Reagent for the high-performance liquid chromatography determination of peroxycarboxylic acids

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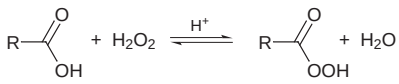
The synthesis and application of a new thiomethoxy-functionalised azo compound for the determination of peroxycarboxylic acids is described. 2-[(3-{2-[4-Amino-2-(methylsulfanyl}phenyl]-1-diazenyl)phenyl)sulfonyl]-1-ethanol reacts selectively with peroxycarboxylic acids in the presence of a large excess of hydrogen peroxide to yield the corresponding sulfoxide. Sulfide and sulfoxide are separated easily using reversed phase HPLC. An important advantage of the new reagent is the absorption maximum of the sulfoxide at wavelengths higher than 400 nm. The cross selectivity towards colored matrix components in real samples is therefore minimised. The method is characterised by an applicable concentration range over more than two decades and low cross reactivity towards hydrogen peroxide and potassium persulfate. External calibration with the respective sulfoxide leads to accurate and reliable results.

Keywords: *Peroxycarboxylic acids; peroxides; derivatisation; high-performance liquid chromatography*

Peroxycarboxylic acids, *e.g.*, peroxyacetic acid (PAA) and *m*-chloroperoxybenzoic acid (*m*-CPBA), are important organic oxidants. PAA is used in industrial processes, including disinfection in the food and beverages industries and bleaching of paper and textiles.[1] Peroxycarboxylic acids are prepared by the reaction of the corresponding carboxylic acid with hydrogen peroxide in the presence of sulfuric acid as catalyst:[2]



Due to this equilibrium, PAA solutions always contain significant amounts of hydrogen peroxide. As peroxycarboxylic acids are strong oxidisers, most analytical techniques for these peroxides are based on the redox properties of these acids. A low cross reactivity towards hydrogen peroxide is therefore a major demand of analytical methods for peracid determination.

An early approach to the determination of peroxyacetic acid involves a two-step titration.[3,4] The major disadvantage of this method is the time dependency of the results.[4] Furthermore, the titration is not suitable for the trace determination of peracids.

Recently, electrochemical[5–8] sensors for PAA determination have been described. Unfortunately, the sensors have to be calibrated using diluted PAA solutions, which are characterised by a limited stability. The peroxide content of the calibration solutions has to be verified using the titration stated above. This is valid as well for photometric methods.[9–16] The accuracy of both groups of methods is therefore limited to that of the reference method.

Some chromatographic methods based on a direct separation of the peroxycarboxylic acids without derivatisation prior to analysis[17–19] have been published. However, these methods have to be calibrated as well using peracid solutions with limited stability. Di Furia *et al*. described a GC method using methyl-*p*-tolyl sulfide (MTS) for the precolumn derivatisation of peroxycarboxylic acids.[20] MTS is oxidised selectively to the corresponding sulfoxide (MTSO):

MTSO is a commercially available solid substance and is used for external calibration. Therefore, calibration with the unstable diluted peracid solutions can be avoided. The transfer of the reaction products from the aqueous to an organic phase is required for GC determination,[20] but can be avoided by employing HPLC for separation.[21] In the latter, detection of MTSO was performed at 230 nm using a UV/VIS detector. Different improvements have been made to avoid the further oxidation of MTS by a large excess of hydrogen peroxide in the solution. Subsequent addition of manganese dioxide[22] or triphenylphospine[23] was used to remove the hydrogen peroxide. In the case of triphenyl phosphine, the corresponding phosphine oxide is formed and can be detected at 225 nm.

Problems may occur due to the low detection wavelengths of the oxidation products in the case of complex matrices. The major objective of the work described here is the development of a new reagent having an absorption maximum above 400 nm for the determination of peroxycarboxylic acids.

Experimental

Safety note

Peroxycarboxylic acids are strong oxidisers and may react with organic substances. Pure peroxycarboxylic acids or their concentrated solutions may cause severe explosions. They should never be mixed with organic substances. The procedures mentioned within this publication have been investigated for peroxycarboxylic acid concentrations of up to 10^{-1} mol l^{-1}.

