

the ordinary commercial applicators are used. The latter fail to deliver uniformly measured doses, since the solvent properties of many materials may destroy rubber, leather, or plastic gaskets in these applicators. In the course of studies with fumigants in pineapple fields under circumstances where depth of application as well as unit dosages were factors, it became

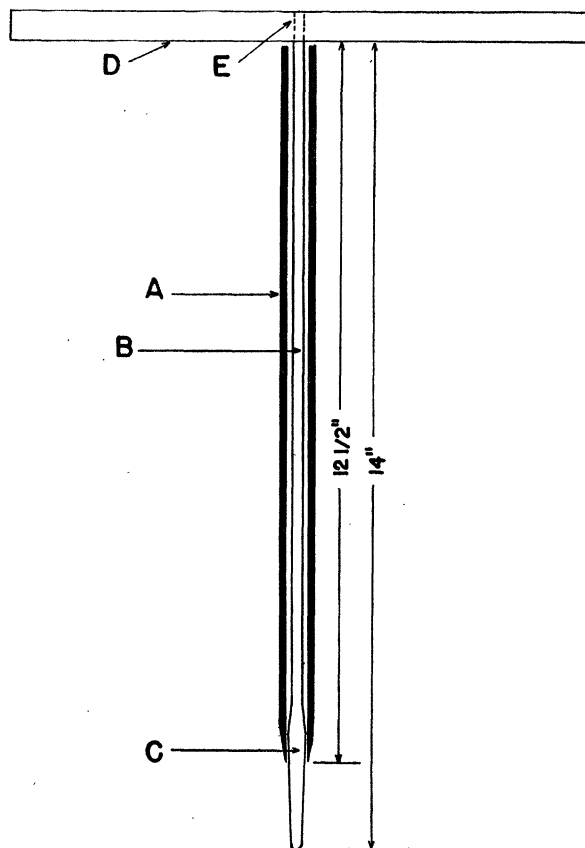


FIG. 1. Assembled injection apparatus. A—standard $\frac{1}{4}$ -inch pipe; B— $\frac{1}{4}$ -inch steel rod; C—enlargement tapering toward point; D—pipe handle; E—weld.

necessary to apply a great variety of materials with considerable precision. The applicator described below has been eminently satisfactory and, being of cheap and simple construction, is worthy of description for the use of other workers in the field.

The device consists of a length of iron pipe of approximately $\frac{1}{4}$ -inch inside diameter, sharpened at one end, and an iron prod with a transverse handle, as shown in Fig. 1. It was found that the device operated with greater ease if the prod was slightly enlarged at the end and tapered toward the tip. The assembled pipe and prod are thrust into the soil to the required depth, the prod withdrawn, and the fumigant poured into the pipe and allowed to drain, after

which the pipe is withdrawn from the soil and the hole closed. In practice it was found desirable to have enough pipes to treat an entire plot without resetting pipes. With pineapple the current standard plot requires 100-unit doses, but this would vary with other crops, depending on the plot size required for calculating significance of results.

A number of measuring devices ranging from simple, graduated cylinders to serological syringes have been used to measure the unit dose of liquid. The most satisfactory method has been the use of glass burettes of 100-ml. capacity, the unit doses being marked with steel or brass bands on the outside of the burette.

This device might also be used by the home gardener or for treating seed beds in glasshouses, where the number of unit doses is sufficiently small not to merit investment in more complicated and expensive equipment.

A Spectrophotometric Method for the Determination of p,p'-DDT

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In 10 minutes 10–50 μ g. of p,p'-DDT may be determined with an error not greater than 10 per cent. A large number of analyses may be run at one time.

PRINCIPLE

When dissolved in 95 per cent ethanol p,p'-DDT absorbs very slightly at 250 m μ . After dehydrochlorina-

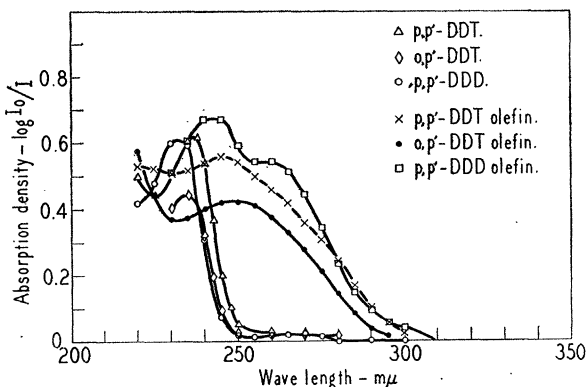


FIG. 1. Ultraviolet absorption curves of 10 μ g./ml. of p,p'-DDT, o,p'-DDT, p,p'-DDD, and their respective olefins dissolved in 95 per cent alcohol.

tion by dilute alcoholic NaOH to the olefin, 2,2-bis(p-chlorophenyl)1,1-dichlorethylene, the solution absorbs strongly at this wave length (see Fig. 1). Measure-

ment of this increase in absorption and comparison with that obtained with a similarly treated standard DDT solution is the basis of the present method. The principal impurity in commercial products (4), *o,p'*-DDT, changes only slightly to its olefin by the present method and is therefore not determined.

