Journal of Chromatography A, 653 (1993) 283–291
Elsevier Science Publishers B.V., Amsterdam

CHROM. 25 439

Sensitive determination of alkyl hydroperoxides by high-resolution gas chromatography–mass spectrometry and high-resolution gas chromatography with flame ionization detection

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(First received January 21st, 1993; revised manuscript received July 15th, 1993)

ABSTRACT

A method for the determination of alkyl-hydroperoxides by high-resolution GC was developed. Alkyl hydroperoxides were synthesized in the gaseous phase and identified in the chromatograms of the reaction mixture using a GC–MS system. Electron impact mass spectra of C_1–C_6 alkyl hydroperoxides were recorded. The hydroperoxides were determined using flame ionization detection (FID). FID response factors of these compounds were calculated using the concept of the effective carbon number. Detection limits of the hydroperoxides ranged from 91 to 127 pg absolute. The system is also useful for the qualitative identification of labile hydroperoxides as, *e.g.*, 1,2-dichloroethyl hydroperoxide.

INTRODUCTION

The identification and determination of hydroperoxides are important owing to their use as oxidants in industrial processes. Further, they play an important role as intermediates in the oxidation of organic compounds in both the liquid and gaseous phases. Hydroperoxides are also atmospheric oxidation products of natural and anthropogenic hydrocarbons. They are considered to damage plants in conjunction with hydrogen peroxide and contribute significantly to the oxidation potential of the atmosphere [1].

The sensitive determination of hydroperoxides is difficult owing to their thermolability and their tendency to undergo heterogeneous catalysed decay. Therefore, only a few sensitive chromatographic methods for the determination of these species exist.

Liquid chromatography was applied by Deelder *et al.* [2] and Kok *et al.* [3]. Kok *et al.* developed a method for the determination of hydrogen methyl and ethyl hydroperoxide and a few hydroxyhydroperoxides using HPLC and postcolumn reaction for the production of fluorescent derivatives. The detection limit was $5 \cdot 10^{-9}$ *M* for hydrogen peroxide.

There have been only a few applications of gas chromatography (GC) for the determination of hydroperoxides. The determination of selected relatively stable species in large amounts has been described by several workers [4–7]. For example, cumene hydroperoxide, ethylbenzene hydroperoxide, *tert.*-butyl hydroperoxide, ethyl hydroperoxide and cyclohexyl hydroperoxide could be determined using packed columns and flame ionization detection (FID). Disadvantages were the low resolution and the low sensitivity achieved with the packed columns and a varying extent of heterogeneous decomposition of the analytes depending on the stationary phase.

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0021-9673/93/$06.00

In this paper, we present a sensitive method for the identification and determination even of complex mixtures of hydroperoxides in the gaseous phase by capillary GC–MS and GC–FID.

EXPERIMENTAL

Fig. 1 gives a schematic diagram of the analytical system. It consists of a glass vessel for the synthesis of hydroperoxides and GC systems for the qualitative and quantitative analysis of the gaseous mixture.

Synthesis of hydroperoxides

Hydroperoxides were synthesized in the gaseous phase using a method according to Warneck and Bächmann [8]. Hydrocarbons are oxidized by hydroxyl radicals produced from photolysis of hydrogen peroxide by UV radiation. The UV source was a mercury lamp (Oriel, Type 6035). The main reaction pathway is as follows [8,9]:

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH$$

$$(H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}O_2H + H_2O)$$

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + {}^{\bullet}O_2H \rightarrow ROOH + O_2$$

$$ROO^{\bullet} + ROO^{\bullet} \rightarrow \text{further oxidation products (ketones, aldehydes, alcohols, ...)}$$

