PB-224 299

ARGENTIMETRIC METHOD FOR DETERMINATION OF MALATHION IN FORMULATIONS

James W. Miles

Public Health Service

Prepared for:

Agency for International Development

1972

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

BIBLIOGRAPHIC DATA SHEET	1. Report No. 614.532-M643	2. PB 224 299

102

4. Title and Subtitle	5. Report Date
"ARGENTIMETRIC METHOD FOR DETERMINATION OF MALATHION IN FORMULATIONS"	1972
	6.
7. Author(s) James W. Miles.	8. Performing Organization Rept. No.
9. Performing Organization Name and Address Center for Disease Control, Savannah, Ga.	10. Project/Task/Work Unit No.
	11. Contract/Grant No. PASA RA(HA) 7-00
12. Sponsoring Organization Name and Address Department of State Agency for International Development Washington, D.C. 20523	13. Type of Report & Period Covered
	14.

15. Supplementary Notes

16. Abstracts

A method has been developed for the determination of malathion in technical grade products by argentimetric titration of the dimethylphosphorodithioateion formed by alkaline cleavage of the molecule. Free dimethylphosphorodithioc acid and other polar impurities are removed by a column of cellulose powder containing 30% moisture. Malaoxon, isomalathion, and diethylmercaptosuccinate do not interfere. However, the methyl ethyl ester of malathion, if present, will titrate as malathion. The method has been adapted to the analysis of formulations of emulsifiable concentrates, water-dispersible powders, and dusting powders. The analyses can be performed potentiometrically by titration to a fixed millivoltage, using a pH meter, or with an automatic titrator operated in the derivative mode. When the method was applied to samples of technical grade malathion, the standard deviation varied from 0.21 to 0.42%. ( )

17. Key Words and Document Analysis. 17a. Descriptors

17b. Identifiers/Open-Ended Terms

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
US Department of Commerce
Springfield, VA. 22151

17c. COSATI Field/Group 614

18. Availability Statement	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 10
i	20. Security Class (This Page) UNCLASSIFIED	22. Price $3.00-1.45

REPRINT NUMBER
PASA-RA(HA) 7-06
522

Technical Development Laboratories
Malaria Program
Center for Disease Control
Box 2167 • Savannah, Ga. 31402

Argentimetric Method for Determination of Malathion in Formulations

By JAMES W. MILES, MARY B. GOETTE, GORDON O. GUERRANT, and FREDERICK C. CHURCHILL, II (Center for Disease Control, Public Health Service, Box 2167, Savannah, Ga. 31402)

A method has been developed for the determination of malathion in technical grade products by argentimetric titration of the dimethylphosphorodithioate ion formed by alkaline cleavage of the molecule. Free dimethylphosphorodithioic acid and other polar impurities are removed by a column of cellulose powder containing 30% moisture. Malaoxon, isomalathion, and diethylmercaptosuccinate do not interfere. However, the methyl ethyl ester of malathion, if present, will titrate as malathion. The method has been adapted to the analysis of formulations of emulsifiable concentrates, water-dispersible powders, and dusting powders. The analyses can be performed potentiometrically by titration to a fixed millivoltage, using a pH meter, or with an automatic titrator operated in the derivative mode. When the method was applied to samples of technical grade malathion, the standard deviation varied from 0.21 to 0.42%.

The colorimetric method of Norris *et al.* (1) is the most widely used procedure for determination of malathion, and a modified version of this method has been adopted by the AOAC (2) for malathion formulations. This method is based on the measurement of the yellow color produced when cupric ion complexes with the phosphorodithioate ion formed by alkaline cleavage of malathion. Recently, Wayne *et al.* (3) reported an improved colorimetric method in which a nonaqueous system is used for development and measurement of the color. Hill *et al.* (4) developed a volumetric method based on the residual iodometric titration of cupric ion after complexation of phosphorodithioate ion with standard copper solution and extraction of the complex with an organic solvent. The instability of the copper complex and possible interference from impurities have limited the accuracy of these methods, although this is minimized in the method of Wayne *et al.* (3). An infrared method for determination of malathion is also described in *Official Methods of Analysis* (5), but this method has the disadvantage that impurities in poor quality products may lead to high results.

The method presented here is based on the formation of a very insoluble precipitate when silver ion reacts with dimethylphosphorodithioate ion formed by alkaline cleavage of malathion (reactions *1* and *2*; p. 1134).

Impurities which form more soluble salts with silver ion do not interfere. In the case of technical grade malathion and malathion emulsifiable concentrates, polar compounds such as *O,O*-dimethylphosphorodithioic acid are removed by passing a hexane solution of the sample through a moistened cellulose powder column. In the case of water-dispersible powder and dust formulations, malathion is extracted with hexane while the polar impurities remain on the clay carrier.