Chemicals

All chemicals were purchased from Aldrich Chemie (Steinheim, Germany) in the highest purity available. Acetonitrile for HPLC and TLC was Merck (Darmstadt, Germany) gradient grade. The laundry detergent Persil Megaperls (contents according to the package label: < 5% phosphonates, soap, polycarboxylates, 5–15% non-ionic surfactants, bleaching agent, 15–30% anionic surfactants, zeolites) is distributed by Henkel (Düsseldorf, Germany).

Instrumentation

Thin-layer chromatography (TLC) was performed on DC-aluminium foils RP-18 F_{254S} from Merck using a mixture of acetonitrile and water (50 : 50, v/v). Proton NMR measurements were performed with the AC 200 spectrometer (200.13 MHz) from Bruker (Bremen, Germany), ^{13}C NMR measurements with the Unity Plus (600 MHz) from Varian (Darmstadt, Germany). Solvent for all NMR investigations was d_6-acetone. COSY spectra of 2-[(3-{2-[4-amino-2-(methylsulfanyl)phenyl]-1-diazenyl}phenyl)sulfonyl]-1-ethanol (ADS) and its oxidation product were recorded to confirm C–H correlation on the Unity Plus instrument from Varian. FTIR spectral information of the products was obtained in KBr pellets by using the IFS 48 from Bruker. Mass spectra (EI, 70 eV) were recorded on the MAT 212 from Varian. The HP 8453 diode array spectrophotometer (Hewlett-Packard, Waldbronn, Germany) with software HP Chem Station 845x biochemical UV/VIS-system was used. UV/VIS spectra were recorded at a concentration of 10^{-5} mol l^{-1} of the sulfide and the corresponding sulfoxide in acetonitrile–water (50 : 50, v/v). A high-performance liquid chromatograph consisting of the following components was used: two LC-10AS pumps (Shimadzu, Duisburg, Germany), SPD-10AV detector (Shimadzu), SIL-10A autosampler (Shimadzu), Class LC-10 Version 1.4 software (Shimadzu), and CBM-10A controller unit (Shimadzu). Injection volume was 5 μl. The column material was Nucleosil C_8 reversed phase (Macherey-Nagel, Düren, Germany) in ChromCart cartriges (Macherey-Nagel): particle size, 5 μm; pore size, 100 Å; column dimensions, 70 × 3 mm. For separation, a binary gradient consisting of acetonitrile and water was used. A flow rate of 1 ml min^{-1} was selected. The linear gradient used 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 the sulfide and the sulfoxide was performed at 427 nm and 410 nm, respectively.