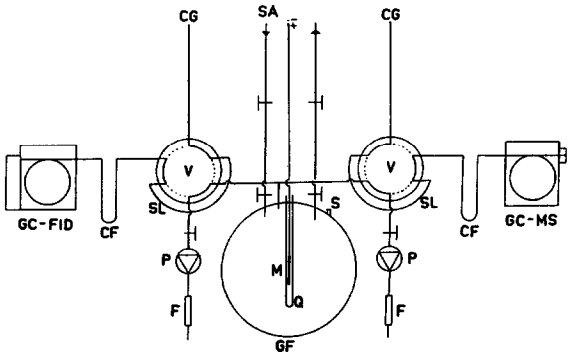

Fig. 1. Schematic diagram of the analytical system. CG = carrier gas; SA = synthetic air; V = six-port valve; F = flowmeter; P = pump; CF = cryofocusing; SL = sample loop; GF = glass flask; Q = quartz glass finger; M = mercury lamp; S = sample injection.

Analytical-reagent grade liquid hydrocarbons and unstabilized 34% hydrogen peroxide were purchased from Merck (Darmstadt, Germany). Gases were obtained from Messer Griesheim at purities of 99.5% or better.

A few micromoles of a single hydrocarbon or a hydrocarbon mixture were injected into a 10-l glass flask (deactivated by treatment with trimethylchlorosilane) followed by unstabilized 34% hydrogen peroxide (molar ratio about 1:1). After a short time for vaporization of the compounds the reaction was started by inserting the mercury lamp into the quartz finger of the reaction vessel.

Gas chromatographic system

The analytical system consisted of two gas chromatographs: a Siemens Sichromat I GC–FID system for quantitative analysis and a Hewlett-Packard GC–MS system (Model 5890/5970 + UNIX chemstation for data analysis) for qualitative analysis. Both gas chromatographs were equipped with 25 m × 0.2 mm I.D. columns with a 0.5-μm Ultra I coating (Hewlett-Packard). The carrier gas was helium at a linear velocity of 45 cm/s (100°C).

The sample was introduced by a six-port valve switching with a sample loop for vapour-phase compounds. In order to avoid hydroperoxide losses due to heterogeneous decay, all connections were made of inert material: the reaction vessel was connected to the valve with a PTFE line and the sample loop was made of Silcosteel (Amchro, Sulzbach, Germany), a stainless-steel tube coated with deactivated fused silica [38 cm × $\frac{1}{8}$ in. I.D. (1 in. = 2.54 cm)]. The analytical column was connected to a precolumn (methylsilyl-deactivated uncoated fused-silica retention gap, 2 m × 0.32 mm I.D.), which was directly connected to the six-port valve through a reduction unit.

Analytical procedure

Vapour-phase samples were taken directly from the reaction mixture in the sample loop (1.4 ml) by a pump, then the transfer of the analytes on to the column was started. The precolumn was cooled to −196°C with liquid nitrogen during transfer of the analytes from the

sample loop to the analytical column in order to provide sharp peaks even of very volatile components (external cryofocusing). Analysis was started by removing the cooling of the pre-column. The separation was carried out with temperature programming, starting at −40°C for 2 min, then increased at 4°C/min to 150°C and maintained at 150°C until all compounds had eluted.

Reproducibility of the sample introduction was tested with mixtures of alkanes, alcohols and ketones. The relative standard deviation of the peak areas was less than 3.2% for all species (five repetitions and FID).

Mass spectrometer analysis

For qualitative analysis, mass spectra were acquired on a Hewlett-Packard Model 5970 quadrupole mass spectrometer with electron impact ionization (electron energy 70 eV). The mass range scanned was 19–200 u at a scan cycle time of 400 ms. Ion abundances of the mass spectrometer were calibrated using perfluorotri-*n*-butylamine (PFTBA). The column was coupled directly to the ion source, the transfer line being kept at 150°C.

Identification

For compound identification a commercially available reference library of mass spectra (NBS–Wiley Library) adopted for the HP 5890/5970 system was used. As only few hydroperoxides were included in the spectral library and the library search for these compounds often failed, the identification was carried out by classical mass spectra interpretation techniques.