METHOD

Reagents

(a) *Potassium hydroxide solution.*—1*N*. Dissolve 28 g KOH in 500 ml ethanol.

(b) *Nitric acid.*—2*N*.

(c) *Silver nitrate solution.*—0.1*N*. Standardize against primary standard NaCl.

(d) *Cellulose powder.*—Reeve Angel No. CF-11.

Apparatus

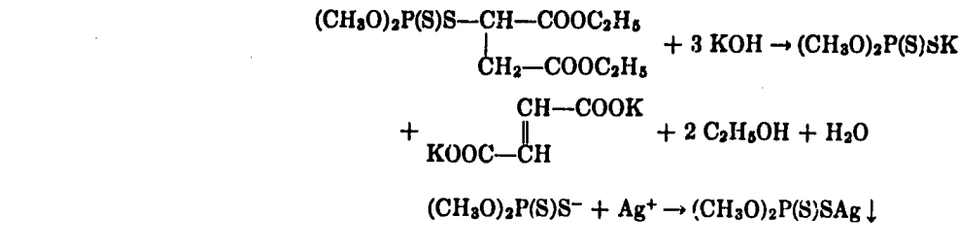
(a) *Potentiometer.*—Recording potentiometric titrator which can be operated in derivative mode (Metrohm Model E336 or E436), or pH meter with millivolt scale.

(b) *Glass reference electrode with Ag/AgCl internal element.*—Corning Glass Works, Catalog No. 476022.

(c) *Silver billet electrode.*—Beckman Instrument Co., Catalog No. 39261.

(d) *Chromatographic tube.*—30 cm × 13.5 mm id.

The use of trade names is for identification purposes only and does not constitute endorsement by the Public Health Service or the U.S. Department of Health, Education and Welfare.



(1)

(2)

(e) *Büchner funnel.*—4.25 cm fitted with fiberglass filter paper.

Preparation of Samples

Technical grade malathion or malathion emulsifiable concentrates.—Place 2 g cellulose powder in 50 ml beaker, add 0.6 g water dropwise, and mix thoroughly. Place plug of glass wool in bottom of chromatographic tube and pack with the wetted cellulose powder. Compress column of cellulose powder to 5 cm with glass rod. Add 5 ml hexane to wet column. Hexane will flow through this column at ca 4 ml/min.

Accurately weigh sample containing 0.5±0.1 g malathion into 250 ml beaker, add 50 ml hexane, and stir 10 min, using magnetic stirrer. Transfer solution to cellulose column and collect eluate in another 250 ml beaker. Use 20 ml hexane to rinse original beaker and then pour it through column; repeat rinse with 2 additional portions of hexane. Carefully evaporate hexane just to dryness. Add 50 ml 95% ethanol or isopropanol and stir with magnetic stirrer; add 20 ml 1*N* KOH and continue to stir 1 min. Add 50 ml water, then 20 ml 2*N* HNO_3, and stir.

Powder formulations.—Accurately weigh sample containing 0.5±0.1 g malathion into 250 ml beaker, add 50 ml hexane, cover with watch glass, and stir vigorously without splashing for 20 min with magnetic stirrer. Filter through paper in Büchner funnel and quantitatively recover filtrate. Thoroughly wash beaker and contents of funnel with 2 additional 20 ml portions of hexane. Quantitatively transfer filtrate to 250 ml beaker and evaporate hexane just to dryness. Add 50 ml 95% ethanol or isopropanol and stir with magnetic stirrer; add 20 ml 1*N* KOH and continue to stir 1 min. Add 50 ml water and 20 ml 2*N* HNO_3, and stir.

Titration

pH meter.—Immerse electrodes in solution and set pH meter to read absolute millivolts. Titrate with 0.1*N* $AgNO_3$ solution until meter reads ca 520 mv. This will bring the titration to within 1-2 ml of end point. Continue titration by dropwise addition of titrant until meter reads 425 mv, which is the end point. As this point is approached, a sharp change in millivoltage will be observed.

Recording potentiometric titrator.—Set instrument in derivative mode and titrate at 2.0±0.2 ml $AgNO_3$ solution/min to within ca 2 ml of expected end point. Decrease speed of delivery of titrant to 0.7±0.1 ml/min and continue titration. The first inflection in titration curve should be taken as the end point.

Calculation.—

$$\% \text{ Malathion} = (V \times N \times 33.04)/W,$$

where V = ml $AgNO_3$ solution, N = normality of $AgNO_3$ solution, W = g sample.