Synthesis of ADS

2-[3′-Aminophenylsulfonyl]ethanol hydrochloride (2.37 g; 10^{-2} mol) was suspended in 5 ml of 6 mol l^{-1} hydrochloric acid. The mixture was cooled to 0 °C. Sodium nitrite (690 mg; 10^{-2} mol) was dissolved in 4 ml water and added dropwise to the mixture under stirring. After 30 min, this solution was slowly added to a suspension of 1.23 ml (10^{-2} mol) of 3-thiomethoxy aniline in 10 ml 1 mol l^{-3} hydrochloric acid. A suspension with a red colour was formed. After stirring for 1 h at 0 °C, the suspension was neutralised with solid sodium carbonate. The precipitate was filtered off and washed with deionised water. For purification, the product was recrystallised from ethanol–water (75 : 25, v/v) and dried to yield 2.4 g (67%) of the red–orange coloured azo dye. Mp 180 °C; TLC R_F = 0.34; ^{1}H NMR 8.30 (m, 1H, H-2), 8.08 (d, 1H, H-4, J = 7.98 Hz), 7.94 (d, 1H, H-6, J = 7.69 Hz), 7.78 (t, 1H, H-5, J = 7.99 Hz), 7.70 (d, 1H, H-3′, J = 8.85 Hz), 6.70 (d, H-6′, J = 2.31 Hz), 6.52 (dd, H-4′, J = 8.85 and 2.31 Hz), 3.93 (t, 2 H, CH_2, J = 6.35 Hz), 3.50 (t, 2H, –CH_2, J = 6.35 Hz), 2.44 (s, 3H, –CH_3) ppm; ^{13}C NMR (C-q: aromatic, quaternary C-atom) 155.00 (C-q), 154.85 (C-q), 147.33 (C-q), 143.05 (C-q), 141.27 (C-q), 131.38 (C-5), 129.17 (C-6), 127.95 (C-4), 122.53 (C-2), 120.41 (C-3′), 111.81 (C-4′), 109.25 (C-6′), 59.48 (–CH_2), 56.98 (–CH_2), 14.60 (–CH_3) ppm; IR (legend: s, strong; m, medium; w, weak) 3423 (m, –OH), 3336 (m, –NH), 3071 (w), 2938 (w), 2877 (w), 1620 (m), 1595 (s, aromatic), 1483 (m, aromatic), 1406 (m, –OH), 1299 (s, –SO_2), 1253 (m), 1232 (m), 1186 (m), 1140 (s), 1049 (m), 906 (w), 875 (w), 737 (m), 696 (m), 604 (m) cm^{-1}; MS *m*/*z* 351 (M$^+$, 3%), 336 (64%), 318 (100%), 227 (13%), 154 (11%), 123 (17%), 94 (27%), 44 (11%). Analysis for $C_{15}H_{17}N_3O_3S_2$: C, 51.31%; H, 4.91%; N, 12.0%. Found: C, 50.91%; H, 4.88%, N, 11.35%.

Synthesis of 2-[(3-{2-[4-amino-2-(methylsulfoxy)phenyl]-1-diazenyl}phenyl)sulfonyl]1-ethanol (ADSO)

ADS (351 mg; 10^{-3} mol) was dissolved in a mixture of 250 ml of acetonitrile and 250 ml water. PAA 110 ml of a 10^{-2} mol l^{-1} solution in water) was added dropwise with stirring. The extent of the reaction was investigated by using TLC and reversed-phase HPLC. After complete evaporation of the solvent at 40–50 °C, the sulfoxide was dissolved in acetone–water (90 : 10, v/v). A very clean precipitate of the sulfoxide was obtained after very slow partial evaporation of the solvent. The precipitate was filtered off and washed with small amounts of water. Finally, it was dried *in vacuo*. The yield was 232 mg (63%). Mp > 140 °C (decomposition); TLC R_F = 0.51; ^{1}H NMR 8.30 (m, 1H, H-2, J = 1.91 Hz), 8.10 (d, 1H, H-4, J = 8.11 Hz), 8.01 (d, 1H, H-6, J = 7.87 Hz), 7.89 (d, 1H, H-3′, J = 8.59 Hz), 7.81 (t, 1H, H-5, J = 7.87 Hz), 7.40 (d, H-6′, J = 2.62 Hz), 6.92 (dd, H-4′, J = 8.82 and 2.62 Hz), 3.94 (t, 2H, –CH_2, J = 6.19 Hz), 3.52 (t, 2H, –CH_2, J = 6.2 Hz), 2.86 (s, 3H, –CH_3) ppm; ^{13}C NMR (C-q: aromatic, quaternary C-atom; C-X: aromatic, non-quaternary C-atom) 155.29 (C-q), 153.91 (C-q), 149.65 (C-q), 143.31 (C-q), 139.90 (C-q), 131.70 (C-X), 130.17 (C-X), 128.07 (C-X), 125.72 (C-X), 122.53 (C-X), 116.40 (C-X), 109.35 (C-X), 59.45 (–CH_2), 57.02 (–CH_2), 44.99 (–CH_3) ppm; IR (legend: s, strong; m, medium; w, weak) 3392 (m, –OH) , 3335(s, –NH), 3232 (s, –NH), 3086 (w), 2914 (w), 2668 (w), 1708 (w), 1657 (m), 1638 (w), 1597 (s, aromatic), 1552 (w), 1485 (m, aromatic), 1432 (m), 1403 (m), 1318 (m), 1303 (s, –SO_2), 1291 (m), 1259 (m), 1238 (m), 1182 (m), 1167 (m), 1129 (s), 1090 (w), 1049 (s, –S=O), 1037 (m), 1005 (s), 961 (w), 889 (w), 877 (w), 821 (w), 782 (m), 736 (m), 673 (m) cm^{-1}; MS *m*/*z* 367 (M$^+$, 0.5%), 352 (1%), 201 (40%), 154 (21%), 107 (11%), 93 (100%), 65 (24%), 18 (29%). Analysis calculated for $C_{15}H_{17}N_3O_4S_2$: C, 49.02%; H, 4.74 %; N, 11.40%. Found: C, 48.65%; H, 4.84%, N, 10.71%.

