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THE CHARACTERIZATION AND QUANTITATIVE ANALYSIS OF DIALKYL AND DIARYL DITHIOPHOSPHATES BY THIN-LAYER CHROMATOGRAPHY AND DENSITOMETRY

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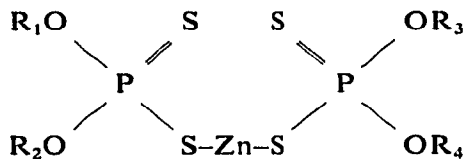
SUMMARY

A method has been devised for the identification of dialkyl and diaryl dithiophosphates (DDPs) by thin-layer chromatography and subsequent quantitative analysis of these compounds by thin-layer densitometry. The DDPs are reacted with an excess of iodine and the reaction product is chromatographed on silica gel. The method offers the following advantages over the methods previously published for the identification of DDPs by thin-layer chromatography. (1) A more definitive spot pattern. (2) Better spot shape. (3) Ease of quantitation.

The method is sensitive and is suitable for additive depletion studies, and performance-to-structure correlations.

INTRODUCTION

Dialkyl and diaryl dithiophosphates (DDPs), in particular zinc dialkyl dithiophosphates (ZDDPs), are commonly used in lubricating oils as antioxidants, bearing corrosion inhibitors and antiwear- or load-carrying additives. Their performance is related to the nature of the alkyl or aryl groups present¹.



where substituent R's are

- (1) Generally the same, either alkyl or aryl groups.
- (2) A mixture of (a) two alkyl groups; (b) two aryl groups; (c) one alkyl, one aryl group.

DDPs made from two different substituents result in a mixture with a maximum of six components.

Thin-layer chromatography (TLC) offers a comparatively simple method for identifying ZDDPs, but previously published methods^{2,3} do not show marked differences between ZDDPs prepared from mixed alcohols and are not easily applicable as quantitative methods.

In the development work done to achieve a more discerning and quantitative method, a brief study was made of the reaction between ZDDPs and iodine⁴, the outcome being the method submitted in this paper.

EXPERIMENTAL

All separations are carried out on Merck pre-coated silica gel plates containing fluorescent F₂₅₄ indicator. Samples are applied to the plates as dilute solutions in *n*-hexane by means of microlitre pipettes or syringes. The positions of the separated components on the dried plate are revealed by (1) inspection under ultraviolet light (254 nm) and (2) spraying with a chromogenic reagent (palladium chloride).

Reagents should be of analytical or equivalent quality unless otherwise stated.

Preparation of reagents

Iodine solution. Weigh 800 mg of iodine into a 100-ml volumetric flask, dissolve the iodine in approximately 50 ml of *n*-hexane, warming if necessary. Dilute to volume with *n*-hexane. Store this reagent in an amber bottle.

Palladium chloride spray reagent. Dissolve 250 mg of palladium chloride in 25 ml of 5 *N* hydrochloric acid, warming if necessary. Cool to room temperature and dilute to 50 ml with acetone and transfer the solution to the reservoir of a spray gun.

Preparation of developing tanks

Pre-wash tank. Add 100 ml of *n*-hexane to a developing tank, apply the cover and allow the atmosphere in the tank to equilibrate for 15 to 20 min before use.

Developing tank. Add 80 ml of carbon tetrachloride to a 100-ml measuring cylinder, add 20 ml of toluene. Stopper the cylinder and mix the two solvents. Add the solvent mixture to a TLC developing tank lined with Whatman No. 1 chromatography paper. Apply the tank cover and allow the atmosphere in the tank to equilibrate for 15 to 20 min before use.

Procedure

Additive concentrates and packages. (1) Weigh approximately 100 mg of sample into a 25-ml volumetric flask. Dissolve the sample in *n*-hexane and dilute to volume with *n*-hexane.

(2) Pipette 1 ml of sample solution into a 5-ml vial. Add 1 ml of iodine solution, cap the vial and allow to stand for approximately 10 min.