Results and Discussion

Analysis of Technical Malathion

A sample of technical grade malathion was hydrolyzed and titrated with $AgNO_3$ according to the above procedure. The millivoltage of the solution was measured with a pH meter set up to read millivolts absolute. A plot of the change in potential with addition of titrant is given in Fig. 1. The titration was repeated on another sample with an automatic titrator operated in the derivative mode. When the titrator is operated at a slow rate (less than 1 ml/min) in the vicinity of the end point, the expected derivative titration curve was obtained (*see* Fig. 2). When the titration was conducted at a high speed (2.5 ml/min), a distorted curve was obtained (*see* Fig. 3). With high quality malathion samples, the first break in the derivative titration curve will be very close to the second break and may appear as a shoulder. Some impure samples will exhibit 3 or more breaks (*see* Fig. 4). In the case of aged or impure samples, the first break in the curve will be distinct and well removed from later breaks.

When malathion is heated or stored for long periods, partial decomposition takes place and diethylmercaptosuccinate is formed as one of the products. In order to determine if diethylmercaptosuccinate would interfere in the determination of malathion, it was synthesized and added to a sample of malathion. The sample was then hydrolyzed and titrated on a recording potentiometer

Received December 13, 1971.

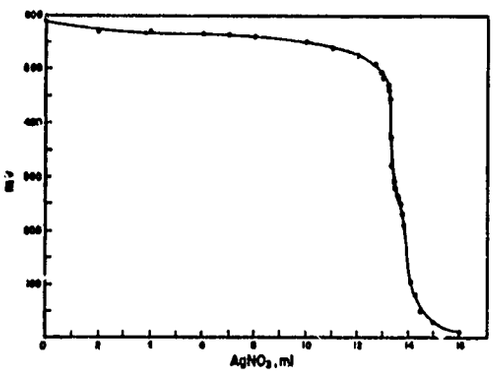


FIG. 1—Argentimetric titration of malathion after cleavage with alkali. Manual titration.

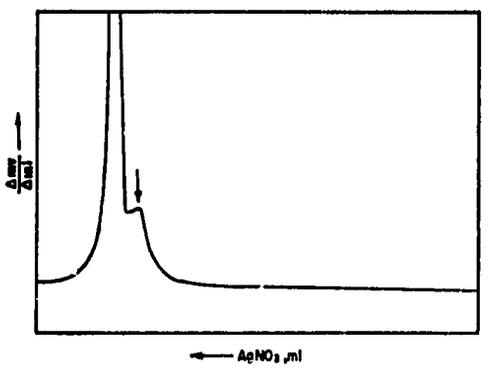


FIG. 3—Argentimetric titration of malathion after cleavage with alkali. Automatic titration with instrument operated in derivative mode. Titrant delivered at 2.5 ml/min throughout titration.

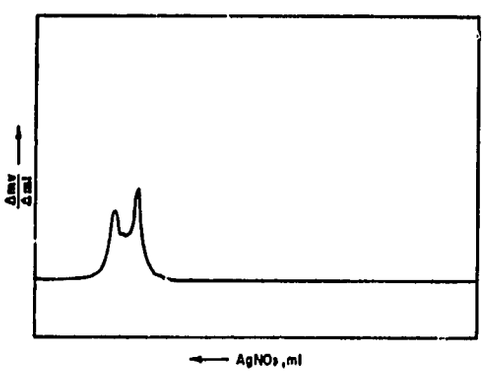


FIG. 2—Argentimetric titration of technical malathion after cleavage with alkali. Automatic titration with instrument operated in derivative mode. Titrant delivered at 0.7 ml/min in vicinity of end point.

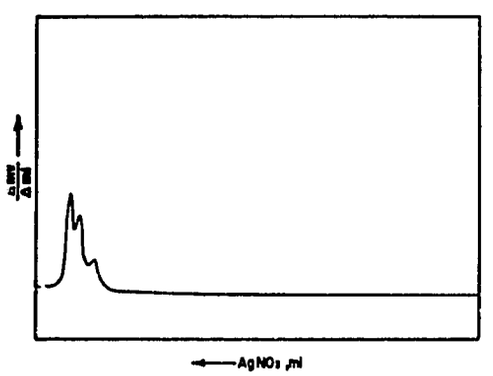
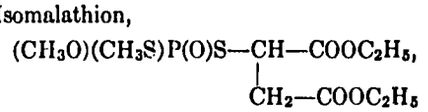


FIG. 4—Argentimetric titration of low quality sample of technical malathion after alkaline hydrolysis. Automatic titration with instrument operated in derivative mode.

operated in a derivative mode. The resulting curve, Fig. 5, shows that diethylmercaptosuccinate does not interfere in the titration of malathion, although it does form a precipitate with silver ion after the precipitation of the dimethylphosphorodithioate ion.