Preparation of the peroxycarboxylic acids

All peroxycarboxylic acids with the exception of PAA and *m*-chloroperoxybenzoic acid (*m*-CPBA) were prepared according to ref. 24. PAA and *m*-CPBA were purchased from Aldrich Chemie. In ref. 24, only the preparation of the peroxycarboxylic acids in the range from C_6 up to C_{18} is described. The method has been adapted for the preparation of the peracids C_3 to C_5. Some modifications have been made. The carboxylic acid was dissolved in concentrated sulfuric acid. The solution was cooled down to −5 to −10 °C. Hydrogen peroxide (35%) was added dropwise and very slowly to the stirred solution. In Table 1 the composition of the reaction mixtures for the preparation of all peroxycarboxylic acids used is shown.

The reaction mixtures were stirred for an additional 3 h at room temperature. The pure peracids were not isolated from their solutions to avoid an explosion hazard.[25] The reaction mixture was diluted with 25 ml acetonitrile–water (80 : 20, v/v) to a concentration range between 10^{-2} to 10^{-1} mol l^{-1}. These solutions were stored at −20 °C. No significant decomposition of the peroxide solutions was observed under these storage conditions during three months.

Table 1 Composition of reaction mixtures for preparation of peroxycarboxylic acids

	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{12}
$n_{\text{carboxylic acid}}$/($10^{-3}$ mol)	1	1	1	2	2	1.5	1.5	1	1
$m_{\text{carboxylic acid}}$/mg	74	88	102	232	260	216	237	172	200
$V_{\text{sulfuric acid}}$/μl	125	125	125	464	464	324	300	430	600
$n_{\text{hydrogen peroxide}}$/$10^{-3}$ mol	1.5	1.5	1.5	3	3	2.25	2.25	1.5	1.5
$V_{\text{hydrogen peroxide}}$/μl	146	146	146	291	291	219	219	146	146

Derivatisation procedure for the peroxycarboxylic acid using ADS

ADS was dissolved in 40 ml acetonitrile–water (50 : 50, v/v). (35.1 mg; 10^{-4} mol) Acetic acid (200 μl of 10^{-1} mol l^{-1}) was mixed with 1000 μl of the ADS solution. A portion (100 μl) of the peroxycarboxylic acid sample (concentration range: 10^{-4}–10^{-2} mol l^{-1}) was added. After a reaction time of 10 min, 100 μl of the reaction mixture were diluted with 1000 μl of acetonitrile–10^{-1} mol l^{-1} acetic acid (50 : 50 v/v). This solution was used for HPLC analysis. For quantification, 36.7 mg (10^{-4} mol) of the prepared standard substance ADSO were dissolved in 40 ml acetonitrile–water (50 : 50, v/v). This ADSO solution was diluted and used for calibration in the HPLC analysis.