(3) By means of a micro-pipette apply 10 μ l of the solution prepared in (2) to a TLC plate.

(4) Place the plate in the developing tank and allow the chromatogram to develop until the solvent front has travelled 15 cm.

(5) Remove the plate from the tank and allow the solvent to evaporate. Spray the plate with the palladium chloride reagent and heat the plate in an oven at 100° for 5 min.

(6) The components of the ZDDP show up as brown spots on a white background. The ZDDP may be identified by comparison with known standards or, if these are unavailable, by comparison of the R_F value with those given in this paper. Alternatively, standards may be prepared by reacting an alcohol with phosphorus pentasulphide and adding iodine solution to a portion of the reaction product.

Unused and used lubricating oils. Extract 20 ml of lubricating oil contained in a 100-ml conical flask with two separate 50-ml portions of methanol. Bulk the methanol extracts in a 150-ml beaker and concentrate by evaporation on a steam-bath.

After removal of all the methanol, dissolve the extract in *n*-hexane and dilute to 25 ml in a volumetric flask. Pipette 1 ml of this solution into a 5-ml vial. Add 1 ml of iodine solution. Cap the vial and allow the solution to stand for approximately 10 min. By means of a micropipette, apply 10 μ l of the solution to a TLC plate. Place the plate in the pre-wash tank and develop until the *n*-hexane front has travelled 15 cm. Allow the solvent to evaporate. Place the plate in the developing tank. When the solvent front has travelled 15 cm, remove the plate from the tank and allow the solvent to evaporate. Spray the plate with the palladium chloride reagent and heat the plate in an oven at 100° for 5 min. Identify the ZDDP as described in the previous section.

Quantitative measurement of ZDDPs in used and unused lubricating oils

In general, quantitative measurements will be made on lubricating oils containing a ZDDP of known composition in either engine test studies or "in-the-field" studies (a) for correlating performance with structure and (b) additive depletion studies. The requisite standards may be prepared from the unused lubricant by dilution with the base oil. Standards and samples are methanol extracted, prepared for application to the TLC plate and the chromatogram developed, as described in the previous section. After removal from the developing tank, the plate is dried, but is not sprayed with palladium chloride reagent. The plate is viewed under UV light (254 nm) and the location of the phosphorothionyl disulphide spot(s) marked lightly with a pencil at the edges of the plate*. The plate is then scanned in a thin-layer densitometer and the absorbance due to each spot is measured and recorded. The results and parameters given in this paper obtain to a Vitatron TLD 100.

A calibration graph of absorbance *versus* concentration is then constructed. It is usual in thin-layer densitometry to measure standards and samples on the same plate in order to achieve the required accuracy and precision. The operating parameters used for the Vitatron TLD 100 in the production of the calibration graph shown in Fig. 4 are given in Table I.

* In some instances, additive degradation products and oil oxidation products in used oils make measurements by fluorescence quenching impracticable. Under these circumstances, the plate is sprayed with palladium chloride reagent and scanned in a thin-layer densitometer.

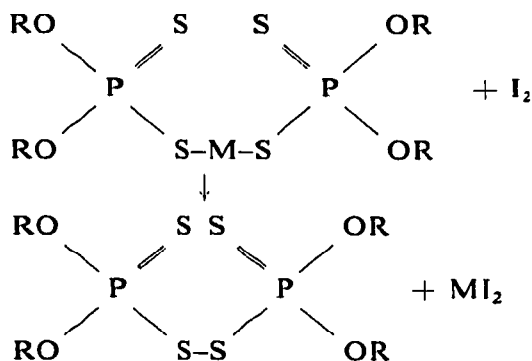
TABLE I

OPERATING PARAMETERS OF THE VITATRON TLD 100 THIN-LAYER DENSITOMETER

Parameter	Fluorescence quenching	Palladium chloride
Mode	log -ve	log -ve
Filter	526 nm	600 nm
Aperture	0.25 mm	0.25 mm
Zero	4.5	3.5
Level	d	c
Span	10	10
x-Oscillation	10 mm	10 mm
y Scan speed	3 cm/min	3 cm/min
Chart speed	4 cm/min	4 cm/min

RESULTS

The reaction between a metal dialkyl dithiophosphate and iodine in organic solvent results in the precipitation of the metal iodide and the formation of a phosphorothionyl disulphide.