Isomalathion,



$$(CH_3O)(CH_3S)P(O)S{-}\underset{\underset{CH_2{-}COOC_2H_5}{|}}{CH}{-}COOC_2H_5,$$

which is sometimes found as an impurity, does not interfere. Isomalathion was cleaved with alkali, and the cleavage products were studied by thin layer chromatography and nuclear magnetic resonance. It was concluded that both P—S and S—C cleavage occurred when the compound was treated with alkali. The P—S cleavage produces $(CH_3S)(CH_3O)P(O)OK$, which does not titrate with silver ion, and diethylmercaptosuccinate. The S—C cleavage produces $(CH_3O)(CH_3S)P(O)SK$, which titrates with silver, and potassium fumarate, which does not. Diethylmercaptosuccinate co-titrates with $(CH_3O)(CH_3S)P(O)SK$, but neither interferes in the titration for malathion. Both compounds titrate after the dimethylphosphorodithioic acid as shown in Fig. 6. Similar experiments were conducted with malaoxon and it, too, was shown not to interfere in the determination of malathion by the argentimetric method.

Dimethylphosphorodithioic acid, if present, would interfere in the determination of malathion; it is removed by the moist cellulose column, along with other polar impurities including α- and β-monoacid derivatives of malathion and desmethyl

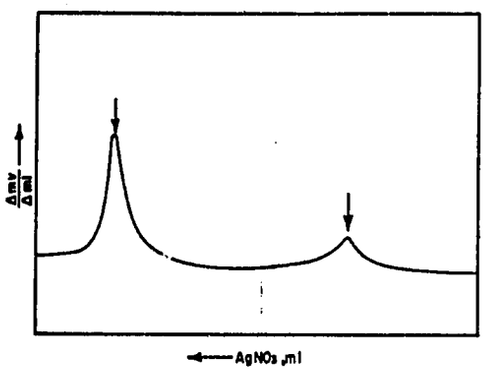


FIG. 5—Argentimetric titration of a mixture of technical malathion and diethylmercaptosuccinate.

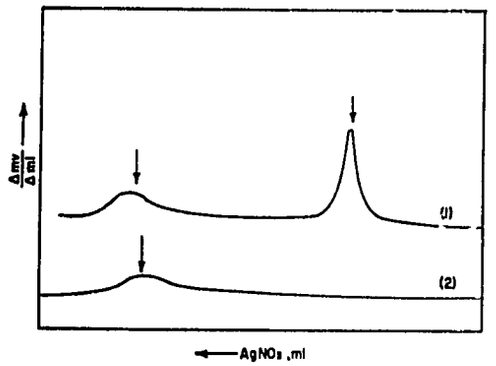


FIG. 6—Argentimetric titration of (1) malathion in the presence of isomalathion and (2) isomalathion in the presence of diethylmercaptosuccinate.

malathion,

$$(CH_3O)(HO)—P(S)S—\underset{\displaystyle CH_2—COOC_2H_5}{\underset{|}{CH}}—COOC_2H_5.$$

The efficiency of the cellulose column was tested on samples of known mixtures of malathion and dimethylphosphorodithioic acid and on an unknown sample of European origin. The free acid content of the samples was determined by the proposed method with the exception that the HNO_3 and KOH were mixed before addition to the sample to prevent hydrolysis of the malathion. The acid content of the samples after passage through the cellulose column was determined in the same manner. The malathion content of several of the samples was also determined before and after passage through the column. In the case of those samples having passed through the column, the free acid found was below the limits of detection of the method. These data, along with data showing recovery of malathion, are shown in Table 1.

The efficiency of the column for removing desmethyl malathion and the α- and β-monoacid derivatives was determined by adding milligram quantities of the respective compounds to hexane and passing the hexane solutions through the cellulose column. Quantitative removal of each of these compounds was confirmed by thin layer chromatography.

If an automatic titrator is used, care must be taken to add the titrant slowly as the end point is approached; otherwise the end point will be overshot and high results will be obtained due to slow electrode response. Data obtained on a single sample run at various rates of addition of titrant are presented in Table 2. Higher values were obtained with increased titration rates. However, when the rate of addition was reduced to less than 1 ml/min within 1–2 ml of the end point, overshooting of the end point did not occur and consistent results were obtained.

