to MTSO.

First investigations with commercially available PAA solutions have resulted in the statement that the cross-selectivity of the method towards hydrogen peroxide when using this method is negligible [13]. More recent results, however, indicate that there may be a more significant cross-selectivity depending on the contents and ratios of PAA, hydrogen peroxide, acetic acid and sulfuric acid in the disinfectant solution. The occurrence of the cross-selectivity and measures to avoid problems when analysing real samples from cleaning-in-place (CIP) disinfection in breweries are presented in this work.

2. Experimental

2.1. Safety note

PAA is a strong oxidizer and may react with organic substances. The procedures described here have only been tested with PAA concentrations up to 2000 mg/l. Concentrated PAA solutions should never be mixed with organic substances, including solvents.

2.2. Chemicals

All chemicals except those specified below were purchased from Aldrich Chemie (Steinheim, Germany) in the highest quality available. PAA solution A is Henkel (Düsseldorf, Germany) P3 Oxonia Aktiv with a nominal concentration of 1–5% PAA, 15–30% hydrogen peroxide and 5–15% organic acid. The PAA concentration was determined as ca. 4.5% and the hydrogen peroxide concentration as ca. 25% by means of titration (for the procedure, see below). PAA solution B was obtained from Aldrich Chemie with a specified concentration of 32% PAA. The PAA concentration was determined as ca. 37% and the hydrogen peroxide concentration as ca. 5% by means of titration (for the procedure, see below). The PAA solutions were diluted to 400 mg/l (ppm) based on the suppliers' concentration specifications. Sol-

vents for HPLC were Merck (Darmstadt, Germany) LiChroSolv gradient grade. Manganese dioxide powder was obtained from Riedel-de Haën (Seelze, Germany).

2.3. HPLC instrumentation

The HPLC instrument consisted of the following components: Knauer (Berlin, Germany) pump Model 64 HPLC, Knauer variable-wavelength monitor, Knauer injection valve, sample loop 5 μl. Data acquisition was performed using a Compaq 286 personal computer and Knauer HPLC Software Version 2.22. The column (Macherey–Nagel, Düren, Germany) was Nucleosil reversed-phase C_{18} (50 × 4.6 mm I.D.), particle size 3 μm, pore size 120 Å. Isocratic elution was carried out with acetonitrile–water (40:60) as the mobile phase at a flow-rate of 2 ml/min.

2.4. Sample preparation and analysis

Real samples and standard solutions were prepared as follows: 1 ml of sample or standard was mixed with 2 ml of a solution of 10 m*M* MTS in methanol in a volumetric flask. Water, methanol or water–methanol mixtures [a total content of 80% (v/v) water was found to be advantageous; see below] were added to a total volume of 10 ml. A 100-mg amount of manganese dioxide was added to each 10-ml sample exactly 1 min after addition of the MTS solution. In this state, the samples could be stored or shipped. Prior to analysis, centrifugation at 3000 rpm was performed for 15 min. After centrifugation, the samples were injected directly into the sample loop. Detection was performed by UV spectrophotometry at 230 nm.

2.5. Titration

The two-step titration is based on the procedures described many years ago [1,2]: 4 ml of a 25% (v/v) H_2SO_4 solution were added to a 10-ml PAA sample. To oxidize hydrogen peroxide, 0.02 *M* $KMnO_4$ solution was added until the colour of the solution turned pale rose. An excess of solid KI was added and the iodide was oxidized by PAA to brownish iodine, then it was titrated with 0.01 *M* $Na_2S_2O_3$ until only a pale brown colour remained. One drop of 1% (w/v) starch solution was added and the titration was continued until complete decolorization occurred.

3. Results and discussion

The separation of MTS and MTSO on a short RP-18 column is shown in Fig. 3. The two substances can be separated easily within only 1 min. The retention time of the analyte is only 0.35 min and that of the reagent is 0.75 min. External calibration is usually performed via sulfoxide standards; additional information about reagent consumption in a sample can be obtained by using sulfide standards. This results in an improved calibration procedure compared with methods that require calibration with the un-

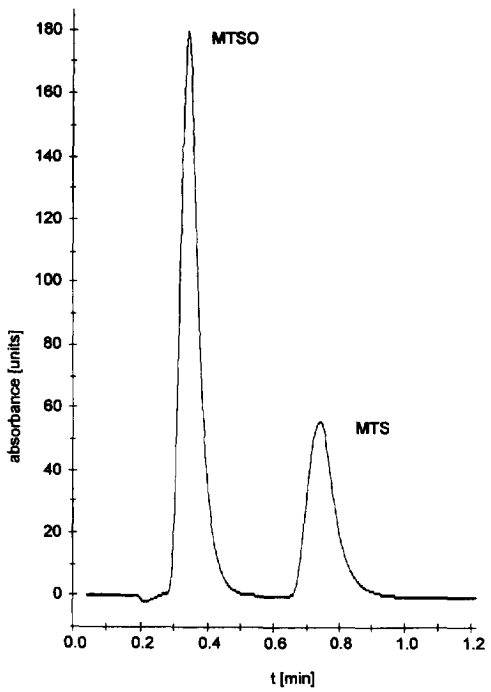

Fig. 3. Chromatogram of MTSO and MTS. Column and chromatographic conditions as specified in the text.

stable PAA itself. For brewery CIP disinfection control, this separation is sufficient. No interferences from other compounds in the disinfectant solutions were observed.