Quantification

Owing to the lack of commercially available standards for the hydroperoxides, we used the effective carbon number (ECN) concept for the calculation of response factors. The ECN of a compound was calculated by using the contributions of different molecular structures as determined by Sternberg *et al.* [10]. Using this method, Scanlon and Willis [11] and Jorgenson *et al.* [12] predicted FID response factors with good accuracy (typical relative standard deviations of *ca.* 2–3%) for a wide variety of compounds. As no recommendations for the calculation of the ECN of alkyl hydroperoxides exist, we treated these compounds like the corresponding alcohols.

TABLE I

CONTRIBUTIONS TO THE EFFECTIVE CARBON NUMBER

Data from ref. 11.

Atom	Type of atom	ECN contribution
C	Aliphatic	1
C	Carbonyl	0
O	Primary alcohol	−0.5
O	Secondary alcohol	−0.75
O	Tertiary alcohol	−0.25

Calibration graphs for *n*-butane, 2-butanone and 2-pentanone based on the peak areas were recorded and used as reference components. The alkanes were determined by means of the *n*-butane calibration and oxidation products by means of the ketone calibration. Contributions of the various types of atoms to the ECN of the uncalibrated compounds used are given in Table I.

The relative mass response factors for uncalibrated compounds were calculated using the following equation:

$$f = \frac{M_{rx}\mathrm{ECN}_r}{M_{rr}\mathrm{ECN}_x}$$

where r = reference compound; x = uncalibrated compound and M_r = molecular mass.

RESULTS AND DISCUSSION

Qualitative analysis

In these investigations the oxidation of C_1–C_6 alkanes was carried out. In all instances alkyl hydroperoxides could be identified as the main reaction product by means of their mass spectra. For *tert.*-butyl hydroperoxide an authentic reference standard (80% *tert.*-butyl hydroperoxide in dibutyl peroxide; Aldrich, Steinheim, Germany) was used in addition and the identity of this compound in chromatograms could be verified by comparing the retention times and mass spectra.

TABLE II

MASS SPECTRA (RELATIVE INTENSITY, %) OF THE ALKYL HYDROPEROXIDES

h.p. = hydroperoxide; H.p. = Hydroperoxy.

m/z	Compound (molecular mass)														
	Methyl-h.p. (48)	Ethyl-h.p. (62)	1-H.p.-propane (76)	2-H.p.-propane (76)	1-H.p.-2-methylpropane (90)	2-H.p.-2-methylpropane (90)	1-H.p.-butane (90)	2-H.p.-butane (90)	1-H.p.-pentane (104)	2-H.p.-pentane (104)	3-H.p.-pentane (104)	1-H.p.-2-methylbutane (104)	1-H.p.-3-methylbutane (104)	2-H.p.-2-methylbutane (104)	2-H.p.-3-methylbutane (104)
19	6.0	3.7		3.0				3.0		1.5				0.5	0.8
20															
21															
22															
23															
24															
25		1.9						1.1							1.0
26		8.8	12.4	4.0	3.0	4.6		10.4	2.9	3.2	10.4	1.5		4.0	4.5
27		33.1	52.9	13.1	30.0	17.7	31.2	34.3	41.2	22.1	41.7	8.2		14.9	13.4
28							1.4	11.2		6.6				3.7	7.5
29	100.0	100.0	60.3	21.2	32.6	30.2	47.1	56.0	63.2	20.9	65.5	59.4	31.9	14.9	26.8
30	20.9	10.6	10.3		5.6		2.5	3.0		0.7	6.0	1.8		0.5	
31	26.9	35.3	100.0	3.3	22.2	23.6	42.2	16.4	41.9	5.1	40.5	11.1	8.9	7.5	1.9
32					19.3					1.2					0.6
33	1.8						4.4								
34							1.9								
35															
36															
37			1.6	2.9	1.5	4.1		2.4		1.6					3.3
38			5.1	4.4	7.4	6.8	3.7	3.0		3.2	3.3	1.5		2.2	5.2
39			17.7	15.7	39.3	39.2	25.0	22.4	40.4	23.5		37.1	47.5	15.2	29.8
40			2.9	3.4	5.5	9.7	4.7	3.3	3.1	4.4				2.7	6.7
41		1.8	52.9	39.6	100.0	100.0	100.0	69.4	100.0	32.6	40.9	100.0	98.1	19.7	46.2
42		6.2	28.5	14.2	36.3	12.8	26.8	11.2	89.7	21.3	14.1	20.0	55.0	11.9	21.6
43		22.1	75.7	100.0	91.9	79.5	45.4	73.9	94.1	100.0	70.7	40.1	100.0	100.0	100.0
44		11.0	7.4	9.7	5.6	4.4	16.2	19.4	38.2	16.2	5.2	5.2	31.2	3.7	25.3
45		30.9	2.9	58.2	7.7	1.8	6.6	100.0	14.0	70.6	3.2	4.2	8.9	3.3	68.5
46		8.1		1.5				3.1		1.9					1.8
47	67.5	17.5	6.9				4.7								
48	77.6														
49						1.3		0.8							
50						5.0		4.5		1.5	1.2			1.5	1.8
51						4.1		3.7		1.9	1.5			1.8	1.6
52								0.8		0.7					
53						4.1		4.2	5.1	4.1	4.2	3.2	1.9	4.5	3.3
54								0.8							