Although the titrations may be run in aqueous as well as alcoholic medium, better results are obtained in the 50% alcoholic solution. Without the addition of alcohol, the precipitate which forms is very fine and tends to coat the electrodes, with resultant loss of sensitivity. The electrodes should be examined periodically and cleaned when necessary.

Samples of technical grade malathion of questionable quality obtained from European sources were analyzed by the proposed argentimetric method, by the copper colorimetric method of Wayne *et al.* (3), and by gas chromatography (GLC). The argentimetric titrations were conducted manually with a Beckman Zeromatic pH meter and also with a Metrohm Model E336 recording potentiometer operated in a derivative mode. Gas chromatographic analyses were made on a Micro-Tek Model 220 instrument equipped with a Melpar flame photometric detector and an Infotronics Model CRS-100 digital integrator. Separation was made on a 180 cm × 4 mm id glass column packed with 3% OV-101 on 100–120 mesh Chromosorb W. The column was temperature programmed from 180 to 230°C at 5°/min. Trithion was used as an internal standard.

The results of the analyses are presented in Table 3. To make a valid comparison between the GLC method and the other methods, we added

Table 1. Dimethylphosphorodithioic acid removed from hexane solutions of malathion by a cellulose column

	Amount Added, %		Acid Found, %		Malathion Found, %	
Sample	Malathion	Acid	No Column	Column	No Column	Column
Mix 1	88.27	3.07	2.75	<0.03		
			3.11	<0.03		
Mix 2	88.05	2.47	2.56	<0.03		
				<0.03		
Mix 3	89.01	1.92	1.81	<0.03		88.3
			1.84			89.5
			1.76			88.7
			1.84			
Unknown sample of European origin			2.1		81.1	79.0
			2.1		80.6	

Table 2. Effect of rate of addition of $AgNO_3$ on the end point in the malathion determination

Rate, ml/min			
Initial	Near End Point	Malathion Found, %	Mean, %
0.6	0.6	94.2, 94.3	94.3
0.8	0.8	94.2, 94.4	94.3
1.4	1.4	94.6, 94.8	94.7
1.9	1.9	95.4	95.4
2.5	2.5	95.6, 95.6	95.6
1.9	0.6	94.2	94.2
2.5	0.8	94.6	94.6

the values for malathion and the methyl ethyl ester of malathion. The only method by which these closely related compounds can be separated is high resolution GLC. If one considers the poor quality of the samples, the agreement among methods was excellent.

Another series of samples of domestic manufacture was obtained and analyzed by the argentimetric procedure. The samples were run manually with end point detection on a pH meter and on an automatic titrator operated in a derivative mode. Comparison of these values with values obtained by the anhydrous copper colorimetric method is made in Table 4.

The reproducibility of the various methods under study was determined by subjecting samples to replicate analyses by several operators. Results obtained on 2 representative samples from domestic production are presented in Table 5.

The standard deviation for the determination of malathion ranged from 0.21 to 0.38% by the manual argentimetric titration, from 0.33 to 0.42% by automatic derivative differential titration, and from 0.70 to 0.84% by the nonaqueous copper colorimetric method.

Analysis of Emulsifiable Concentrates

Samples of malathion, emulsifiable concentrates of various concentrations, were analyzed by the proposed argentimetric method and by the colorimetric method of Wayne *et al.* (3). When the samples were eluted through the cellulose column according to the proposed procedure, the surfactants in the formulations were removed along with the polar phosphorus compounds. Results obtained on 4 samples are presented in Table 6. Good reproducibility was obtained; however, there was some variation between methods.

Analysis of Water-Dispersible Powders

In the first application of the argentimetric method to a 50% water-dispersible powder, the analysis was carried out without extraction of the malathion from the clay carrier. Results were high and the automatic titration curve did not correspond to that obtained with technical malathion. Malathion was then extracted from another sample with acetonitrile, which was the solvent of choice used by Upham (6). The titration curve was essentially that obtained on the unextracted powder. A less polar solvent, hexane, was then used to extract the powder and the titration curve of the recovered malathion was similar to that of technical malathion. Also, the malathion content agreed more closely with the expected value.

A study of malathion extraction from a partially decomposed powder was made on a sample prepared by heating a 50% water-dispersible powder 72 hr at 90°C. A sample of the heat-treated powder was extracted with hexane and analyzed by the proposed argentimetric method

This paper was presented at the 85th Annual Meeting of the AOAC, Oct. 11–14, 1971, at Washington, D.C.