After reaction a sample of the mixture may be applied directly to a silica gel plate. In the solvent system used to develop the plate any unreacted ZDDP remains at the origin, while the phosphorothionyl disulphides formed are eluted. Besides being less polar than their parent ZDDP the sulphides exhibit fluorescence quenching on TLC plates impregnated with F_{254} phosphor, which is a major contribution to the quantitative measurement of the disulphides.

The thin-layer chromatogram of ZDDPs prepared from a single alcohol results in a single component being eluted, the R_F value being proportional to the molecular weight (Fig. 1). ZDDPs prepared from mixed alcohols exhibit multiple components characteristic of (a) the difference between the number of carbon atoms in each component alcohol and (b) the relative proportions of each alcohol used in the manufacture of the ZDDP (Fig. 2).

Table II shows the relationship between the R_F value and the chain length of the alkyl groups of several commercial ZDDPs.

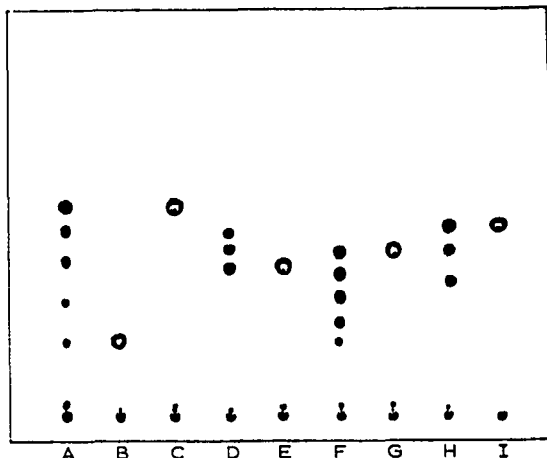
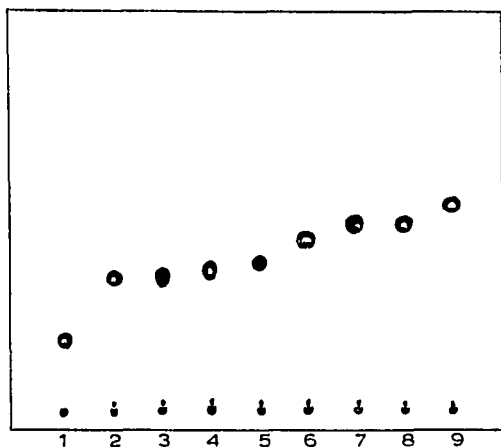


Fig. 1. Thin-layer chromatogram of alkyl ZDDPs prepared from (1) C_3 = isopropyl alcohol; (2) C_4 = isobutyl alcohol; (3) C_4/C_5 = isobutyl, isoamyl alcohols; (4) C_4/C_5 = isobutyl, *n*-pentyl alcohols; (5) C_6 = MIBC; (6) C_8 = capryl alcohol; (7) C_8 = trimethylpentyl alcohol; (8) C_8 = 2-ethylhexyl alcohol; (9) C_{12} = dodecyl alcohol.

Fig. 2. Thin-layer chromatogram of ZDDPs prepared from mixed alcohols compared with those of ZDDPs prepared from the individual alcohol. (A) C_3/C_8 = isopropyl alcohol, 2-ethylhexyl alcohol; (B) C_3 = isopropyl alcohol; (C) C_8 = 2-ethylhexyl alcohol; (D) C_4/C_8 = isobutyl alcohol, 2-ethylhexyl alcohol; (E) C_4 = isobutyl alcohol; (F) C_3/C_6 = isopropyl alcohol, MIBC; (G) C_6 = MIBC; (H) C_3/C_8 = isopropyl alcohol, capryl alcohol; (I) C_8 = capryl alcohol.