55				8.6	10.6	11.2	11.9	68.4	39.7	19.3	36.4	69.8	35.8	26.1
56				11.9	19.4	40.5	19.7	14.7	2.2	1.5	43.1	9.6	1.8	1.6
57		6.2		35.3	73.3	50.1	43.3	29.4	2.5	55.0	66.9	19.3	4.2	2.2
58		12.2	4.8		22.1	1.5	4.0	14.7	2.9	25.3	11.9	4.5	13.4	
59		14.4	1.9		78.1	0.8	16.9		1.7	100.0			23.8	
60		7.4			3.1		0.7			3.1			0.7	
61			4.5				11.2		5.9					5.9
62	24.3													
63	0.7													
64														
65														
66														
67														
68									0.7					
69								13.2	0.7			1.5		0.9
70								30.1	8.8	6.0	18.6	23.8	6.3	5.2
71						2.2		17.6	16.9	23.8	12.6	11.9	22.4	19.3
72				8.9		5.6	6.0		0.8	1.2			3.7	2.7
73							1.5		4.7				11.2	4.8
74				3.7										
75					6.6					12.6			10.4	
76		4.4	6.7											
77														
78														
79														
80														
81														
82														
83														
84														
85														
86									4.3	6.0				3.3
87									0.3					
88														
89													1.0	
90					1.5	1.5	2.3							
91														
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93														
94														
95														
96														
97														
98														
99														
100														
101														
102														
103														
104									1.3	2.2			0.4	
105														
106														

The mass spectra obtained with the GC–MS system used here differ in relative intensities from the mass spectra in the NBS–Wiley Library and literature data [13]. Nevertheless, all characteristic fragments are present and the identity of the hydroperoxides is unambiguous.

Fig. 2 shows a chromatogram with FID for a reaction mixture of alkanes and hydrogen peroxide after a reaction time of 25 min. All possible simple hydroperoxides are present in the reaction mixture. Chromatographic separation of 1-hydroperoxy-2-methylpropane and 2-hydroperoxybutane could not be achieved under the conditions used here, but the overlap of the two peaks could be recognized by means of the MS analysis.

Fig. 3 and Table II presents the mass spectra of the hydroperoxides detected, normalized on PFTBA.