Table 3. Results of analyses of poor quality malathion samples from European sources by gas chromatographic, colorimetric, and argentimetric methods

	Gas Chromatography			Malathion, %		
Sample	Malathion, %	Methyl Ethyl Ester, %	Total as Malathion, %	Nonaq. Cu^{++} Colorim.	Argentim. Auto. Deriv.	Argentim. mv Manual
1	75.1	5.5	80.6	78.1	81.4	80.9
2	85.0	1.2	86.2	84.5	86.0	85.7
3	82.1	1.9	84.0	81.8	83.8	83.5
4	79.1	7.1	86.2	86.3	86.9	86.7
5	78.3	7.0	85.3	85.1	87.6	85.7
6	76.4	2.6	79.0	79.7	83.9	82.7
7	85.3	1.5	86.8	86.3	87.3	86.3

Table 4. Results of analyses of domestically produced malathion by argentimetric titration with an automatic titrator and a pH meter and by the anhydrous copper colorimetric method

	Malathion, %		
	Argentimetric		Colorim.
Sample	mv Manual	Auto. Deriv.	Nonaq.
1	94.2	94.7	94.7
2	94.3	93.7	94.0
3	94.4	95.2	95.0
4	93.2	94.2	93.5
5	94.7	95.5	94.7
6	94.9	95.2	94.9
7	94.6	95.1	95.2

with an automatic titrator operated in the derivative mode. Another sample of the same powder was titrated after hydrolysis of the sample in a 50% alcohol medium without extraction. A comparison of the resulting titration curves is presented in Fig. 7.

The efficiency of extraction of malathion from an aged 50% water-dispersible powder was studied by making repetitive determinations on a sample (Sample A, Table 7) that had been in semitropical storage for 4 years. Similar recoveries were obtained on samples extracted with acetonitrile, diethyl ether, benzene, and hexane when determined by the argentimetric method. These values were also comparable to those found by GLC after extraction of the samples with acetone. In addition, comparative data were obtained on a 50% water-dispersible powder partially decomposed by heating 72 hr at 90°C (Sample B, Table 7) after extraction with both tetrahydrofuran and hexane. These data indicate that hexane is a suitable extractant for malathion in water-dispersible powders.

As a further test of extraction efficiency, duplicate samples of several heat-treated formulations of malathion on different carriers were extracted with acetone and with hexane. The acetone extracted samples were analyzed by GLC after further dilution of aliquots with isooctane. The hexane extracts were analyzed by the argentimetric differential titration method. Comparable recovery values were found by the 2 methods (Table 8). Hexane was then used in subsequent analyses of water-dispersible powders by the argentimetric and nonaqueous copper colorimetric methods.

Four 50% water-dispersible powder laboratory formulations were analyzed by the argentimetric, the nonaqueous colorimetric, and the Hill *et al.* (4) copper titrimetric methods. The Hill method was modified by addition of a preliminary hexane extraction to eliminate impurities. The average results of duplicate determinations are presented in Table 9 for comparison. Formulations C and D contain Micro-Cel E and Celite 209 (Johns-Manville Corp., N.Y.), whereas formulations E and F contain Zeosyl 10 (J. M. Huber, Edison, N.J.) and Pikes Peak clay, 9S66 (Lowe's, Inc., Cassopolis, Mich.). In addition, the formulations were analyzed after heating 20 hr at 90°C, an accelerated test of long-term tropical storage stability. These results are also presented in Table 9. The mean difference between the results from the argentimetric method and the copper colorimetric method is −0.9% for the original sample and −0.6% for the sample after 20 hr at 90°C. The respective differences between the argentimetric method and the modified Hill methods are −0.6 and −1.0%.

The results of analyses of 50% water-dispersible powder formulations of recent manufacture before and after heat treatment are shown in Table 10. Results obtained by the argentimetric titration method with a pH meter for end point

Table 5. Results obtained on replicate determinations of malathion by argentimetric titration and by the anhydrous copper colorimetric method

Sample	Operator	Instrument	Replicates	Range, %	Mean, %	Std Dev., %
A	W	pH meter	4	93.9–94.7	94.3	0.34
	S	pH meter	7	94.1–95.1	94.4	0.38
	G	titrator	12	94.0–95.2	94.7	0.33
	S	Cu colorim.	12	93.0–95.6	94.7	0.84
B	S	pH meter	4	94.1–94.6	94.4	0.21
	G	pH meter	4	94.4–95.2	94.7	0.36
	G	titrator	5	94.7–95.8	95.2	0.42
	S	Cu colorim.	4	94.0–95.5	95.0	0.70

Table 6. Results of analyses of malathion emulsifiable concentrates (EC)

Sample	Malathion, % Colorim. Nonaq. Cu^{++}	Malathion, % Argentim. Auto. Deriv.
50% EC	50.2	52.5
	50.2	52.3
57% EC	61.3	60.5
	61.3	60.5
80% EC	83.4	83.2
	83.4	83.6
50% EC[a]	41.1	43.6
	41.3	43.3
		43.7

[a] Formulation which had been stored 3 years.