TABLE II

R_F VALUES OF PHOSPHOROTHIONYL DISULPHIDES OF ZDDPs

Carbon No. alkyl chain	Alcohol	$R_F \times 100$
3	Isopropyl	24
4	Isobutyl	46
4/5	Isobutyl, <i>n</i> -pentyl	47
6	Methylisobutylcarbinol (MIBC)	50
8	1-Methylheptyl (capryl)	58
8	2,2,4-Trimethylpentyl	63
8	2-Ethylhexyl	64
12	Dodecyl (lauryl)	69

Table III exhibits the effect of differences in the number of carbon atoms present in mixed-alkyl DDPs and the proportion of each component alcohol. This table also shows the relationship between R_F value and alkyl chain length in aryl and aralkyl DDPs and shows that the aromatic ring does not influence the R_F value.

Fig. 3 shows a typical chromatogram of aryl and aralkyl DDPs.

The fluorescence-quenching property of the phosphorothionyl disulphides, mentioned previously, forms the basis of the quantitative measurement of these compounds by thin-layer densitometry.

A calibration graph for a C_6 alkyl ZDDP is shown in Fig. 4, the concentration of the ZDDP (μg) is plotted against the peak area (integrator units).

TABLE III
RELATIONSHIP BETWEEN R_F VALUE AND CARBON NUMBER OF THE ALKYL OR ARYL CHAIN OF THE ZDDP

ZDDP	$R_F \times 100$		Carbon No.								
	C_3	C_4	C_6	Aryl C_7	Capryl C_8	TMP C_8	2EH C_8	Aryl C_8	Aryl C_9	Lauryl C_{12}	Aryl C_{12}
<i>Mixed alkyl</i>											
Isopropyl	22	34	46		56						
2-Ethyl hexyl											
Isobutyl	29	36	44	50	56						
2-Ethyl hexyl											
Isopropyl	31	41	51		58						
MIBC											
Isopropyl											
Capryl											
<i>Alkyl</i>											
Isopropyl	23										
Isobutyl			46								
MIBC				50							
Capryl					58						
Trimethylpentyl						63					
2-Ethylhexyl							64				
Lauryl										69	
<i>Aryl-aralkyl</i>											
Heptylphenyl				64							
Octylphenyl								64			
Nonylphenyl									67		
Dodecylphenyl											69
Isopropyl	20	33	46		56			64			
Octylphenyl											
2-Ethylhexyl											
Octylphenyl								63			
2-Ethylhexyl			40	50							
Cresyl								62			

Thin-layer densitometer chart recorder outputs are shown in Fig. 5. (1) Is a composite showing the peak positions relative to the baseline of the chromatogram for single-component ZDDPs, and can be compared with Table I, because peak positions are directly related to R_F values. Chromatograms (2), (3), (4) and (5) are those of mixed-alcohol ZDDPs which are given in Fig. 2 and Table II and represent C_3/C_8 isopropyl-2-ethylhexyl, C_3/C_8 isopropyl-capryl, C_3/C_6 isopropyl-MIBC and C_4/C_8 isobutyl-2-ethylhexyl, respectively.

CONCLUSION

The reaction of metal dialkyl dithiophosphates with iodine to form phosphorothionyl disulphides followed by thin-layer chromatography provides a sensitive and definitive method for their identification. However, the method will not distinguish

