Pakistan J. Sci. Ind. Res., Vol. 13, No. 4, December 1970

SPECTROPHOTOMETRIC DETERMINATION OF PETKOLIN FROM PLANT SURFACES

SHAHID H. ASHRAFI, S.N.H. NAQVI, F. YASMEEN, S.A. MUZAFFAR and M.K.A. KHAN

P.C.S.I.R. Laboratories, Karachi 39

(Received March 31, 1969; revised January 14, 1970)

Spectrophotometric determination of residues of Petkolin was done on the cotton leaves, according to the method described by Avens *et al.*,[12] after certain modifications. Different concentrations and different volumes of the Petkolin emulsion were used for spraying and the amount of residue was calculated on the basis of colorimetric estimations by using Fat dye as an agent. It was found that the residue of Petkolin persisted for 5-7 days in all the replicates and patterns.

Although much work has been done on different aspects of Petkolin[1] by various workers[2–8] no work has been done on its residual effect. During the residual studies of Petkolin on crop it was found desirable to develop a chemical method for determining its traces quantitatively on plants. Various methods[9–12] were tried but the method described by Avens *et al.*[12] for the determination of mineral oil deposits on plants, with certain modifications, was found most suitable for the analysis of Petkolin (Chlorinated Petrol).

Materials and Methods

Preparation of Dyed Petkolin.—One hundred millilitres of dyed Petkolin was prepared by dissolving 4 mg of Fat Red dye per ml. This mixture was heated at a low temperature (40°C) with intermittent shaking for 1 hr. Thus the deeply red coloured Petkolin was obtained and it was allowed to stand overnight at room temperature (23°C). Next day it was again heated for 1 hr and filtered through a sintered glass filter. This filtered, coloured Petkolin was taken as stock solution. From this stock solution 40% emulsifiable concentrate of coloured Petkolin was prepared and then the emulsion of 0.5, 1.0, 2.0 and 3.0% for spraying on plants.

Application and Extraction Method.—The experiments were designed in two different sets. In the first set 1 ml emulsions of coloured Petkolin per leaf, of different concentration, ranging from 0.5 to 3.0%, were sprayed on the upper surface of the leaves of cotton plant (in field) by the help of De-Vilbiss atomizer. In the second set, 1,2,3 ml per leaf of 1% emulsion of coloured Petkolin were sprayed. The cotton plant leaves of approximately equal size (average area 16.5 in^2) were used during the experiment. Each concentration was sprayed on five leaves separately and each set of experiments was replicated thrice. After spraying coloured Petkolin the samples were randomly taken at 24, 48, 72, 120, 144 and 168 hr. interval for residue analysis. The leaves were stored in a deep-freeze chamber until the time of extraction. The extraction was done in 100 ml petroleum ether by using Soxhlet apparatus, for 2 hr. The extract was subsequently removed in an Erlenmeyer flask and was made up to 250 ml by adding further quantity of petroleum ether.

Colour Measurement.—The transmission measurements were taken by the help of Beckman Model DB 620 Spectrophotometer with 5 ml cell size. Petroleum ether was used as reference during colorimetric determination. The wavelengths were varied from 410 to 580 mμ to find the optimum wavelength at which maximum absorption takes place. This was found to be 520 mμ in the case of Fat Red dye as against 515 mμ described by Avens *et al.*[12] for oil red 'O' dye. Therefore, all the determinations were done at 520 mμ wavelength. Transmittancy value graph (Fig. 1) for measuring the quantity of residues colorimetrically was prepared by dissolving different quantities of Fat Red dye in petroleum ether.

Blank or check values were determined by extracting samples of unsprayed material and making the measurement as in the case of sprayed samples. Values from check material were then deducted from those obtained from the sprayed material to give the net Petkolin present.

