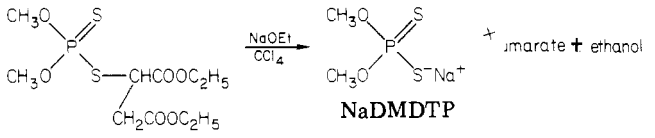
Determination of Malathion in Formulations

A method for the determination of malathion in formulations has been described. Malathion, dissolved in carbon tetrachloride, is hydrolyzed at room temperature by sodium ethoxide to get sodium dimethyl dithiophosphate (NaDMDTP). This NaDMDTP was converted into its bismuth complex by adding Bi(III) in acid medium. The complex was extracted into carbon tetrachloride. Excess bismuth(III) in aqueous solution was determined by complexometric titration employing ethylenediaminetetraacetic acid. Thiourea functioned as the indicator. The amount of DMDTP generated as a consequence of hydrolysis was obtained as a difference between the concentrations of the substance present in the formulation before and after hydrolysis.

Malathion undergoes quantitative hydrolysis in carbon tetrachloride with sodium ethoxide as reported by Clark and Qazi (1980):



malathion

Sodium dimethyl dithiophosphate (NaDMDTP) is converted into its light yellow bismuth complex in acidic aqueous solution. This complex is extracted into carbon tetrachloride.

Norris et al. (1954) dissolved malathion in a mixture of ethanol and carbon tetrachloride, and it was hydrolyzed by sodium hydroxide. The method suffers from two drawbacks: (i) the color of the complex fades quickly and (ii) a slight increase in the contact time of the copper(II) solution and the hydrolysis product of malathion contribute to a large decrease in the absolute absorbance as reported by Zweig (1973). Roussow (1961) found that the color is stable for 15–45 min if the temperature is maintained between 16 and 20 °C. Hill et al. (1967) proposed a method for the determination of malathion in formulations. This is an extension of the method of Norris et al. (1954). We report here a modification of the analytical procedure published by Clark and Qazi (1979) for the determination of malathion in formulations.

EXPERIMENTAL SECTION

Materials. The following compounds were used: bismuth(III) nitrate, 0.02 M solution in dilute nitric acid; carbon tetrachloride, redistilled commercial-grade sample (BDH); ethylenediaminetetraacetic acid (EDTA), 0.02 M AR (BDH); nitric acid, 3 N AR (BDH); sodium ethoxide (0.5 g of freshly cut sodium was dissolved in 50 mL of pure ethanol; a fresh sample of the solution was prepared for every determination); thiourea (Hungary); malathion samples (50% emulsifiable concentrate and 95% technical grade samples were supplied by Cyanamid India, Ltd., Bombay).

Sample Preparation. The 50% emulsifiable concentrate and 95% technical-grade samples that were expected to contain 0.8–1.0 g of pure malathion were weighed accurately and dissolved in 50 mL of carbon tetrachloride. *O,O,O,O*-Tetramethyl pyrophosphorotrithioate and the esters of malathion, *S*-[(1-carboxy-2-carbethoxy)ethyl]-*O,O*-dimethyl phosphorodithioate and *S*-[(1-carbethoxy-2-carboxy)ethyl] *O,O*-dimethyl phosphorodithioate, were present as trace impurities. These do not interfere with the present determination.

Procedures. *Determination of Total O,O-Dimethyl Dithiophosphate.* A 10-mL aliquot of the sample solution and 2 mL of 1% sodium ethoxide solution were taken in a 100-mL separating funnel. The mixture was swirled gently and allowed to stand for 45 min. The mixture was acidified with 3 N nitric acid. A total of 20 mL of carbon tetrachloride and 20 mL of bismuth(III) solution were then added, and the mixture was shaken thoroughly for 2–3 min and allowed to separate. The carbon tetrachloride layer was discarded. The aqueous layer was extracted with 10-mL portions of carbon tetrachloride until the carbon tetrachloride washings were colorless. The aqueous layer was transferred into a 250-mL conical flask, and the separating funnel was washed with two 5-mL portions of distilled water. The aqueous layer was titrated against 0.02 M EDTA solution. Thiourea was used as the indicator (Fritz, 1954).

Determination of Free O,O-Dimethyl Phosphorodithioate. A mixture of 10 mL of sample solution, 20 mL of carbon tetrachloride, and 20 mL of bismuth(III) solution was taken into a 100-mL separating funnel. The mixture was shaken vigorously for 2–3 min and allowed to separate into two layers. The slightly yellow carbon tetrachloride layer was discarded and the aqueous layer was extracted with 10-mL portions of carbon tetrachloride until the carbon tetrachloride washings were colorless. The aqueous layer was transferred into a 250-mL conical flask and the separating funnel was washed with two 5-mL portions of distilled water. The aqueous layer was titrated against 0.02 M EDTA solution to a thiourea end point.

The percentage of malathion in the above formulations was also determined by using the copper method (Hill et al., 1967).

