residues equivalent to the control value, the sensitivity of the method when applied to milk is considered to be 0.005 p.p.m.; when applied to animal tissues, except fat, 0.02 p.p.m.; and when applied to fat, 0.03 p.p.m.

Recovery experiments were carried out by adding known amounts of Guthion or its oxygen analog at the initial blending step and processing by the procedure described above. The recoveries for various animal products given in Table I indicate that the method is satisfactory for both Guthion and its oxygen analog.

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METHOD OF ESTIMATION

Estimation of Malathion by Oxidation with Chloramine-T

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Recently a titrimetric method for the estimation of parathion by oxidation with chloramine-T was described. A rapid titrimetric method based on the oxidation of O,O-dimethyl dithiophosphoric acid by chloramine-T has been worked out for the estimation of malathion.

MALATHION [*S*-(1,2-dicarbethoxyethyl) *O,O*-dimethyl dithiophosphate] is an important pesticide widely used in plant protection. Its determination is therefore of great interest.

Polarographic (*2*) and colorimetric (*4*) methods are available for the estimation of malathion. The colorimetric method is based on its decomposition in carbon tetrachloride–ethyl alcohol solution by alkali to give sodium dimethyl dithiophosphate and sodium fumarate. The sodium dimethyl dithiophosphate is extracted into water and converted into the copper complex of dimethyl dithiophosphoric acid, which is then extracted into carbon tetrachloride and determined colorimetrically at 418 mμ.

A rapid titrimetric method based on the oxidation of *O,O*-dimethyl dithiophosphoric acid by chloramine-T has been worked out for the estimation of malathion, similar to the one for parathion (*3*).

The thio compounds of various oxy acids of phosphorus react with water to give hydrogen sulfide by a process in which sulfur is replaced by the oxygen of the water (*5*). This hydrogen sulfide can be oxidized quantitatively to sulfuric acid in acid medium (*6*) by an excess of chloramine-T, which can then be estimated iodometrically.

Reagents

Malathion. Samples of 95% and 99.50% purity supplied by the American Cyanamid Co., New York, N. Y.

Chloramine-T (0.1*N*). About 15 grams of recrystallized sample of pure chloramine-T is dissolved in 1 liter of water and stocked in an amber-colored bottle. The solution is standardized iodometrically in an acid medium (*1, 5*).

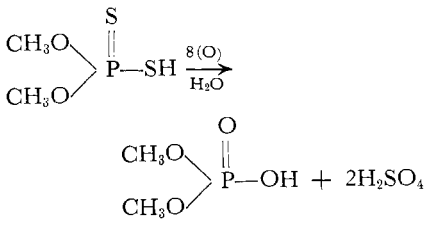
Sodium thiosulfate, 0.1*N*.
Dilute sulfuric acid, 2*N*.
Potassium iodide, 5% (w./v.)
Ethyl alcohol (aldehyde-free)
Alcoholic potassium hydroxide, 1*N*.

Procedure

Fifty to 80 mg. of the malathion sample are accurately weighed into a 250-ml. round-bottomed flask, and 30 ml. of alcoholic potassium hydroxide are added and refluxed gently on a water bath for 30 minutes. After cooling, the alkali is neutralized by dilute sulfuric acid and 25 ml. of acid are added in excess. Then 50 ml. of chloramine-T are added to the flask, which is well shaken and kept aside for about 30 minutes. At the end of this period, 25 ml. of potassium iodide solution are added and the liberated iodine is titrated with sodium thiosulfate using starch as the indicator. The amount of chloramine-T consumed by the malathion is obtained from the titer value and the number of equivalents of the oxidant required per mole of malathion is calculated. No blank correction is necessary, as it is less than 0.05 ml. of thiosulfate.

The analytical values are reproducible and the results of a few experiments are given in Table I.

It appears that 16 equivalents of chloramine-T react with 1 mole of *O,O*-dimethyl dithiophosphoric acid formed from 1 mole of malathion as indicated by the equation



Therefore 1 ml. of 0.1*N* chloramine-T is equivalent to 2.064 mg. of pure malathion.

When malathion is estimated in commercial formulations, impurities may consume chloramine-T and the value reported may be too high. This limitation has to be kept in mind before applying this method of analysis for such samples.

