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Note

Qualitative and quantitative determination of hydroperoxides by high-performance liquid chromatography

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Hydroperoxides are increasingly being used as intermediates or as reagents in industrial processes[1–6]. Apart from iodometric titration, no reliable methods are available for the routine analysis of hydroperoxides that are suitable for process control purposes. Gas chromatographic analysis is known to be extremely troublesome, since at the high temperatures needed for the separation of hydroperoxides from other products, the hydroperoxides are invariably decomposed into the corresponding alcohols and ketones. This leads to complications in the analysis of the latter compounds, which are always found as by-products in the formation (and consumption) of hydroperoxides. In principle, this problem may be overcome by using a completely PTFE-lined* gas chromatograph[7] at low temperatures but, because of its complicated nature, this method is unsuitable for routine analyses.

High-pressure liquid chromatography has a number of advantages over GLC, *viz.* (1) It is applicable to non-volatile or thermally unstable compounds (such as hydroperoxides), (2) chemically inert support materials can be used which do not catalyse the homolysis[8] or heterolysis[9] of the hydroperoxides, and (3) reversed-phase elution offers the advantage that the separation is only affected by the proper choice of the eluents[10] so that complications in routine analyses resulting from variations in support/stationary phase composition can be avoided.

On the basis of these considerations we have developed a rapid procedure for the qualitative and quantitative analysis of hydroperoxides.

EXPERIMENTAL

Reversed-phase gradient elutions were carried out using a Hewlett-Packard Model 1010B liquid chromatograph with options 004, 005, 007, and 008, provided with a Hewlett-Packard Model 1030B variable wavelength UV detector set at 225 nm and a Philips LCM-2 wire detector. Stainless-steel columns (2 × 25 cm × 3 mm I.D.) provided with one Chrompack snubber with one removable metal frit (5 μm) per column, were used. The columns were filled with Merckosorb ST 60 (silanized, 10 μm) using the equal density filling technique[11]. Spectro-grade (Uvasol, Merck, Darmstadt, G.F.R.) acetonitrile and demineralized water were used as solvents. Samples of 5 μl

* The decomposition of hydroperoxides at high temperatures is catalysed by metal surfaces[8].

of a 5% solution of hydroperoxide in acetonitrile were injected directly into the solvent stream.

RESULTS AND DISCUSSION

Alkyl hydroperoxides were gradient eluted with acetonitrile–water mixtures starting with acetonitrile–water (0.2:1.8) (2 ml/min) isocratic for 4 min followed by a linear gradient (2 min) to acetonitrile–water (0.4:1.6) and subsequent isocratic elution. The chromatogram shown in Fig. 1 was obtained after injection of a mixture of alkyl hydroperoxides dissolved in acetonitrile. Under similar conditions (for gradient data, see Figs. 1–3) mixtures of alkylaryl hydroperoxides were separated (Fig. 2). As can be seen from the chromatograms, small differences in hydroperoxide structure result in considerable differences in retention times. As shown in Fig. 3, separation of a certain hydroperoxide, *viz.* 1-phenylethyl hydroperoxide (ethylbenzene hydroperoxide, EBHP), from its homolytic decomposition products (1-phenylethanol and acetophenone) can be easily achieved. Under no circumstances was any decomposition of hydroperoxides observed. We were unable to detect acetophenone by means of the LCM-2 wire detector, apparently because of evaporation due to the formation of an azeotrope with water.

We have also studied the quantitative analysis of EBHP using 1-phenylethanol as a reference compound. With EBHP solutions in the concentration range of about 1 M to 10^{-2} M the following linear relationships between EBHP concentrations (g/l) in the sample and the detector response (peak heights) were derived (see Fig. 4):

