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Note

Determination of organic peroxyacids and hydroperoxides by gas chromatography

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The quantitative analysis of organic peroxides, hydroperoxides and peroxyacids by gas chromatography is of considerable interest for these substances are important intermediates in the oxidation of organic compounds in solution and in the gas phase, and they are also widely used as oxidants.

While the determination of organic peroxides is relatively simple, there are difficulties in estimating hydroperoxides and, in particular, peroxyacids. There is often decomposition of the oxygenated compound prior to injection and in the injection port, and, further, there is generally decomposition on the packing material, leading to multiple peaks or, at the best, considerable peak distortion.

The nature of the liquid phase in the packing material does not appear to be of great significance in the estimation of hydroperoxides for esters (*e.g.* dinonyl^{1,2} and didecyl³ phthalate, and tricresyl phosphate⁴), silicones⁵⁻⁸, mixtures of an ester and a silicone⁹ and of an ester and a hydrocarbon^{10,11}, and β,β' -oxydipropionitrile⁸, have all been used to determine relatively stable hydroperoxides (*e.g.* *tert.*-butyl hydroperoxide).

On the other hand, successful quantitative determination of the lower alkyl hydroperoxides and peroxyacids has not been reported in detail. For example, methyl hydroperoxide was found to decompose in the metal inlet port and both the hydroperoxide and methanol were eluted on a dinonyl phthalate column¹², while peroxyacetic acid, although eluted on a similar column, gave a grossly distorted peak¹³.

EXPERIMENTAL

Samples of peroxyacetic acid and peroxypropionic acid were prepared by the gas-phase oxidation of the corresponding aldehydes^{14,15} and ethyl hydroperoxide by oxidation of propanal¹⁴. A sample of *tert.*-butyl hydroperoxide, prepared by Laporte Industries, Luton, Great Britain, was further purified using a preparative gas chromatograph (Pye Model 105). The glass column (1.5 cm length, 6 mm I.D.) was filled with Gas-Chrom Q (Phase Separations, Queensferry, Great Britain) with a liquid phase of 20% (w/w) Apiezon L (Apiezon Products, London, Great Britain) and 11.6% (w/w) dinonyl phthalate (BDH, Poole, Great Britain)¹¹. The authenticity of the compounds

was confirmed by mass spectrometry^{14,16} and their concentrations were determined by iodometric titration.

All chromatograms were obtained using a Pye 104 Model, equipped with a flame ionization detector. Glass columns (1.5 m \times 4 mm I.D.) were used throughout the studies. Nitrogen was the carrier gas.

RESULTS AND DISCUSSION

We report that we are able to separate and estimate quantitatively aliphatic peroxyacids using Gas-Chrom Q (100–120 mesh) coated with 20% (w/w) dinonyl phthalate, and that alkyl hydroperoxides can also be determined successfully. The packing material was conditioned for 60 h at 110°.

At first, the compounds, following preparation in an all-glass apparatus, were vaporized and swept into the gas chromatograph with nitrogen via a short length of steel tubing. It was found, for example, that the area of the peak for peroxyacetic acid did not follow a linear relationship with the concentration of acid, as determined by titration (Fig. 1). As the latter determination was carried out using an all-glass apparatus, it appeared that the peroxyacid was decomposing in the steel tubing leading to the chromatograph. On substituting a glass connector between vaporizer and chromatograph, a linear relationship between peak area and concentration for peroxyacetic acid was obtained (Fig. 1).

Four columns have been prepared over the last three years, all giving satisfactory results, and data from three of them (A, B, C) are presented (Figs. 1–3). The peak shape for peroxyacetic acid (Fig. 2) is symmetrical and that of peroxypropionic

