contrast for copying. The high-voltage technique seems to offer a number of advantages, as present work in this laboratory on the separation of incompletely inverted sucrose has already shown. The high degree of resolution and the great saving of time are only two of them.

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Analysis of Organic Hydroperoxides in the Presence of Hydrogen Peroxide

The problem of identifying and estimating accurately organic hydroperoxides in the presence of hydrogen peroxide has recently been solved in these laboratories by two different techniques.

It has been found possible, by the use of filter paper chromatography, to resolve synthetic mixtures of hydrogen peroxide with such peroxides as methyl- or *t*-butyl hydroperoxides. The experiments were carried out with Whatman No. 1 papers placed, in the usual way, between two glass plates. Hydrogen peroxide and methyl peroxide were then separated by developing the chromatogram with ether, and showing the positions of the rings with a thiocyanate reagent. Hydrogen peroxide and *t*-butyl peroxide were conveniently separated with propyl alcohol, and the rings shown up with the usual reagents. The R_F values found were: in ether, hydrogen peroxide 0·4, methyl peroxide 1·0; in *iso*-propyl alcohol, hydrogen peroxide 0·74, *t*-butyl peroxide 1·0.

The first method is mainly qualitative, unless the chromatograms are compared with others obtained with standard mixtures of peroxides. The polarographic method has been applied to the quantitative estimation in two ways. One of these depends on the observation that in an alkaline medium (0·1 *M* lithium sulphate, 0·01 *M* lithium hydroxide), hydrogen peroxide gives two waves. There is first an anodic step with $E_{1/2} = -0 \cdot 1$ V. (against a standard calomel electrode), and then the well-known, slowly rising cathodic step, with the approximate relation $E_{1/2} = -0 \cdot 9$ V. The diffusion currents of hydrogen peroxide which correspond to these steps have equal and opposite values. The presence of organic hydroperoxides has been found to contribute only to the second, cathodic step, though with different diffusion currents (these results will be published in a later communication). It is thus possible to derive the total concentration (hydrogen + organic peroxides) from the cathodic step, and that of hydrogen peroxide only from the anodic step.

If the concentration of hydrogen peroxide is much greater than that of the organic peroxides, then the following modification is more suitable. The hydrogen peroxide is precipitated, in an alkaline medium of 0·2 *M* lithium sulphate and 0·05 *M* lithium hydroxide, by reaction with lanthanum acetate (0·01 *M*). An irreducible basic peroxide of lanthanum is formed, so that a polarogram now reveals only the presence of the organic peroxide. The hydrogen peroxide can then be liberated by acidifying the solution. The lower limit of detection is *c.* 10^{-5}–10^{-6} *M* peroxide.

The methods described are now being applied to the analysis of combustion products.

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Kinetics of Porphyrin-catalysed Chemiluminescent Decomposition of Peroxides, and the Mechanism of Photosensitized Oxidation

A reciprocal relation between photochemical and chemiluminescent reactions is to be expected. In one case, absorbed light leads to chemical action, and in the other, chemical processes result in light emission. As part of a study of the mechanism of dye-sensitized photo-oxidations we have therefore investigated the kinetics of the chemiluminescent reaction between certain dyes and organic peroxides which was discovered by Helberger[1]. For example, magnesium phthalocyanine will catalyse the decomposition of tetralin hydroperoxide in hot hydrocarbon solvents, and this catalysis is accompanied by a bright chemiluminescence[1,2]. Zinc tetraphenylporphine and chlorophyll will also luminesce in these hot hydrocarbon–peroxide systems[2–4].

The reaction between zinc tetraphenylporphine[5] and tetralin hydroperoxide[6] was studied at 149° C. in *tert.*-butylbenzene solvent, chosen because of its high boiling point and low chain transfer constant[7]. All materials were carefully purified, solutions were rigorously de-oxygenated on the vacuum-line and reactions were run in sealed-off tubes. The dye was followed spectrophotometrically, the peroxide by a precise iodometric titration[8], and the emitted light measured by a photomultiplier photometer.

Typical results are given in the accompanying figure and table, showing respectively the catalytic effect of the porphyrin on the peroxide decomposition and data on the time course of the luminescence. The falling-off of the catalytic effect with time is

Chemiluminescent Reaction between Tetralin Hydroperoxide and Zinc Tetraphenylphorphine
Run, *L*-3; temperature, 149° C.; solvent, *t.*-butylbenzene

Tube No.	Time (min.)	[Tetralin hydroperoxide] $\times 10^2$ mol. $l.^{-1}$	[Zinc tetraphenylporphine] $\times 10^5$ mol. $l.^{-1}$	Light intensity ΔG (photometer reading)	$\frac{k_I [P][D] \times 10^8}{\Delta G}$
0	0	1·900	9·20	172	1·02
3	31·5	1·813	6·79	124	0·99
2	66·5	1·702	4·67	78	1·02
1	99·5	1·631	3·32	49	1·11