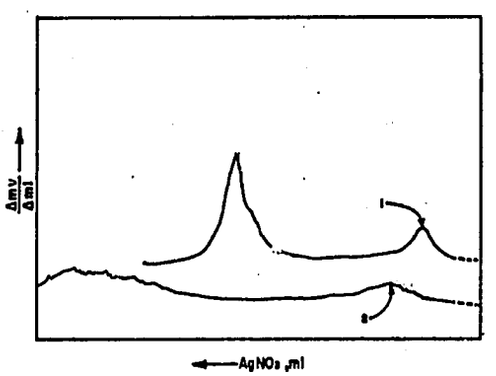


FIG. 7—Titration curve of malathion water-dispersible powder heated 72 hr at 90°C with (1) and without (2) hexane extraction.

detection are compared to those obtained on an automatic titrator operated in derivative mode.

The mean difference between the values obtained by the manual titration as compared to the automatic titration is 0.3% for the sample without heat treatment. The mean difference between the results from the argentimetric and the nonaqueous copper colorimetric methods is −0.6% for the samples as received and −0.2% for the samples after 20 hr at 90°C.

The results indicate the argentimetric method is reliable for the determination of malathion in water-dispersible powder formulations. Many of the polar impurities present in malathion formulations are not extracted by hexane and can thus be separated to minimize subsequent interference with the determination of malathion. Although malathion has limited solubility in hexane and care must be taken to quantitatively dissolve it, hexane is preferred for extraction over the more commonly used polar solvents.

Analysis of Dusting Powder Formulations

Malathion dusting powders have a higher ratio of carrier to malathion and may be formulated with diluents different from those used in the manufacture of water-dispersible powders. In the case of dilute dusts, there is a possibility that the interaction between the carrier and the malathion could affect extraction efficiency. Bowman *et al.* (7) have shown that the mechanism of adsorption of malathion upon montmorillonite clay was by hydrogen bonding interaction between the carbonyl oxygen atoms and the hydration water shells of the saturating cations of the clay. To test

Table 7. Extraction of malathion from partially decomposed water-dispersible powders with various solvents

Sample	Solvent	Malathion, %	Mean, %
A[a]	acetonitrile	29.2, 29.1	29.1
	diethyl ether	29.2, 29.3	29.2
	benzene	28.6, 29.0	28.8
	hexane	27.7, 28.0, 29.2, 29.7	28.6
B[b]	tetrahydrofuran	19.6	19.6
	hexane	19.6, 19.8	19.7

[a] Four-year-old powder. Malathion found by GLC, 28.9%.
[b] 50% water-dispersible powder heated 72 hr at 90°C.

Table 8. Comparison of recoveries obtained by GLC and argentimetric methods on malathion powders after heating 72 hr at 90°C

Carrier	Malathion, % GLC[a]	Malathion, % Argentim.[b]
Celite 209 + Micro-Cel E	23.7	24.9 25.6
Micro-Cel E	32.9	33.1 33.5
Celite 209	12.1	13.6 13.5
Attaclay	3.0	3.0

[a] Extracted with acetone.
[b] Extracted with hexane.

Table 9. Results of analyses of laboratory-formulated malathion 50% water-dispersible powders, per cent malathion found[a]

Sample	As Prepared: Colorim. Nonaq. Cu^{++}	As Prepared: Titrim. Ag^{+b}	As Prepared: Titrim. Cu^{++c}	After 20 hr at 90°C: Colorim. Nonaq. Cu^{++}	After 20 hr at 90°C: Titrim. Ag^{+b}	After 20 hr at 90°C: Titrim. Cu^{++c}
C	49.6	52.2	51.5	47.3	48.3	46.9
D	52.0	51.6	51.5	45.2	46.7	45.1
E	50.9	50.2	49.5	45.0	45.5	44.9
F	48.0	50.1	49.3	46.6	47.2	46.8
Diff.[d]	−0.9		−0.6	−0.6		−1.0

[a] Mean of 2 values.
[b] Argentimetric manual titration.
[c] Method of Hill *et al.* (4) modified by preliminary hexane extraction.
[d] Mean difference between Ag^+ automatic derivative titrimetric results and nonaqueous copper colorimetric or Hill *et al.* (4) methods.