Chromatographic MTS method

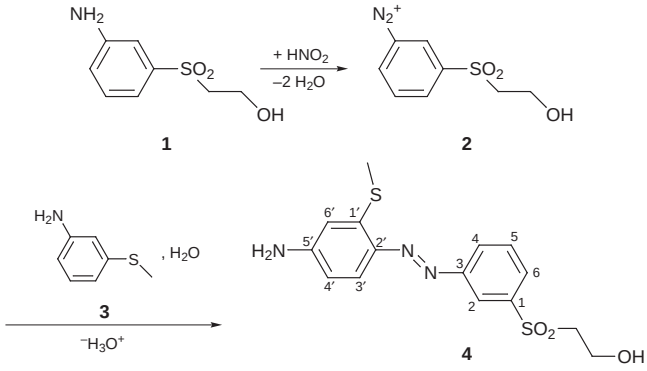
Chromatographic measurements using MTS as a reagent for the selective determination of peroxycarboxylic acids were carried out.[23] Detection of MTSO was performed at 230 nm.

Photometric [2,2′-azinobis(3-ethylbenzothiazoline)-6-sulfonate] diammonium salt (ABTS) method

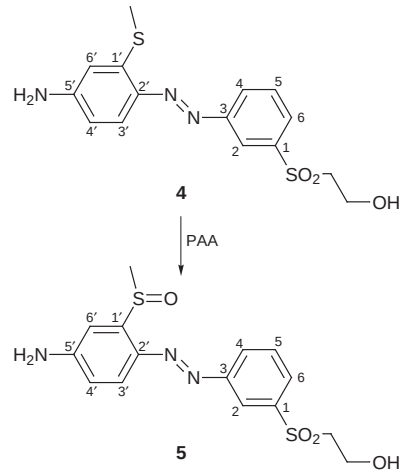
Photometric measurements were carried out as stated in ref. 16. A detection wavelength of 405 nm was selected. The molar absorptivity ε (405) = 3.16×10^4 l mol^{-1} cm^{-1} was used for the quantitative determination.[16]

Results and discussion

A systematic synthesis strategy was developed at the beginning of the project. The most important requirements for a new precolumn derivatising agent are a high reaction rate with peracids in media, low cross reactivity towards hydrogen peroxide, an absorption maximum at a wavelength higher than 400 nm and good chromatographic properties of the sulfide and the sulfoxide. To achieve a good solubility of the reagent in water, polar functional groups should be incorporated into the molecule. On the other hand, some strongly polar groups tend to exhibit tailing in reversed-phase chromatography and require the addition of buffers to the eluent. These functional groups should be avoided if possible. Here, an aliphatic hydroxyl and a sulfonyl group lead to sufficient water solubility of the molecule without negative influences on the chromatographic properties of the molecule. In order to consider these demands, ADS (**4**) was synthesised as described above in detail. 2-[3′-Aminophenylsulfonyl-]ethanol (**1**) was used as starting material. The aromatic amine (**1**) was treated with sodium nitrite in acidic media to yield diazonium ion (**2**). After coupling with thiomethoxy aniline (**3**) in the presence of diluted hydrochloric acid, the azo compound ADS (**4**) was formed.



ADS **(4)** is oxidised selectively to the corresponding sulfoxide (ADSO) by peroxycarboxylic acids. The presence of a large excess of hydrogen peroxide does not interfere. Using the conditions stated above, no formation of the corresponding sulfone was observed. Calibration was performed by using the self-prepared ADSO standard. ADSO was prepared by addition of peroxyacetic acid to a solution of (**4**) in acetonitrile–water as stated above.



The UV/VIS spectra of the sulfide and the corresponding sulfoxide are presented in Fig. 1. For the sulfide, an absorption maximum at 427 nm can be observed. The oxidation of the organic sulfide to the corresponding sulfoxide leads to a shift of the absorption maximum to slightly shorter wavelengths. A broad band in the absorption spectrum of ADSO is observed at 410 nm. Further absorption maxima for both compounds are located at shorter wavelengths. In order to minimise interferences by coeluting compounds in complex matrices, 410 nm was selected as a suitable wavelength for the detection of ADSO.

