The analysis of (nC_1–C_{12}) *p*-alkylphenols by a thin-layer chromatographic method

Long chain *p*-alkylphenols are often present in lubricating oils and a rapid means of identifying such phenols in these formulations would be of considerable value, particularly as the quantitative analysis of phenols by ultraviolet spectroscopy depends on a knowledge of the identity of the phenols concerned. Mass spectrometry has been used for the analysis of *p*-alkylphenols but, as only small parent peaks are obtained, it can be difficult to identify the individual components in a mixture of phenols. The paper chromatographic analysis of simple phenols (uncombined, or as azo dyes formed by reaction with diazotized amines) is well established, particularly on paper impregnated with amines[1–4]. The use of thin-layer chromatography for the separation and identification of phenolic materials is described in the literature[5–8] but the emphasis is on phenols not usually encountered in petroleum products. A thin-layer chromatographic (TLC) method for the separation of simple phenols has been described[9] in which the phenols are coupled to form *o*- and *p*-nitrophenylazo dyes that are separated by two-dimensional chromatography on thin layers of alkali-treated silica gel. Thin-layer chromatography does not appear to have been used for identifying the long chain *p*-alkylphenols encountered in lubricating oils. We have therefore investigated its application in this connection and have developed a method for identifying (C_1 to C_{12}) *p*-alkylphenols.

Experimental and results

Adsorbent/solvent system/locating agent. In preliminary experiments with acid, basic and neutral silica gel, and alumina there was little, if any, separation with various developing solvents. However, separations could be obtained on polyamide layers and two solvent systems gave good separations of the phenols when used in conjunction with the polyamides (Table I). The systems were water–dimethyl formamide–formamide (60:40:10, v/v/v) and aqueous *N* sodium hydroxide–methanol

TABLE I

THE SEPARATION OF *p*-ALKYLPHENOLS ON POLYAMIDE WITH TWO SOLVENT SYSTEMS

Solvent system	R_F *values of p-alkylphenols*						
	Methyl	*Ethyl*	*Butyl*	*Heptyl*	*Octyl*	*Nonyl*	*Dodecyl*
Water–dimethylformamide–formamide (60:40:10, v/v/v)	—	0.79	0.68	0.48	0.45	0.34	0.08
N sodium hydroxide—methanol (70:30, v/v)	0.95	0.90	0.81	0.45	0.36	0.22	0.05

(70:30, v/v). The latter system was selected since it gave better separations and is relatively non-toxic. A solution of 0.5 % wt. Fast Blue Salt B (a stable diazonium salt) in water was the most suitable locating reagent; the phenols appeared as brown spots on a white background when sprayed with this reagent.