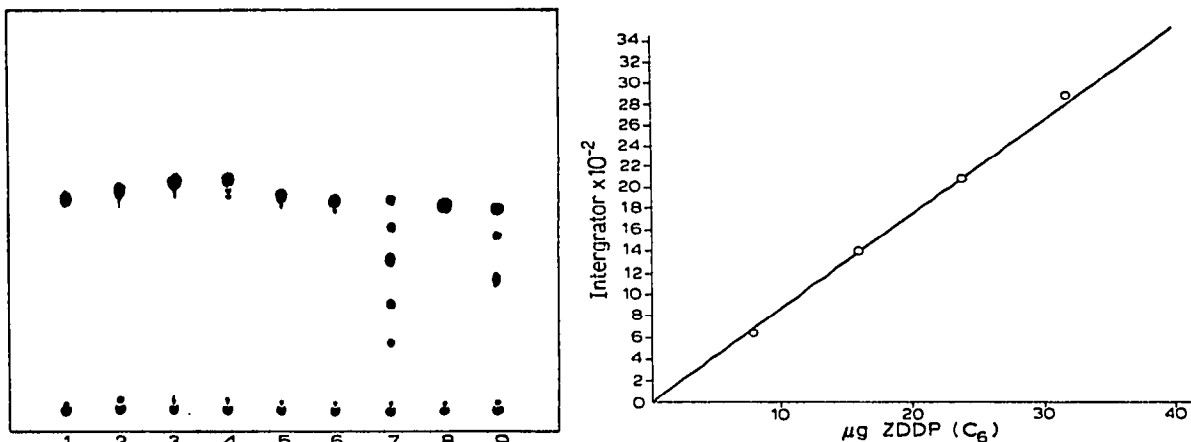


Fig. 3. Thin-layer chromatogram of aryl and aralkyl ZDDPs. (1) Octylphenyl alcohol; (2) nonylphenyl alcohol; (3) and (4) dodecylphenyl alcohol; (5) and (6) heptylphenyl alcohol; (7) isopropyl, octylphenyl alcohols; (8) 2-ethylhexyl, octylphenyl alcohols; (9) 2-ethylhexyl, methylphenyl alcohols.

Fig. 4. Calibration graph derived for C₆ ZDDP (methyl isobutyl carbinol).

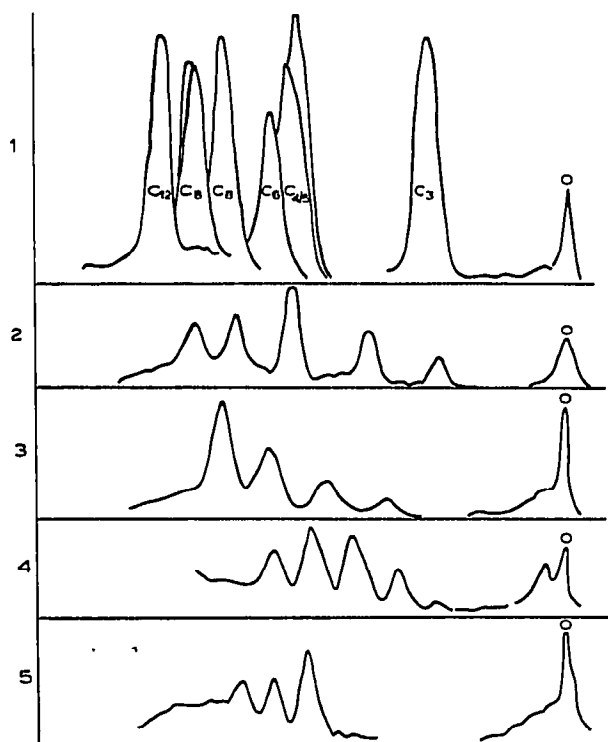


Fig. 5. Thin-layer densitometer chart recorder output. (1) A composite showing the peak positions relative to the baseline of the chromatogram, for single component ZDDPs. (2), (3), (4) and (5) are the traces obtained from mixed alcohols given in Fig. 2. The peak positions can be compared directly with those of single component ZDDPs.

between alkyl and aralkyl DDPs without corroborative evidence such as infrared spectroscopy, because the aromatic nucleus has no influence on the R_F value. The method will only signify differences in homologues when the number of carbon atoms differs by a number greater than one.

The procedure is easily made quantitative by virtue of the fluorescence quenching property of the phosphorothionyl disulphides, which also enables a fingerprint chromatogram of metal dialkyl dithiophosphates to be made by means of a thin-layer densitometer.

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