RESULTS

The percentage of malathion in the sample was calculated by using the formula

$$\text{malathion \% (w/w)} = \frac{\omega(V_b - V) \times 10.21 \times 100}{W}$$

ω is the weight in grams of bismuth(III) nitrate pentahydrate to which 1 mL of EDTA solution is equivalent, V_b is the volume in milliliters of EDTA solution required by the bismuth(III) solution remaining after reaction with the unhydrolyzed malathion sample, V is the volume in milliliters of EDTA solution required by the bismuth(III) solution remaining after reaction with the hydrolyzed malathion sample, and W is the weight in grams of malathion taken for analysis.

The figure 10.21 takes into account that three molecules of *O,O*-dimethyl dithiophosphate derived from three molecules of malathion bind one molecule of bismuth(III) nitrate pentahydrate, and only one-fifth of the malathion weighed is used in each determination. The results relating to the present work and that of the copper method (Hill et al., 1967) are presented in Table I.

DISCUSSION

The results in Table I show that the bismuth method yields results that are identical with those that could be obtained by the copper method. Further, the former method has certain distinct advantages: (i) fewer reagents

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Table I. Comparative Study of the Copper Method (Hill et al., 1967) and the Present Method

sample no.	malathion content: 50% e.c. (w/w)	95% technical grade (w/w)	50% e.c. (w/w)	95% technical grade (w/w)
1	48.7	93.9	48.8	94.0
2	49.3	94.5	49.3	94.4
3	48.6	94.5	48.8	94.5
4	50.5	95.2	50.2	95.1
av	49.3	94.5	49.3	94.5

Table II. Determination of Malathion with Percentage of Relative Error

sample no.	amount of malathion: taken W,[a] g	found, g: 50%	found, g: 95%	relative error, %: 50% sample	relative error, %: 95% sample
1	0.2000	0.1874	0.1934	6.3	3.3
2	0.3000	0.2844	0.2934	5.2	2.2
3	0.4000	0.3824	0.3952	4.4	1.2
4	0.5000	0.4815	0.4973	3.7	0.53
5	0.6000	0.5850	0.5968	2.5	0.52
6	0.7000	0.6888		1.6	
7	0.8000	0.7887	0.7958	1.41	0.52
8	0.9000	0.8874		1.40	
9	1.0000	0.9860		1.40	

[a] W is the weight in gram of malathion taken for analysis.

are needed: (ii) reducing substances do not interfere with the determination; (iii) isomalathion does not interfere. Hence, the bismuth method could be used in the place of the copper method for the determination of malathion in formulations.

The method is applicable only for the determination of malathion in malathion formulations. The results of the present investigation (Table II) also point out that the method fails to yield accurate results when the expected amount of malathion is less than 0.8 g in the case of 50% formulations and 0.5 g in the case of 95% formulations.

Finally, the method may be used to determine other DMDTP-containing compounds.

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Registry No. Malathion, 121-75-5; NaDMDTP, 26377-29-7; dimethyl dithiophosphate·$^1/_3$bismuth(III), 30903-97-0.

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Mutagenicity Assays with (2,4-Dichlorophenoxy)acetic Acid–Amino Acid Conjugates

The mutagenic effects of five amino acid conjugates of (2,4-dichlorophenoxy)acetic acid (alanine, aspartic acid, leucine, methionine, and tryptophan) on five *Salmonella typhimurium* strains (TA97, TA98, TA100, TA1535, and TA1538) were investigated. The tested compounds did not increase the reversions of any of the tester strains' 2-fold over the spontaneous controls nor did they show a dose–response effect and, therefore, were considered to be not direct-acting mutagens under these conditions.

The aspartic acid conjugate of indoleacetic acid (IAA) has been reported in plants for many years (Andreae and Good, 1955). Amino acid conjugates are now recognized as major metabolites of (2,4-dichlorophenoxy)acetic acid (2,4-D) (Feung et al., 1972, 1975), (2,4-dichlorophenoxy)-butyric acid (2,4-DB) (Smith, 1979), and (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) (Arjmand et al., 1978). Seven amino acid conjugates were isolated and identified from soybean callus tissue (Feung et al., 1975). The glutamic and aspartic acid conjugates predominated; however, the alanine, valine, leucine, phenylalanine, and tryptophan conjugates were also identified. Feung et al. (1976) have also isolated the glycine, alanine, and valine conjugates of IAA from Boston ivy (*Parthenocissus tricuspidata*) crown gall tissue culture. Glutamic acid and aspartic acid conjugates were isolated as metabolites of 2,4,5-T in soybean callus tissue. In residue studies of greenhouse grown soybean plants sprayed with 0.45 kg/a.i. (active ingredient) propylene glycol butyl ether esters of 2,4-D per 0.4 ha (hectare), the glutamic and aspartic acid conjugates of 2,4-D were found to be present after 4 days at a level of 125 ppm (Zama and Mumma, 1983). These data suggest that amino acid conjugates may be more prevalent than once thought and that we should examine the toxicological

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