no specificity for the fumigant vapor. Figure 4 shows similar results when adsorption data of Figure 2 are reduced to a unit surface basis. These data also indicate that, when adsorption is considered on a unit surface basis, kaolinitic and illitic soils tend to act similarly toward the dibromochloropropane molecule.

The adsorption capacity of soil for dibromochloropropane, however, cannot be fully explained by the external surface area. Figure 5 shows that adsorption is also influenced by the clay mineral present in the soil. Comparison of the two mean adsorption isotherms based on unit surface indicates that montmorillonitic soils adsorb slightly greater amounts of dibromochloropropane vapor at lower P/P_o values, but kaolinitic and illitic soils possess greater adsorptive capacities at higher P/P_o values. These data on dibromochloropropane adsorption by dry soils correspond closely with the adsorption data of ethylene dibromide (8) indicating similarity in the adsorption mechanism of these two molecules. Additional studies are now in progress to determine the clay mineral effect on vapor adsorption.

Heat of Adsorption

The parameter C of Equation 1 is related to the average heat of adsorption, E_1, of the first layer by 2.30 RT log $C = E_1 - L$, where R is the gas constant, T is absolute temperature, and L is the heat of liquefaction of the adsorbent. The value of C is obtained when experimental data are plotted according to Equation 2. The usefulness of E_1, as a measure of surface energetics, is limited to a qualitative index because of the simplified model used in the derivation of Equation 1 (5). The $E_1 - L$ values, shown in Table I, indicate that montmorillonitic soils have a slightly greater adsorptive force for the fumigant molecules than do kaolinitic or illitic soils. The heat of liquefaction of dibromochloropropane is approximately 12 kcal. per mole at 23° C. (3). Therefore, the average heat of adsorption on the less active, roughly homogeneous, fraction of the surface varied from 13.2 to 13.7 kcal. per mole on the seven soils studied.

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INSECTICIDE DETERMINATION

Color Reaction of 2,6-Dibromo-N-chloro-p-quinoneimine with Thiophosphate Insecticides on Paper Chromatograms

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A simple and rapid detection paper chromatographic method for sulfur-containing phosphate ester insecticides was found by spraying the developed chromatogram with 2,6-dibromo-N-chloro-p-quinoneimine. As low as 1 γ of material was detected for some of the insecticides studied. This color reaction is useful for rapid identification of a wide variety of thiophosphate insecticides from plant or animal residues.

PAPER CHROMATOGRAPHY is widely used for separation and identification of mixtures of organic insecticides and their metabolites, but the detection of spots on chromatograms is often difficult. Many useful insecticides are esters of phosphoric acid. These can be detected by oxidation to inorganic phosphate and formation of molybdenum blue (6), but this method usually requires several hours for the hydrolysis and fails to detect quantities of less than 25 γ.

The sulfur-containing phosphate ester insecticides can be detected by spraying the chromatogram with N-bromosuccinimide (2). The spots react with the active bromine, and subsequent spraying with fluorescein gives yellow fluorescent

Table I. Detection of Various Phosphate Ester Insecticides on Paper Chromatograms at 110° C. for 7 Minutes

Compound[a]	Micrograms	Color
Systox	1	Red-brown
Isosystox	2	Yellow
Parathion	2	Red-brown
Isoparathion	20	None
Trithion	1	Orange-brown
Thimet	1	Orange-brown
Malathion	2	Orange-brown
Dow ET-14	5	Red-brown
Guthion	2	Orange-brown
Dipterex	20	None
Phosdrin	20	None

[a] Structures of these insecticides are as follows: Systox is O,O-diethyl O-ethyl-2-mercaptoethyl phosphorothionate. Isosystox is O,O-diethyl S-ethyl-2-mercaptoethyl phosphorothiolate. Parathion is O,O-diethyl O-p-nitrophenyl phosphorothioate. Isoparathion is O,S-diethyl O-p-nitrophenyl-phosphorothioate. Trithion is S-(p-chlorophenylthio)-methyl O,O-diethyl phosphorodithioate. Thimet is O,O-diethyl S-(ethylthio)methyl phosphorodithioate. Malathion is S-[1,2-bis(ethoxycarbonyl)ethyl] O,O-dimethyl phosphorodithioate. Dow ET-14 is O,O-dimethyl O-(2,4,5-trichlorophenyl) phosphorothioate. Guthion is O,O-dimethyl S-(4-oxo-3H-1,2,3-benzotriazine-3-methyl) phosphorodithioate. Dipterex is O,O-dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate. Phosdrin is O,O-dimethyl (1-carbomethoxy-1-propen-2-yl) phosphate.

spots on a pink background of brominated fluorescein. This method can detect less than 2 γ but requires careful adjustment of reagent concentrations and two successive sprayings.