A solution of 10^{-2} mol l^{-1} PAA was derivatised using ADS. The reagent and the resulting sulfoxide were separated by reversed phase HPLC as stated above. The respective chromatogram recorded at 410 nm is presented in Fig. 2. As additional wavelength, 230 nm (relative maximum for MTSO in the UV/VIS spectrum) was chosen to demonstrate the advantages of the new reagent.

Both compounds can be separated easily within 3 min. The first relevant peak can be assigned to the formed sulfoxide, and the second peak results from the excess of the reagent. For the detection wavelength of 410 nm, not even an increase in the baseline due to increasing acetonitrile concentration is observed.

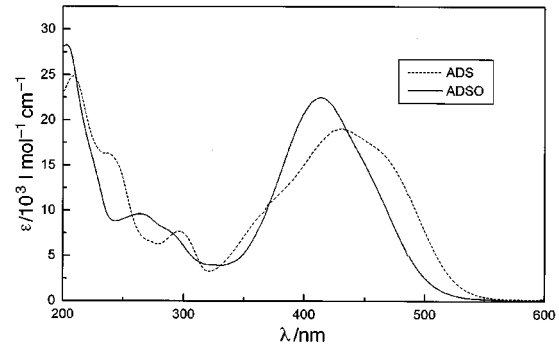


Fig. 1 UV/VIS spectra of ADS and ADSO (for concentrations see Instrumentation).

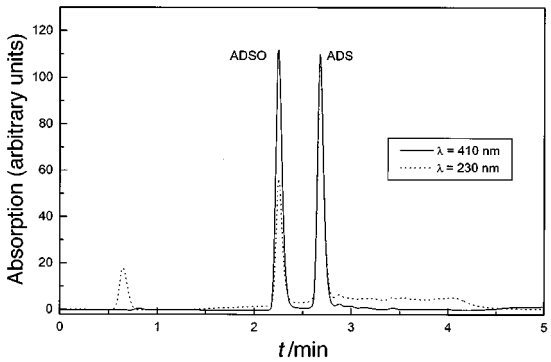


Fig. 2 Chromatogram of the separation of ADS and ADSO. A 10 mmol l^{-1} PAA solution was derivatised according to the text.

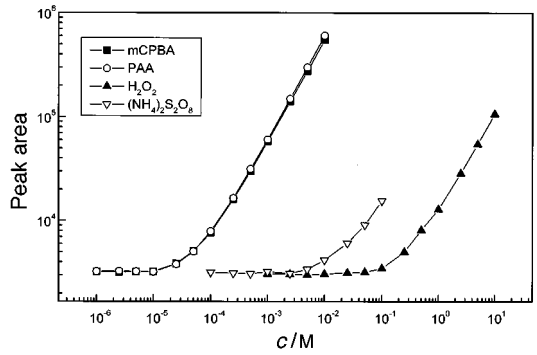


Fig. 3 Calibration curve for PAA and *m*-CPBA using ADS, including the interferences for hydrogen peroxide and potassium peroxodisulfate.

Calibration curves were recorded for the determination of *m*-CPBA and PAA. Both peroxides were diluted and derivatised as stated above. Additionally, the cross reactivity of ADS towards hydrogen peroxide and ammonium peroxodisulfate was investigated. The results are presented in Fig. 3.

The calibration functions of *m*-CPBA and PAA are comparable. Linearity is observed over more than two decades. As can be seen from Fig. 3, the lower limit of detection is limited by the sulfoxide blank in the sulfide ADS, as is the case for the MTS method. Significant cross reactivity towards potassium persulfate is observed for concentration above 10^{-2} mol l^{-1}.

The cross reactivity of ADS towards hydrogen peroxide is negligible, as can be seen in Fig. 3. To achieve the same ADSO peak area, the concentration of hydrogen peroxide has to be higher by a factor of 1000. In typical disinfection solutions, however, the concentrations of hydrogen peroxide rarely exceeds the PAA concentration by a factor of 10.