PROCEDURE

(A) Three ml. of solution of DDT in 95 per cent alcohol containing 2–20 μ g. DDT/ml. is pipetted into a 30- to 50-ml. test tube and placed in a 37° C. water bath. Five-tenths ml. of 0.7 N alcoholic NaOH (or KOH) is added, and after five minutes the alkali is neutralized with 0.1 ml. (3 drops) of 4 M acetic acid.

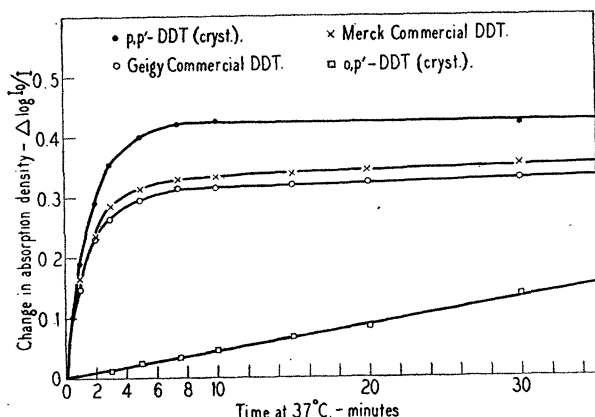


FIG. 2. Change in absorption value at 250 $m\mu$ with time of dehydrochlorination in 0.1 M NaOH in 95 per cent alcohol at 37° C. of crystalline pure *p,p'*-DDT, *o,p'*-DDT, and two commercial preparations.

(B) In this sample, which is a control or blank, the quantities of alkali and acid indicated in A are mixed before addition of the 3-ml. aliquot of DDT solution.

(C) This sample is merely the solvent control. To 3 ml. of 95 per cent alcohol is added 0.5 ml. of 0.7 N NaOH (alcoholic) and 0.1 ml. of 4 M acetic acid.

SPECTROPHOTOMETRIC MEASUREMENT¹

Samples C, B, and A, in this order, are placed in a Beckman D U photoelectric spectrophotometer and the absorption measured at 250 $m\mu$. C, the solvent, is used in balancing the spectrophotometer. The difference between the absorption of B and A is due to the olefin formed by dehydrochlorination of the *p,p'*-DDT by alcoholic NaOH. The weight of *p,p'*-DDT corresponding to the difference in absorption is read directly from a standard curve.

RESULTS

Table 1 contains the analyses of different dilutions

¹ Neal, *et al.* (5) described a spectrophotometric method for determining DDT, but it was applicable only to solutions free from any other material absorbing in the region of 237 $m\mu$.

of several different preparations of DDT. The starting solutions were all 2 per cent by weight of DDT dissolved in commercial kerosene. The change in absorption increases linearly with the concentration of material in accordance with Beer's law. The lower values in Table 1 and Fig. 2 for the commercial preparations are in agreement with the findings of Haller, Bartlett, Drake, *et al.* (4) that commercial preparations contain about 70 per cent *p,p'*-DDT. These results also show that the change in absorption is directly proportional to the concentration of *p,p'*-DDT.

SPECIFICITY OF THE METHOD AND INTERFERING SUBSTANCES

The work of Busvine (1) and of Cristol (3) led to the present method, which is relatively specific for *p,p'*-DDT. These workers showed that *o,p'*-DDT and *p,p'*-DDD (the dichlorethane analogue of DDT) dehydrochlorinate at much lower rates than does *p,p'*-DDT. The quantity of *p,p'*-DDD in commercial preparations is apparently small, whereas the *o,p'*-DDT is 15–20 per cent (4).

Results of experiments to determine the time at which the largest proportion of *p,p'*-DDT was dehydrochlorinated with a minimum of change in the *o,p'* isomer are shown graphically in Fig. 2. After five minutes at 37° C. in 0.1 N alcoholic NaOH, pure *p,p'*-DDT is 95 per cent converted to its olefin, whereas *o,p'*-DDT was changed only 5–10 per cent. Busvine (1) also found that the *o,p'*-DDT was much lower in its biological action than *p,p'*-DDT.