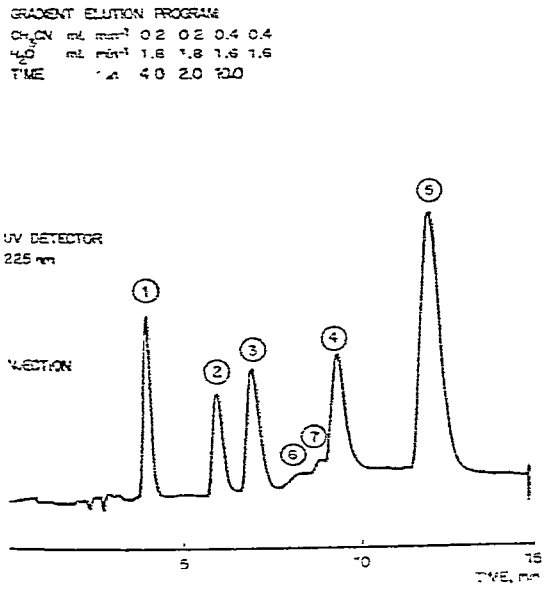
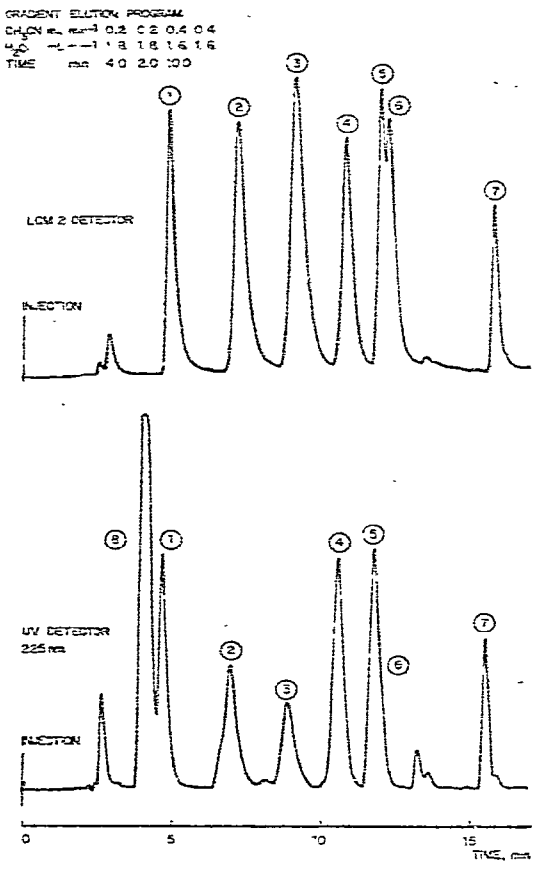


Fig. 1. Chromatogram of (1) *tert.*-butyl hydroperoxide, (2) 1,1-dimethylpropyl hydroperoxide, (3) ,1,2-trimethylprop-2-enyl hydroperoxide, (4) 1,1,2-trimethylpropyl hydroperoxide, and (5) 1,1,2-rimethyl-2-bromopropyl hydroperoxide. 6 and 7 are contaminants present in 4 and 5, respectively.



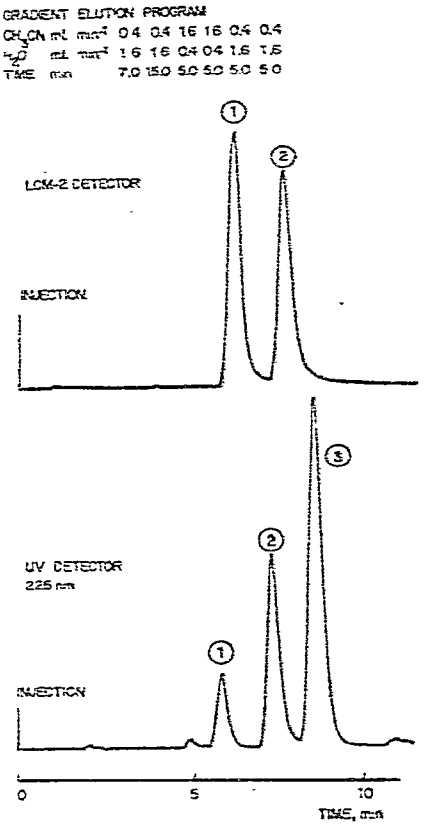


Fig. 2. Chromatogram of (1) cyclohex-2-enyl hydroperoxide, (2) EBHP, (3) cumyl hydroperoxide, (4) tetraline hydroperoxide, (5) *p*-cymyl hydroperoxide, (6) 2-phenylethyl hydroperoxide, and (7) *p-tert.*-butylcumyl hydroperoxide. Note the "false peak" 8 due to a trace contaminant with a very high molar extinction coefficient.