To optimize the reaction time of the sample with the sulfide, the mixture was multiply injected into the HPLC system at close time intervals after mixing. The reaction kinetics of the oxidation are dependent on the solvent and are presented in Fig. 4. It is obvious that a high water content in the reaction mixture is very important to obtain a fast reaction. A mixture with a high water content [water–methanol (60:40, v/v)] reaches 95% of its final sulfoxide peak area after 3 min, whereas the 95% reaction time of a solution with a lower water content [water–methanol) (20:80, v/v)] is ca. 15 min. Therefore, solutions with a high water content are preferred to solutions with a high methanol content. The total analysis time, including sampling and chromatography, can be minimized to less than 5 min. It should be noted that the methanol content in these mixtures results exclusively from the sulfide reagent solutions, because the sulfide is only slightly soluble in water. The methanol content can only be reduced, but not completely avoided.

During the oxidation reaction, PAA is consumed. Owing to the acid-catalysed equilibrium of hydrogen peroxide and acetic acid, new PAA may be formed. Although hydrogen peroxide itself does not lead to the oxidation of MTS, the equilibrium reaction may provide new PAA and therefore an increase of the MTSO signal after storage of the samples. We have found this effect to occur especially in strongly acidic solutions and in solutions with a very high hydrogen peroxide content.

To minimize this influence, we tried to decompose hydrogen peroxide catalytically as soon as the oxidation of MTS to MTSO by PAA was completed. We prepared a platinum catalyst on a solid sorbent by storing quartz-wool in hexachloroplatinate(IV) solution for several minutes and subsequently heating the coated quartz-wool in a burner flame. The catalyst was very active in the decomposition of pure hydrogen peroxide solutions. This platinum catalyst on a solid sorbent, however, did not decompose hydrogen peroxide in the disinfectant solution which con-

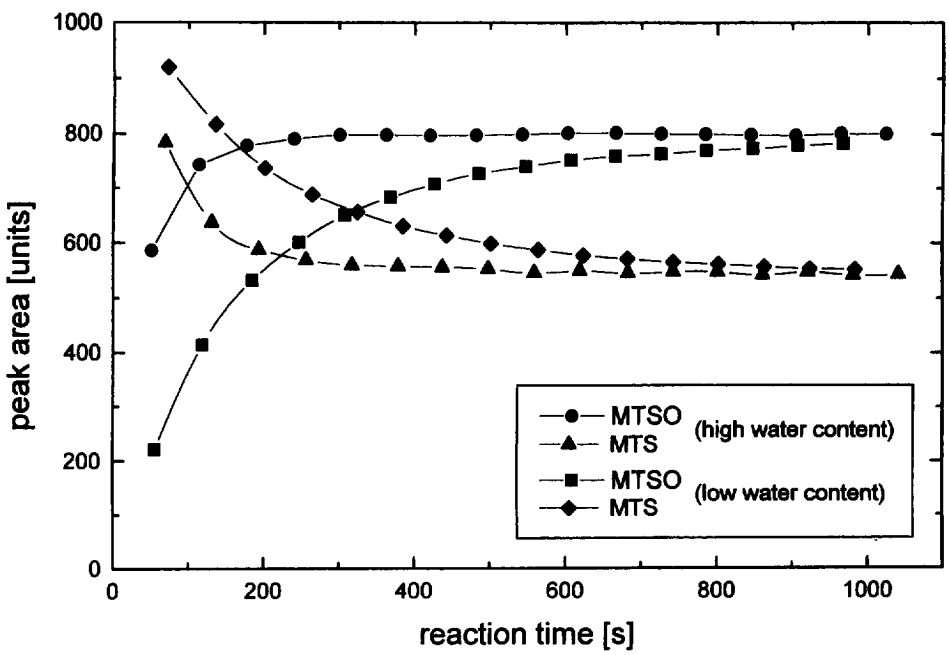

Fig. 4. Reaction kinetics of PAA and MTS in solvents with different water and methanol contents.

tained MTS and MTSO. This may be due to the formation of platinum–sulfide bonds which result in a reduction of the active surface of the catalyst. The application of ammonium iron(II) sulfate was successful concerning the decomposition, but the formation of iron(III) resulted in precipitation of $Fe(OH)_3$. The addition of manganese dioxide was more advantageous: the catalytic properties were excellent and the catalyst could be removed by centrifugation or filtration prior to HPLC analysis.