Other materials analyzed to determine their possible interference were: bis(*p*-chlorophenyl) acetic acid, bis(*p*-chlorophenyl) sulfone, and 2-trichlor-1-*o*-chlorophenylethyl-*p*-chlorobenzene sulfonate. No interference was encountered other than a rise in the blank value in some instances.

Many substances, crude kerosene in particular, absorb strongly in the region of 250 $m\mu$, causing high blank values. However, in the sprays as ordinarily employed (2–5 per cent DDT in commercial kerosene) the absorption by kerosene has not been high enough to reduce the precision of the measurement (see Table 1). If the proportion of kerosene is increased so that the blank or B absorption value is high compared to that derived from the DDT olefin, then the error in estimating the DDT will increase. Dilutions were always made in the nonabsorbing solvent, 95 per cent ethanol.

EFFECT OF CERTAIN VARIABLES ON ABSORPTION VALUE

(1) The effect of the concentration of DDT on the absorption value is linear.

(2) The wave length setting is important, particularly if a standard solution is not analyzed simul-

taneously, for, as may be seen from Fig. 1, the absorption curve of the DDT sample rises abruptly below 250 m μ .

(3) The time of heating should be within 0.25 minutes of 5.

APPARATUS

The Beckman quartz ultraviolet photoelectric spectrophotometer (2) has been used throughout this work. The wave length scale was standardized, as recommended, with the hydrogen 656-m μ line. It was

TABLE 1
SPECTROPHOTOMETRIC ANALYSIS OF DIFFERENT DDT PREPARATIONS

DDT/ml. in μ g.	Absorption Density—Log I ₀ /I											
	3 \times Crystallized p,p'-DDT			Merck Commercial			Geigy Commercial			Artificial Mixture 75% p,p'-DDT and 25% o,p'-DDT*		
	A	B	Δ	A	B	Δ	A	B	Δ	A	B	Δ
2	.14	.082	.06	.12	.08	.04	.115	.06	.055	.1	.06	.04
5	.32	.155	.165	.275	.165	.11	.275	.155	.12	.285	.145	.14
10	.63	.31	.32	.565	.295	.27	.56	.31	.25	.55	.32	.23
20	1.23	.62	.61	1.07	.58	.49	1.12	.60	.52	1.08	.6	.48

* This and most of the other related pure chemicals were kindly placed at our disposal by S. J. Cristol and H. L. Haller, of the Agricultural Research Administration, Beltsville, Maryland.

(4) The reaction is bimolecular, and the rate is proportional to the hydroxyl ion concentration.

(5) The temperature of the reaction should be controlled to a few tenths of a degree. The results of the work of Cristol (3) indicate a temperature coefficient of about 3 for 10° C.

(6) The time of standing after neutralization of the alkali causes no appreciable change up to several hours.

EXTINCTION

The extinction, $E_{1\text{ cm.}}^{1\%}$, for pure p,p'-DDT olefin at 250 m μ , close to a peak of absorption, is about 550, and the molecular extinction, ϵ , is about 18,000. The peak of absorption for pure p,p'-DDT is at 237 m μ , the extinction in this case being 550, and ϵ , 20,000.

checked in the ultraviolet region by determining the absorption maxima of a 0.02-per cent benzene solution in iso-octane. The three highest maxima were observed at 261, 245.5, and 249 m μ , which are within 1 or 2 m μ of the values in the International Critical Tables.

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Letters to the Editor

The Ascorbic Acid Content of Some Malpighia Fruits and Jellies

In a recent issue (*Science*, 1946, **103**, 219) Asenjo and Freire de Guzmán reported the exceptionally high ascorbic acid content of the West Indian cherry (*Malpighia puniceifolia* L.). These workers found that the fruits, when fully ripe, contain an average of 1,707 mg. of ascorbic acid per 100 grams of edible material and, when unripe, 2,963 mg.

Apparently some confusion exists as to the identity of the species of Malpighia grown in southern Florida and commonly referred to as the Barbados cherry. Mowry and his associates (*Fla. agric. Exp. Sta. Bull.*, 1941, 109,

65-67) have applied this common name to *M. glabra*, whereas Sturrock, in his *Tropical fruits for southern Florida and Cuba and their uses* (1940), has applied it to *M. puniceifolia*.

In the present investigation, fruits and herbarium material were collected from four plants, three of which were thought by their growers to be *M. glabra* and one, *M. puniceifolia*. The latter bush is located at the U. S. Plant Introduction Garden, a few miles south of Miami, Florida. All of these herbarium specimens were identified by H. A. Gleason and his associates, of the New York Botanical Garden, as *M. puniceifolia*. Fruits were also collected from a plant of *M. coccigera* and from an un-