The limit of detection which is achieved when diluting down ADSO standard solutions is 5×10^{-8} mol l^{-1} with a linear calibration curve over four decades up to 5×10^{-4} mol l^{-1}. However, to estimate a realistic LOD for practical use, it has to be considered that the ADS standard typically contains 0.2% ADSO, which causes a blank. Provided that at least two-fold excess of ADS is required for analysis, this will limit the effective linear range for PAA determination to two decades. Regarding the conditions for the determination of PAA in disinfectant solutions as stated above, a linear range from 10^{-4} to 10^{-2} mol l^{-1} with a limit of detection at 3×10^{-5} mol l^{-1} is obtained. Significantly lower LOD may be achieved easily by diluting down the ADS reagent solution. It should be noted that the time required for quantitative reaction of ADS with PAA will increase in this case.

Furthermore, the reproducibility of the derivatisation and the chromatographic analysis was investigated. Therefore, a 5×10^{-3} mol l^{-1} PAA solution was derivatised ten times, diluted and analysed by HPLC as stated above. The obtained relative standard deviation was only 1.7%. Ten-fold injection of the same sample leads to a standard deviation of 0.4% related to the chromatographic analysis.

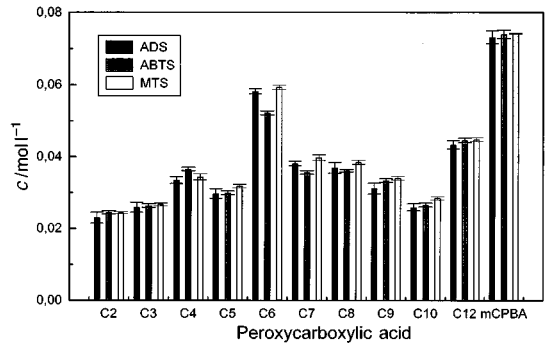


Fig. 4 Comparative measurements of different peroxycarboxylic acids.

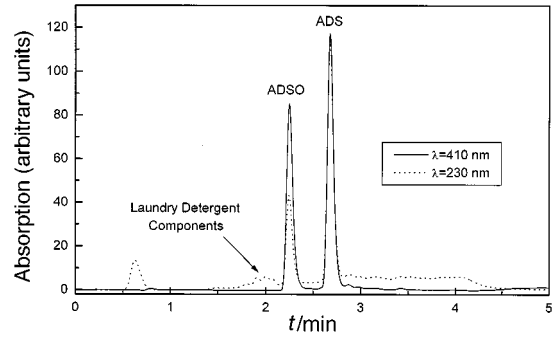


Fig. 5 Chromatogram of the separation of ADS and ADSO. A sample of 2% Persil Megaperls in water was derivatised according to the text.

The reaction of other peroxycarboxylic acids in the range between C_3 and C_{12} with ADS was investigated as well. The ADSO standard was again used for external calibration. The chromatographic MTS method using the commercially available MTSO standard[23] and the photometric ABTS method[16] were used to compare the results of the ADS method to independent methods. The results obtained are presented in Fig. 4.

It is obvious that the three methods correlate excellently in the case of all investigated peroxycarboxylic acids. The advantages of the new reagent become apparent in the case of peroxycarboxylic acid determination in laundry detergents: 2 g of the laundry detergent Persil Megaperls were added to 100 ml stirred water at 20 °C. After 10 min, a sample of 100 µl was derivatised as stated above. The solutions were centrifugated for 5 min at 10 000 rpm to remove the turbidity. The chromatogram recorded at 410 and 230 nm is presented in Fig. 5.

No interferences occur at 410 nm as detection wavelength in contrast to 230 nm, thus proving that ADS is well suited as a new reagent for the determination of peroxycarboxylic acids in disinfection and bleaching solutions.

Financial support of parts of this work by the FAZIT-Stiftung (Frankfurt, Germany) and the Fonds der Chemischen Industrie (Frankfurt, Germany) is gratefully acknowledged.

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Paper 8/01697F
Received March 2, 1998
Accepted May 29, 1998