Two different commercially available PAA solutions were tested concerning the long-term stability of the MTSO signal with and without the addition of the manganese dioxide catalyst. The results are presented in Fig. 5. It is obvious that the storability of PAA solution A (see specification above) is increased strongly by addition of manganese dioxide. Without the addition of the catalyst, this sample should be analysed immediately after sampling. PAA solution B shows only a weak increase in the MTSO signal after addition of the catalyst. The sample can be stored for several hours after sampling without catalyst and for several days when manganese dioxide has been added. Therefore, the addition of manganese dioxide can be recommended strongly for solutions with low pH and high hydrogen peroxide contant which have to be stored before HPLC analysis. Note that manganese dioxide catalyses the rapid decomposition of hydrogen peroxide, not of PAA. Therefore, the time of manganese dioxide addition does not influence the results if it is performed slightly before, simultaneously with or slightly after addition of MTS. However, excellent results were obtained by adding manganese dioxide 1 min after the addition of MTS.

Several factors may influence the effectiveness of manganese dioxide addition. We found that the amount of manganese dioxide added and the time of addition of manganese dioxide before or after the addition of MTS are important factors. In Table 1, the dependence of the amount of manganese dioxide is presented. If the amount of manganese dioxide is a minimum of 100 mg for a 400 ppm sample with a 10-ml volume, the signal increase within the following 20 h is negligible.

A linear calibration graph from $1.3 \cdot 10^{-4}$ to $2.6 \cdot 10^{-2}$ mol/l PAA (10–2000 ppm) was

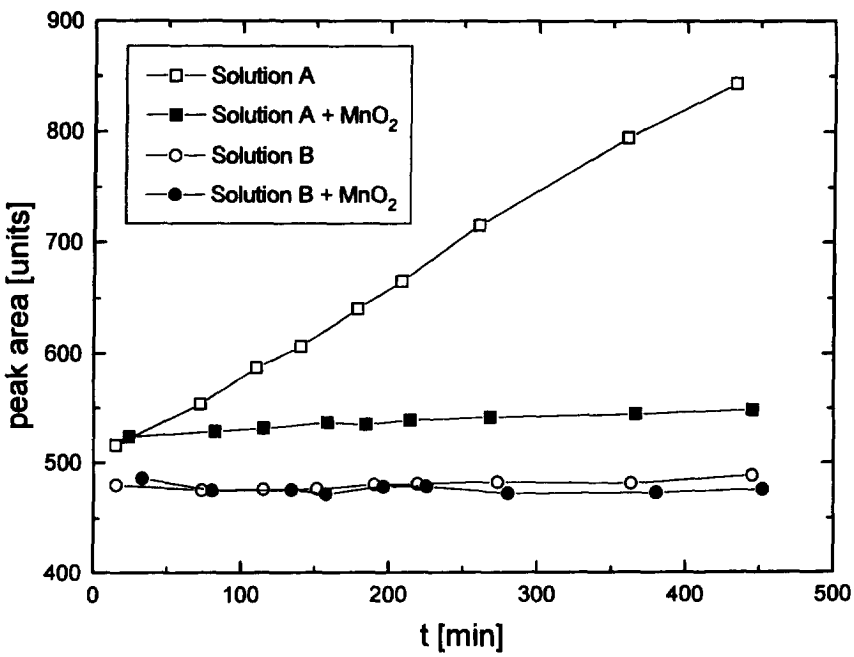

Fig. 5. Long-term stability of the MTSO signal without and after addition of manganese dioxide for two different PAA solutions.

Table 1
Dependence of the MTSO signal on the amount of manganese dioxide (peak area, average for three samples, range for all values ±2%)

MnO_2 added (mg)	Reaction time (h)		
	1	2	20
0	551	593	925
1	550	598	866
10	535	556	585
100	527	527	524
500	517	508	510

Data were obtained using solution A.

obtained. The range of the single values was ca. ±2% of the mean for repetitive measurements ($n = 3$) at all concentration levels. It can be varied by changing the level of dilution. The limit of detection was determined to be $4 \cdot 10^{-7}$ mol/l (30 ppb).

Interferences from other oxidants (e.g., other peroxycarboxylic acids, inorganic peroxides, hypochlorite, chlorine, hypobromite, bromine, permanganate) may occur. However, no interferences of these compounds should occur due to the known composition of the disinfection solutions.

Real samples from different disinfection locations in a brewery (CIP vessel of the bottling plant, keg filling plant and yeast storage vessel) were analysed by titration and the HPLC method described above. HPLC analysis was performed directly at the brewery site and after storage and transport of the sample to another laboratory overnight. The data obtained by titration, by direct HPLC analysis without the addition of manganese dioxide and by HPLC analysis after storage over manganese dioxide corresponded excellently, although the concentrations determined by HPLC were in general a few per cent higher than those obtained by titration.

4. Conclusions

An extremely rapid and reliable HPLC method for the determination of PAA in brewery disinfection samples has been developed. Sampling and analysis can be performed within less than 5 min. Even difficult PAA samples with a high hydrogen peroxide content and low pH can be stored and transported for at least 2 days if manganese dioxide is added to decompose excess hydrogen peroxide. Sampling and analysis can be performed in any standard analytical laboratory without special equipment owing to the use of a very simple but reliable chemical reaction and basic HPLC instrumentation.

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