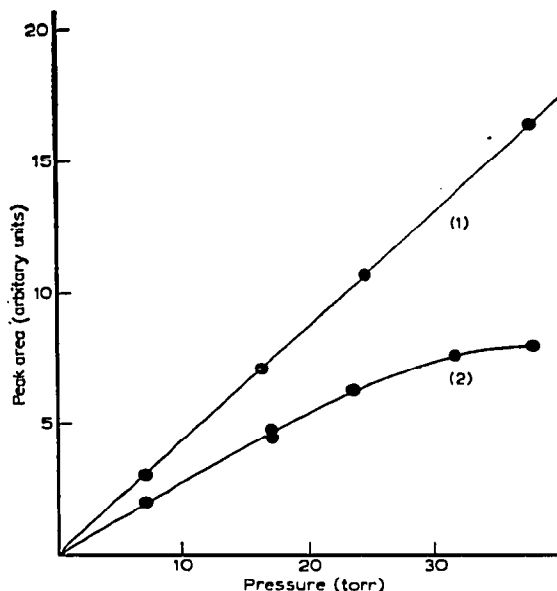


Fig. 1. Plot of concentration of peroxyacetic acid *versus* peak area. Column A at 50°. 1 = All-glass apparatus; 2 = steel connection prior to inlet.

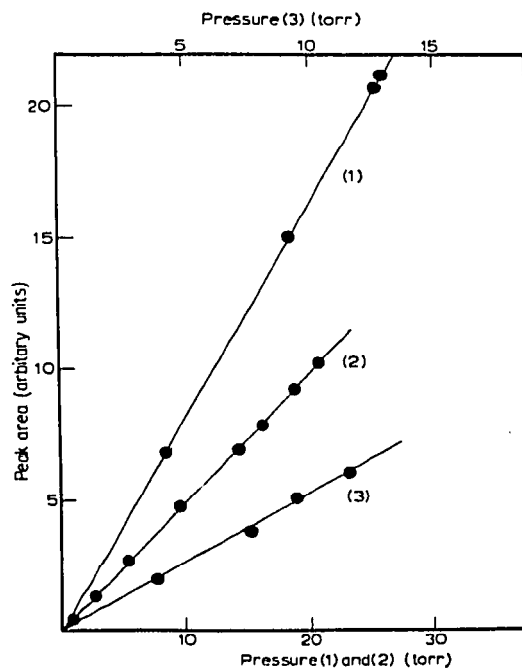
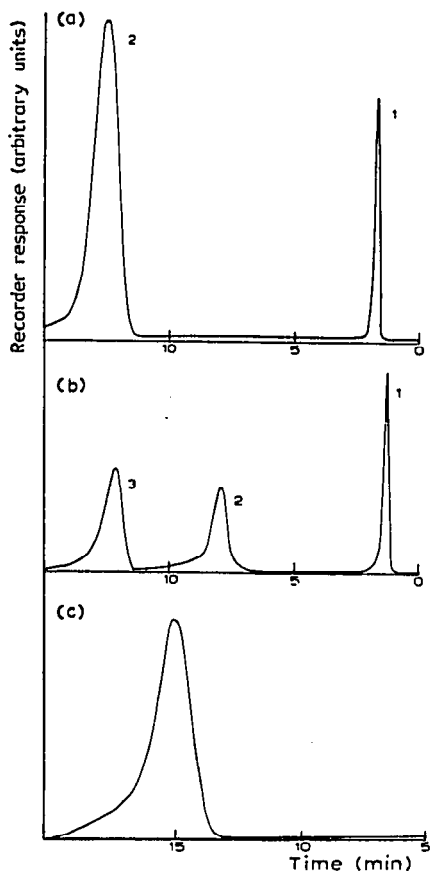


Fig. 2. (a) Elution of peroxyacetic acid on column B at 50°. Nitrogen flow-rate, 25 ml/min. 1 = Acetaldehyde; 2 = peroxyacetic acid. (b) Elution of ethyl hydroperoxide and peroxypropionic acid on column C at 60°. Nitrogen flow-rate, 50 ml/min. 1 = Propanal; 2 = ethyl hydroperoxide, 3 = peroxypropionic acid. (c) Elution of *tert.*-butyl hydroperoxide on column C at 60°.

Fig. 3. Plots of concentrations *versus* peak area. (1) Peroxyacetic acid on column B at 50°; (2) peroxypropionic acid; (3) *tert.*-butyl hydroperoxide on column C at 60°.

acid, although there is slight tailing, also gives good reproducible data (Fig. 3). The shapes for the hydroperoxides are satisfactory and the compounds can be estimated quantitatively.

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