A simpler detector solution for many sulfur-containing phosphate ester insecticides is a 0.5% solution of 2,6-dibromo - N - chloro - p - quinoneimine (DCQ) in cyclohexane. The chromatogram is sprayed and then heated in an oven at 110° C. for 7 minutes. Spot colors range from yellow to brownish red, and as little as 1 γ of some insecticides can be detected. Table I lists the limits of detection of spots of various sulfur-containing phosphate ester insecticides on paper strips (coated with either silicone or β-methoxypropionitrile for chromatography).

2,6 - Dibromo - N - chloro - p - quinoneimine is a sensitive color reagent for phenols in dilute solution (3, 5). It has been used as a color reagent for uric acid (4), and a 1% solution in 95% ethyl alcohol has been used as a spot

detector for uric acid and creatinine on paper chromatograms (1). Colors ranging from yellow to brown were observed with spots of tryptamine, indole-3-acetic acid, and other compounds on paper chromatograms (1). In this laboratory, 2,6 - dibromo - N - chloro - p - quinoneimine has been used to detect glutathione and cysteine on paper chromatograms, and with it various other reducing agents—such as catechol, iodide, and thiosulfate—have been observed to give yellow to brown spots, even at room temperature. Gibbs (5) had shown that this spot detector reacts with reducing agents.

On paper chromatograms, however, very few substances are likely to be present that will interfere with the detection of the sulfur-containing phosphate ester insecticides. Insecticides having the phosphorus-sulfur linkage give a reddish color. The carbon-sulfur-carbon linkage gives a yellowish color. The phosphorus-sulfur-carbon linkage apparently does not give color, but the

only example of this type tested was the S-ethyl isomer of parathion (isoparathion). Phosphate ester insecticides that contain no sulfur give no color. Metabolites of the sulfur-containing insecticides may also fail to give color if the sulfur is oxidized—e.g., from a thioether to a sulfoxide.

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FOOD ANTIOXIDANT ANALYSIS

Infrared Analysis of Commercial Butylated Hydroxyanisole

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Butylated hydroxyanisole (BHA) is a widely used food antioxidant consisting of a mixture of 2- and 3-tert-butyl-4-hydroxyanisole. The 3-tert-butyl-4-hydroxyanisole isomer is reported to be a more effective antioxidant than the 2-tert-butyl-4-hydroxyanisole isomer, so a means of controlling the isomeric composition of the commercial product is important. An infrared method has been developed which allows the isomers to be determined with a standard deviation of approximately $\pm1\%$. The method is rapid and requires very little recalibration and has been used for several years as a convenient and effective quality control measure on commercial butylated hydroxyanisole.

COMMERCIAL BUTYLATED HYDROXYANISOLE (BHA), a widely used food antioxidant, is essentially a mixture of 2-tert-butyl-4-hydroxyanisole (2-BHA) and 3-tert-butyl-4-hydroxyanisole (3-BHA). As it has been reported that 3-tert-butyl-4-hydroxyanisole is a more effective antioxidant when added to lard than 2-tert-butyl-4-hydroxyanisole (7, 4), it is important that the isomeric composition of commercial butylated hydroxyanisole be known.

Mahon and Chapman (2) described a colorimetric method for estimating the proportion of the isomers in commercial butylated hydroxyanisole, as well as in that which is removed from fats and antioxidant preparations. The method is based upon the fact that when 3-tert-butyl-4-hydroxyanisole reacts with 2,6-dichloroquinonechloroimide–borax reagent, it produces 5.2 times as much ab-

sorbance at 620 mμ as does 2-tert-butyl-4-hydroxyanisole, whereas the latter isomer, on reaction with ferric chloride-1,1'-bipyridine reagent, produces 1.1 times as much absorbance at 515 mμ as does the former isomer. Otis (3) has used an infrared method to analyze crude butylated hydroxyanisole for the two isomers and for one or more impurities which were present in these samples. In order to handle this complex system, simultaneous equations and absorbance values taken at three or four selected wave lengths were used.

As part of the quality control of the commercial antioxidant being produced on a plant scale, a simple and rapid method for the determination of the isomer ratio was desired. As the product at this point was essentially pure butylated hydroxyanisole, it appeared that a simplified version of the infrared

method might give the desired results. In the current investigation, the ratio of the absorbances at 10.74 and 10.92 microns of a carbon disulfide solution of butylated hydroxyanisole provided a reliable value for the isomeric composition of the commercial product.

Apparatus and Materials

Spectrophotometer. A Baird double-beam recording spectrophotometer equipped with a scattered light filter and a 2X slit mechanism was employed. Cells of approximately 0.2 and 0.4 mm. were used with a 1.3-cm. rock salt plate in the reference beam.

2- and 3-tert-Butyl-4-hydroxyanisole. Samples of each of the pure isomers were available from earlier development work on the preparation of butylated hydroxyanisole. The melting point of the