The intensity of the molecular ion peaks decreases significantly from C_1 to C_6 hydroperoxides. The relative stabilities of the molecular ions decreased in the order *sec.*-hydroperoxides ≥ *tert.*-hydroperoxides > primary hydroperoxides. For primary C_5 and all C_6 hydroperoxides molecular ions could not be detected.

The characteristic fragments resulting from elimination of HO_2 (M − 33) and H_2O_2 (M − 34) are present in the mass spectra of all alkyl peroxides with more than two carbon atoms and the M − 33 peak is more intense than the M − 34 peak. Elimination of H_2O (M − 18) and OH (M − 17) is also observed in most spectra, the former peak being more intense than the latter.

Ions resulting from α-fragmentation are generally less intense but give important information on the position of the hydroperoxide group in the molecule. Alkyl hydroperoxides with the hydroperoxide group in the 2-position yield fragments at *m/z* 45 ($C_2H_5O^+$) and the hydroperoxide group in the 3-position results in fragments at *m/z* 59 ($C_3H_7O^+$).

The base peaks in most of the mass spectra of hydroperoxides are typical hydrocarbon fragments; in some instances a contribution of oxygen-containing fragments to the base peak cannot be excluded (*e.g.*, *m/z* 29 in ethyl hydroperoxide and *m/z* 43 in 2-hydroperoxypropane).

Using this system, hydroperoxides of alkyl-substituted aromatic compounds and chlorinated hydrocarbons could also be synthesized, but only in low yields. Fig. 4 shows the mass spectrum of 1,2-dichlorohydroperoxyethane as an example.

Quantitative analysis

In order to recognize losses of hydroperoxides during the analytical procedure and to verify the applicability of the ECN concept to alkyl hydroperoxides, reaction mixtures of single hydro-

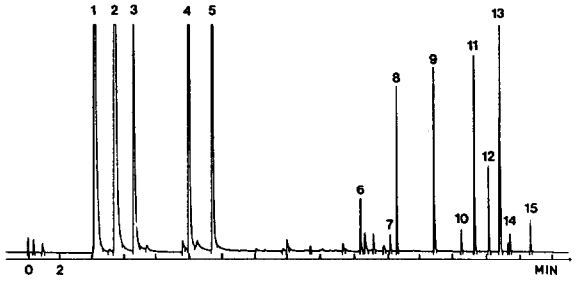

Fig. 2. Chromatogram of a reaction mixture of alkanes and hydrogen peroxide obtained using FID. 1–5 = alkanes (propane, isobutane, *n*-butane, isopentane, *n*-pentane). 6–15 = Alkyl hydroperoxides: 6 = 2-hydroperoxypropane; 7 = 1-hydroperoxypropane; 8 = 2-methyl-2-hydroperoxypropane; 9 = 2-hydroperoxybutane; 10 = 1-hydroperoxybutane; 11 = 2-methyl-2-hydroperoxybutane; 12 = 2-methyl-3-hydroperoxybutane; 13 = 2- and 2-hydroperoxypentane; 14 = 2-methyl-1-hydroperoxybutane and 3-methyl-1-hydroperoxybutane; 15 = 1-hydroperoxypentane. Peaks not marked = other oxidation products (mostly ketones).

TABLE III

DETECTION LIMITS (3σ) FOR ALKYL HYDROPEROXIDES

Compound	Detection limit	
	pg[a]	ppb (v/v)[b]
2-Hydroperoxypropane	127	27
Primary C_4 hydroperoxides	103	18
2-Hydroperoxybutane	108	19
tert.-Butylhydroperoxide	98	17
Primary C_5 hydroperoxides	94	14
Secondary C_5 hydroperoxides	98	15
Secondary C_6 hydroperoxides	91	12

[a] Absolute detection limits.

[b] Resulting detection limits for the vapour-phase concentration in the reaction vessel.