Table I. Moles of Chloramine-T Required per Mole of Malathion

Moles of Malathion Taken for Experiment × 10^4	Equivalents of Chloramine-T Required, × 10^4	Equivalents Required per Mole of Malathion
1.248	20.09	16.10
2.300	36.98	16.08
1.656	26.68	16.11
1.069	17.32	16.20
1.254	20.30	16.19
2.313	37.35	16.14
2.124	34.20	16.10
1.342	21.50	16.03
1.753	28.35	16.12
0.925	14.85	16.06

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FOOD FUMIGATION

Bromide Residues from Methyl Bromide Fumigations of Cocoa Beans, and Processed Fractions from Fumigated Beans

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Cocoa beans were fumigated with methyl bromide in a series of studies. Bromide residues were determined on the beans and their fractions after milling. Under the conditions used, bromide residues in cocoa beans did not exceed the tolerance of 50 p.p.m. after fumigation 5 times with 1.5 pounds of methyl bromide per 1000 cubic feet for 24 hours, 7.5 pounds in one fumigation, or with 4.5 pounds for 24 hours followed by 4.5 pounds for 12 hours. The shells from fumigated beans contained 4 to 6 times the amount of residue in the whole bean. Cocoa had a residue level about the same as the fumigated beans, and the other fractions all had lower residues. Reducing the chamber load from 75% to 15% did not affect the residue deposition.

IN THE harvesting, storage, shipping, and other handling of cocoa beans prior to processing, there is ample opportunity for infestation by insects or rodents. One of the most effective ways of controlling these pests is by fumigation with methyl bromide—for example, Phillips *et al.* (*5*) reported on the fumigation of cocoa beans for control of the tobacco moth.

A tolerance for residues of inorganic bromide in cocoa beans resulting from fumigations with methyl bromide has been established by the U. S. Food and Drug Administration at the level of 50 p.p.m. (*2*). This permits legal use of the fumigant under conditions which are effective in solving these problems. Under some conditions, because of length of storage or handling, reinfestation can occur, making it necessary to fumigate more than once. Some pests require higher concentrations of fumigant than others.

This study was undertaken with the cooperation of members of the cocoa industry to determine the levels of bromide residues resulting from single and multiple fumigations with methyl bromide at different dosages and to determine the pattern of residue deposition in the fractions from fumigated cocoa beans after processing.

Experimental Procedure and Results

Series I. The cocoa beans used in the first experimental series were fumigated in a 36-cu. foot vault, using 1.5 pounds of methyl bromide per 1000 cu. feet (*1*). The exposure period was 16 hours at 75° to 80° F. and 50% relative humidity. After fumigation the beans were removed from the vault, placed on a table in the laboratory, and allowed to air 24 hours before sampling. The sample to be analyzed was sealed in a screw-capped glass jar, and total bromide was determined by the Shrader method (*6*) as soon as possible.

The experiment was carried out so that the beans were exposed to the fumigant four times, each time followed by determination of bromide. Results of the analyses are given in Table I. Aeration of 7 days was allowed between fumigations.

Series II. Cocoa beans for the second series were obtained from the 1964 Nigerian main crop, shipped in commercial 4.4-cu. foot burlap bags, each weighing approximately 120 pounds. The shipment was handled to ensure that the beans would not be fumigated before arrival at the laboratory.

The fumigations were carried out in an air-tight 27-cu. foot chamber, 44 inches long and 35 inches in diameter. A vacuum was drawn on the chamber after samples were introduced and a weighed quantity of methyl bromide was swept in with the air as the pressure in the chamber was brought to atmospheric. A circulating fan in the chamber was run to assure mixing of the gas. After the fumigation period, air was drawn rapidly through the chamber and exhausted through a stack to remove the fumigant from the air prior to opening the chamber.

The fumigations were carried out with five bags in the chamber each time. After each fumigation, one bag was removed and another added. Table II shows the loading scheme. This plan gave duplicate bags of cocoa beans fumigated with 1.5 pounds of methyl bromide 1, 2, 3, 4, and 5 times. The load level of 75% full was kept constant for all of the fumigations in this series.

After aeration for 2 to 3 days, the beans from each bag to be sampled were poured into a fiber drum with several

Table I. Residues of Bromide in Cocoa Beans Fumigated with Methyl Bromide after 24 Hours' Aeration

(Series I)

Number of Fumigations				
0	1	2	3	4
Total bromide, p.p.m.				
19	19	29	36	43
15	10	35	32	33