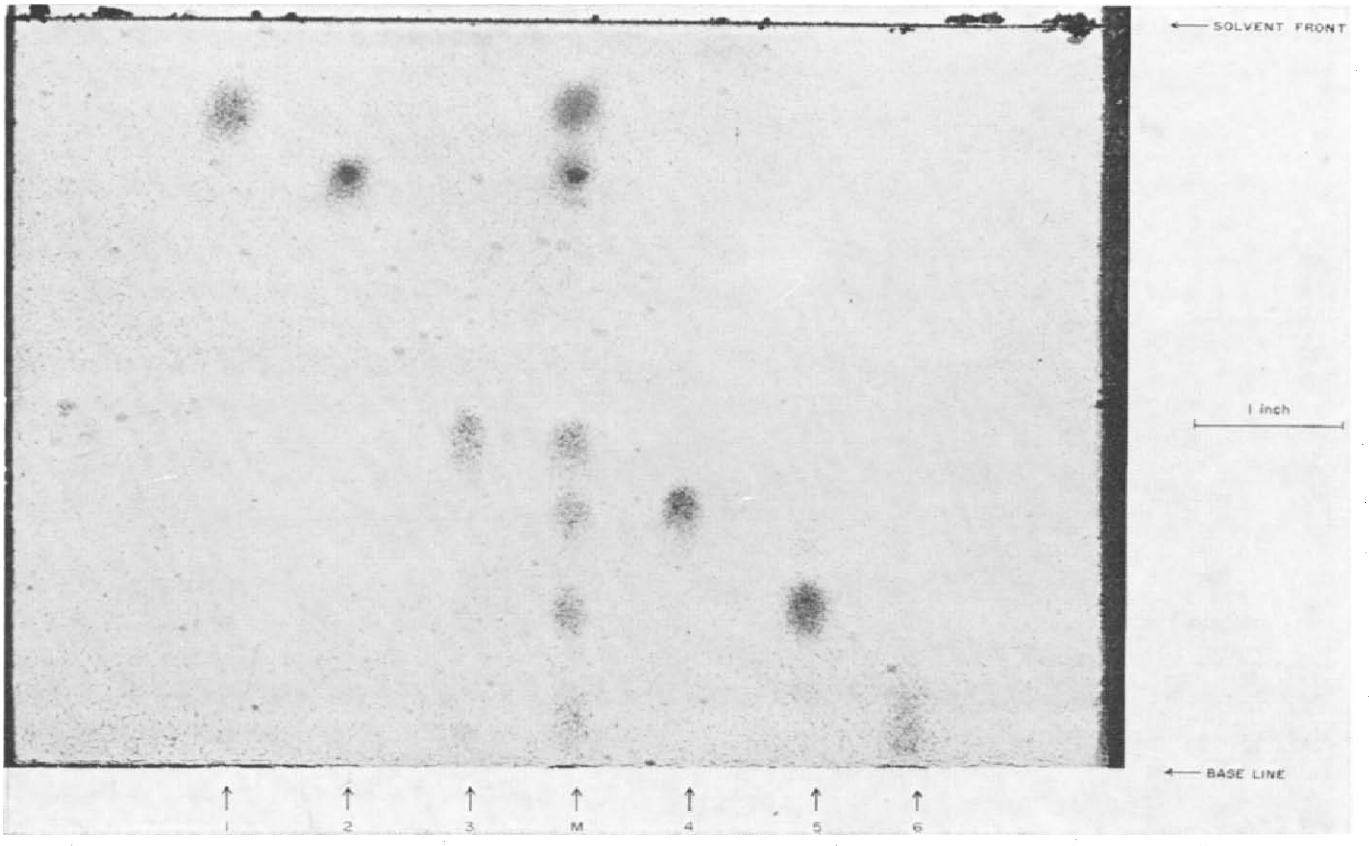

Fig. 1. Thin-layer separation of *p*-alkylphenols. 1 = *p*-Ethylphenol; 2 = *p*-butylphenol; 3 = *p*-heptylphenol; 4 = *p*-octylphenol; 5 = *p*-nonylphenol; 6 = *p*-dodecylphenol; M = mixture of 1–6.

Separation procedure. Solutions containing 0.1 % w of the phenols in chloroform are spotted 1 cm apart on the TLC plate of polyamide (250 μm thickness). The plates are developed in the alkaline methanol solvent and, after the solvent has been allowed to evaporate at room temperature, are sprayed with Fast Blue Salt B solution. The plates are then warmed gently for a few minutes to locate the separated phenols as brown spots on a white background. Typical results, given in Table I and illustrated in Fig. 1, show that the *p*-alkylphenols are well separated. It can be seen also that as the alkyl chain length increases the R_F value approaches zero, so that there is little

TABLE II

IDENTIFICATION OF *p*-ALKYLPHENOL IN LUBRICATING OILS

Formulation	R_F *value of alkylphenol zone*	*Inference*
A	0.04	*p*-Dodecylphenol or higher homologue
B	0.04	*p*-Dodecylphenol or higher homologue

separation between phenols having alkyl groups greater than C_{12}. A complete analysis takes about one hour and as little as 5 μg of each phenol can be detected.

Applications of the method to lubricating oil formulations. Two lubricating oil formulations, suitably diluted with chloroform, were spotted on a TLC plate which was then treated according to the procedure described above. The results given in Table II indicate that *p*-dodecylphenol or a higher homologue is present in each formulation.

It is preferable, but not essential, to use a concentrate of the phenol; such a concentrate can often be obtained by column chromatography; its use reduces the risk of zone elongation which can be caused by the presence of polymers and other additives.

"Shell" Research Ltd., Thornton Research Centre, Chester (Great Britain) P. F. DIAMOND

1 G. B. CRUMP, *J. Chromatog.*, 10 (1963) 21.
2 J. MACAK AND J. KUBES, *Collection Czech. Chem. Commun.*, 25 (1960) 101.
3 W. N. MARTIN AND R. M. HUSBAND, *Anal. Chem.*, 33 (1961) 840.
4 E. SUNDT, *J. Chromatog.*, 6 (1961) 475.
5 G. PASTUSKA AND H. J. PETROWITZ, *Chemiker-Ztg.*, 86 (1962) 311.
6 T. FURUKAWA, *J. Chem. Soc. Japan*, 80 (1959) 387.
7 E. STAHL, *Arch. Pharm.*, 292 (1959) 411.
8 G. PASTUSKA, *Z. Anal. Chem.*, 179 (1961) 355.
9 G. B. CRUMP, *Anal. Chem.*, 36 (1964) 2447.

Received August 16th, 1967