Table 10. Results of analyses of commercially formulated malathion 50% water-dispersible powders, per cent malathion found[a]

Sample	As Received: Colorim. Nonaq. Cu^{++}	As Received: Argentimetric Auto. Deriv.	As Received: Argentimetric mv Manual	After 20 hr at 90°C: Colorim. Nonaq. Cu^{++}	After 20 hr at 90°C: Auto. Deriv. Ag^+
1	52.4	52.1	51.8	48.3	49.7
2	50.7	52.2	52.6	49.9	49.5
3	50.3	52.2	52.3	50.0	49.7
4	51.2	51.8	52.4	49.5	49.9
5	50.7	51.0	51.8	48.0	48.4
6	51.4	51.0	51.1	47.4	47.6
Diff.[b]	−0.6		+0.3	−0.2	

[a] Mean of 2 values.
[b] Mean difference between Ag^+ differential titrimetric results and nonaqueous copper colorimetric or manual argentimetric methods.

Table 11. Extraction of malathion from bentonite clays with various solvents

Extn Solv.	Malathion Recovered, % 95% Olancha (5)[b]	23% Pikes Peak 9T66[a] (46)	23% Pikes Peak 9T66[a] (48)
Hexane	2.7	45.5	47.2
Benzene	4.4	45.7	47.8
Acetonitrile	4.9		
Tetrahydrofuran	4.5		

[a] Balance of formulation was Micro-Cel E.
[b] % malathion added.

the effectiveness of hexane for extraction of malathion from a carrier containing montmorillonite to which a portion of the active ingredient is chemically bound, a 5% formulation was prepared on Olancha clay (Cyprus Mines Corp., Trenton, N.J.) which is a bentonite or impure montmorillonite. Hexane, benzene, acetonitrile, and tetrahydrofuran were used for extraction; recoveries are presented in Table 11. Hexane did not completely extract malathion from the dusting powder as indicated by the lower results when compared to results obtained with acetonitrile and tetrahydrofuran. Essentially complete extraction was obtained with benzene, which penetrates the inner layer region of montmorillonite and replaces malathion due to mass action. At higher malathion concentrations of 46 and 48%, recoveries from Pikes Peak clay (9T66) were only slightly lower with hexane than with benzene as shown in Table 11. Higher extraction efficiencies observed in the case of Pikes Peak clay (9T66) may also be due to the fact that this form is calcined and thus does not chemically bind the malathion as do the non-calcined montmorillonoid clays.

In practice, most malathion dusts are prepared with non-sorptive carriers and all commercial formulations encountered to date have been extracted with hexane without difficulty. For example, samples of a 2 and a 3% dust obtained from European sources were analyzed by GLC after extraction with acetone and by the argentimetric method after extraction with hexane. The malathion content of the 3% powder was found to be 3.30% by GLC and 3.38% by the titration. The 2% powder was found to contain 2.38 and 2.52% by the 2 methods, respectively.

Although the proposed argentimetric method has been validated for use on formulations containing malathion only, a number of other or-

ganophosphorus compounds have been subjected to the method and only those which yield dialkyl phosphorodithioates upon hydrolysis appear to interfere.

Acknowledgments

The assistance of James E. Woehst and Freeda B. Stanford in performing analyses is gratefully acknowledged.

These studies were accomplished as a part of a contractual agreement between the Center for Disease Control and the Agency for International Development.

REFERENCES

(1) Norris, M. V., Vail, W. A., & Averell, P. R. (1954) *J. Agr. Food Chem.* 2, 570–573
(2) *Official Methods of Analysis* (1970) 11th Ed., AOAC, Washington, D.C., secs. 6.265–6.269
(3) Wayne, R. S., Groth, W. C., Miles, J. W., & Guerrant, G. O. (1972) *JAOAC* 55, 926–938
(4) Hill, A. C., Akhtar, M., Mumtaz, M., & Osmani, J. A. (1967) *Analyst* 92, 496–500
(5) *Official Methods of Analysis* (1970) 11th Ed., secs. 6.261–6.264
(6) Upham, S. D. (1960) *JAOAC* 43, 360–364
(7) Bowman, B. T., Adams, R. S., Jr., & Fenton, S. W. (1970) *J. Agr. Food Chem.* 18, 723–727

CHANGES IN ADDRESS

Associate and General Referees—Has your address changed since the list of Officers and Standing Committees of the AOAC was published in the March issue of JAOAC? This list is used as the basis of a mailing list—to notify people of items of interest and also to remind people of the deadline for reports and papers to be presented at the AOAC meeting. It is essential that this list be kept up to date. If your address has changed, please notify the AOAC Business Office.