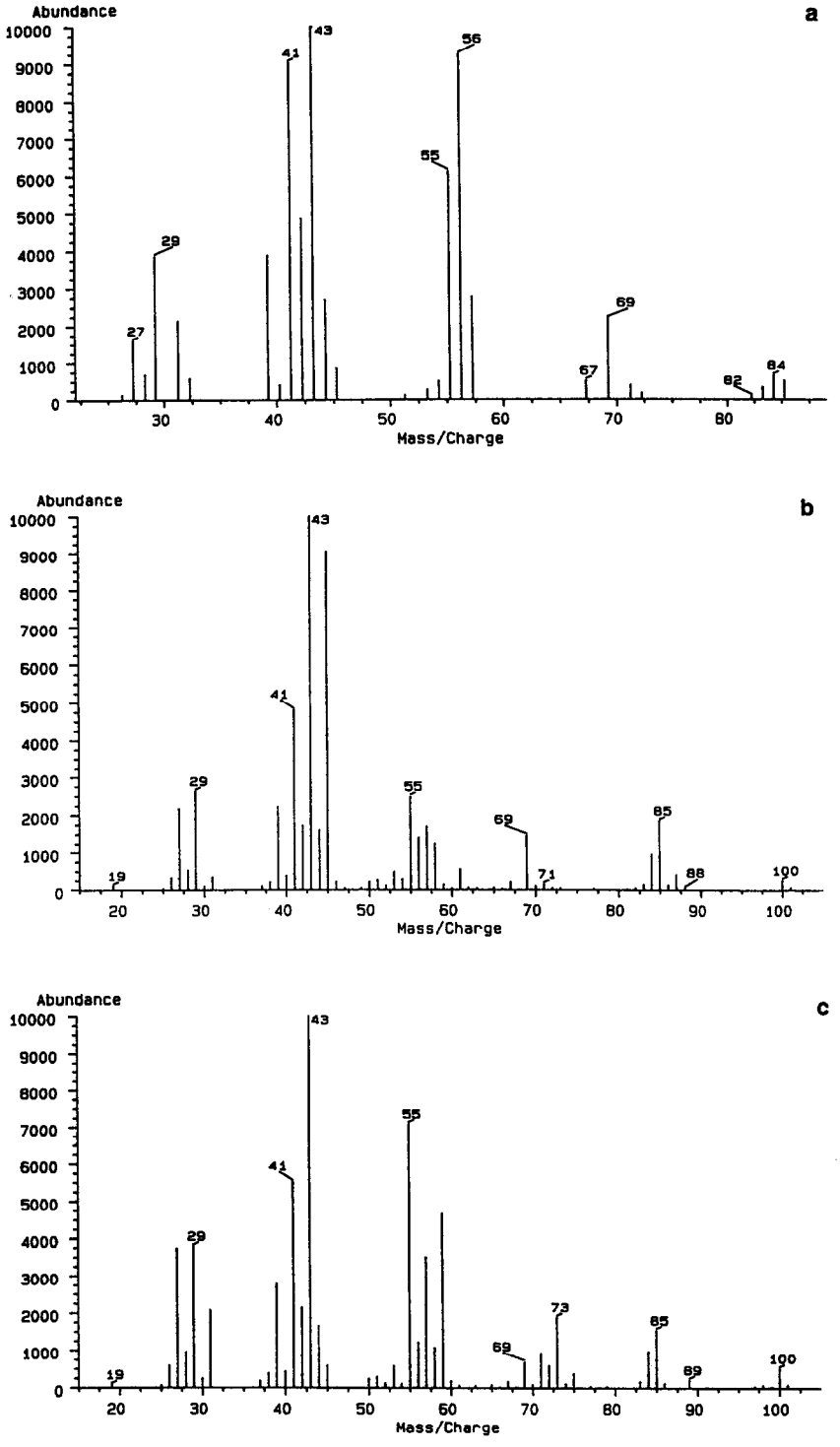

Fig. 3. Mass spectra of the hydroperoxides derived from the oxidation of *n*-hexane. (a) 1-Hydroperoxyhexane, $CH_3(CH_2)_5OOH$ (M_r 118); (b) 2-hydroperoxyhexane, $CH_3CH(OOH)(CH_2)_3CH_3$ (M_r 118); (c) 3-hydroperoxyhexane, $CH_3CH_2CH(OOH)(CH_2)_2CH_3$ (M_r 118).