Fig. 3. Chromatogram of: (1) 1-phenylethanol, (2) EBHP, and (3) acetophenone. Note that acetophenone is not detected by the LCM-2 detector.

UV detector

$$[\mathrm{ROOH}] = (351.1 \pm 3.4)\, E + 4.14$$

in which

$$E = C\,[\mathrm{ROH}]\,\frac{E_{\mathrm{ROOH}}}{E_{\mathrm{ROH}}}$$

and

$$C = \frac{E_{\mathrm{ROH}}}{[\mathrm{ROH}]} = 2.94.\ 10^{-3}{}^{*}$$

* As determined from a number of independent measurements.

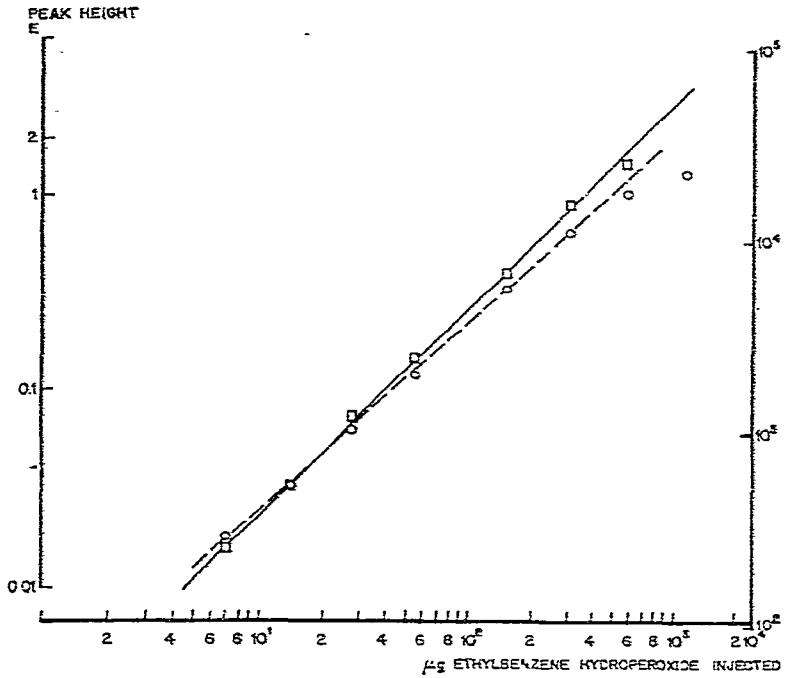


Fig. 4. Quantitatitive analysis of EBHP with 1-phenylethanol as reference compound. ○, LCM-2 detector; □, UV detector set at 225 nm.

LCM-2 detector

$$[\mathrm{ROOH}] = (0.0289 \pm 0.0005)\, R - 0.4$$

in which

$$R = C\,[\mathrm{ROH}]\,\frac{R_{\mathrm{ROOH}}}{R_{\mathrm{ROH}}}$$

and

$$C = \frac{R_{\mathrm{ROH}}}{[\mathrm{ROH}]} = 103.8^{*}$$

All concentrations are in g/l; E = extinction; R = LCM-2 detector response.

These linear relationships are valid up to 330 μg of hydroperoxide injected. However, above this level some deviation from linearity was found (Fig. 4), apparently due to overloading of the column and subsequent peak broadening. Peak surface integration should extend the region of linear detector response. The good linearity of the plots (coefficients of determination: UV detector, 0.9991; LCM-2 detector, 0.9978) substantiates the suggestion that under the conditions of the analysis no decomposition of EBHP to 1-phenylethanol takes place.

Observed standard deviations: UV detector, $\pm$ 2%; LCM-2 detector, $\pm$ 3%. Limits of detection (signal to noise ratio $>$ 3): UV detector, $<$ 0.5 μg injected; LCM-2 detector, 2 μg.

* As determined from a number of independent measurements.

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