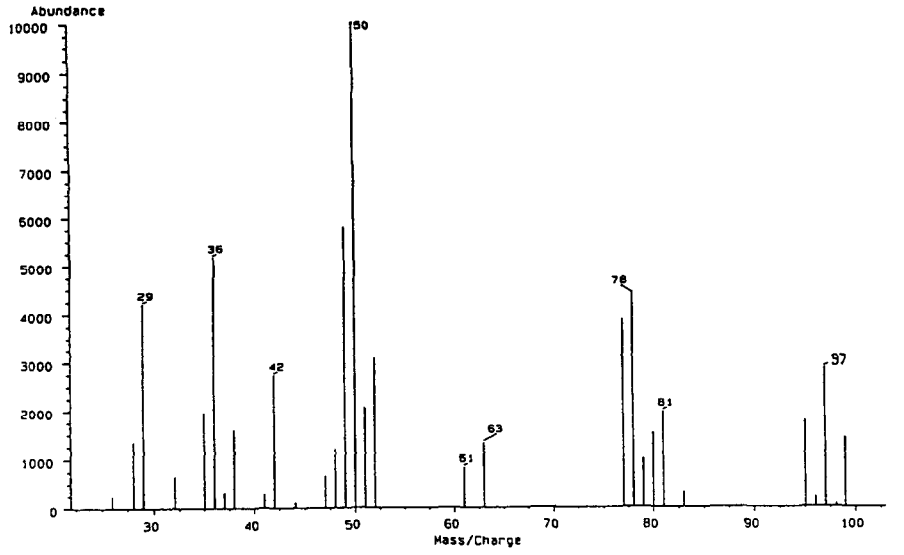

Fig. 4. Mass spectra of 1,2-dichloroethyl hydroperoxide and characteristic fragments (a molecular peak could not be detected).

Elimination of	Molecular mass for the 3 possible chlorine compositions and their relative intensities in parentheses		
	130 (10:)	132 (6,5:)	134 (1)
O_2H (M − 33)	97	99	101
H_2O_2 (M − 34)	96	98	100
^{35}Cl	95	97	–
^{37}Cl	–	95	97
OH and ^{35}Cl	78	80	–
H_2O and ^{35}Cl	77	79	–
OH and ^{37}Cl	–	78	80
H_2O and ^{37}Cl		79	81

carbons were investigated. Reaction mixtures of propane, isobutane, *n*-butane, isopentane, *n*-pentane and *n*-hexane were analysed before starting the reaction and after a reaction time of 25 min. Using the amount of degradation of the educt and the amount of products, mass balances for carbon were established. Recoveries of 94–102% were determined for these alkanes. Therefore, the ECN concept was applicable to the determination of hydroperoxides.

For methane and ethane no carbon balances could be established because cold trapping and the column capacity for these very volatile compounds were insufficient. Peak splitting and peak broadening occurred and quantitative analysis was impossible.

In Table III the detection limits of the hydroperoxides are listed. Detection limits (3σ) were derived using the ECN concept. The detection limits of this system might be improved if sample loops of larger volumes are applied.

CONCLUSION

A sensitive GC method for the identification and determination of alkyl hydroperoxides has been developed. Mass spectra of C_1–C_6 hydroperoxides have been recorded. Detection limits of the hydroperoxides ranged between 91 and 127 pg absolute. With this system, very unstable hydroperoxides such as chlorinated hydroperoxides could also be synthesized and determined.

ACKNOWLEDGEMENT

We are grateful to the Eurotrac subproject Lactoz for financial support.

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