Calculation of the Quantity of Petkolin Deposits.—The amount of Petkolin deposited is calculated from the equation given below:

$$Q = K \log \frac{100}{\% T}$$

where Q is the quantity of Petkolin per 50 ml sample; %T is the per cent transmittance measured by the spectrophotometer; K is a constant, which is characteristic of dyed Petkolin being determined; K_1 is calculated for dyed Petkolin used in the following manner.

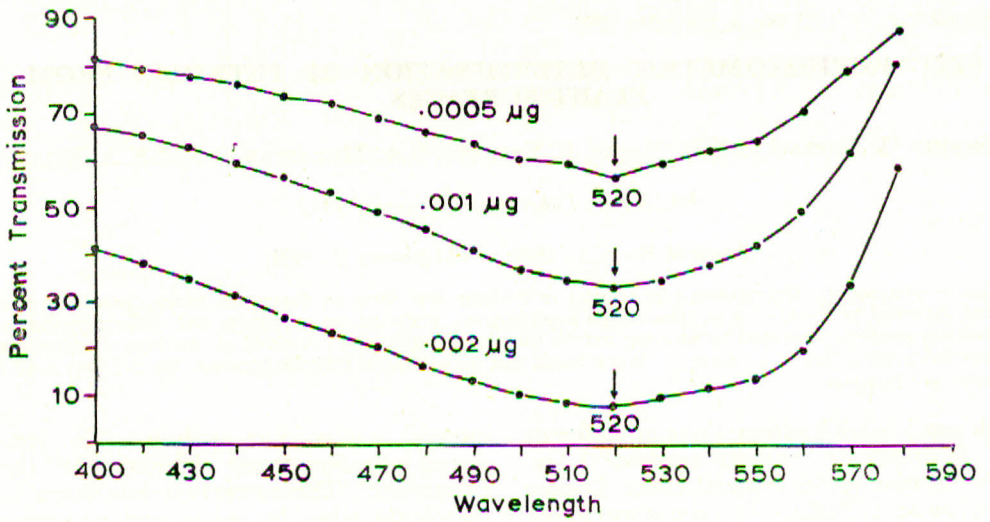

Fig. 1.—Standard graph of Fat Red Dye for quantitative extimation.

Value of Q and K.—The dyed Petkolin (200 mg) was accurately weighed in a weighing bottle and transferred with the aid of petroleum ether to 1-l volumetric flask. The per cent transmittance of this solution was determined. The constant K was calculated from the above equation.

Values of sample and blank were determined by measuring the per cent transmittance of several extracts of sprayed and unsprayed leaves and substituting the average per cent transmittance in the above formula using the K for the oil being determined according to Avens *et al.*[12]

Results

Experiments were performed and repeated five times. Net amount of Petkolin residue recovered was calculated as described above. Calculated values, based on colorimetric determination and actual weight of the Petkolin sprayed, have been compared in the Tables 1 and 2. These tables represent the data of two sets of experiments. Set No. 1 comprises the spraying of 5 ml of 0.5%, 1%, 2% and 3% solution in each case and their amount of residue left after 24, 48, 72, 96, 120, 144 and 168 hr. Set No. 2 comprises the spraying of 5, 10 and 15 ml of 1% solution in parts of 5 ml and their residue left after 24, 48, 72, 96 and 120 hr.

Discussion

The data indicate that the residual effect of Petkolin persists for 7 days, in the first method of spray and for 5 days in the second method of spray (Tables 1 and 2). The half life was found to be 3-5 days for different ocncentrations in the first method while 2 days in the second method. The half life of DDT on citrus foliage have been reported as 39 days while that of Malathion as 3 days on foliage.[13] However, the half life of Petkolin is quite near to that of Malathion.

The calculated values and the actual weight of the residue differ, but this difference may be due to some loss during the experiments. It was also noted that by the increase of concentration (Set 1) the increase in the amount of residue was more prominent than the increase in volume (Set 2). This may be due to greater loss during spraying in more than one dose. Percentage loss in Set 1 was low at higher concentration though the quantity increased. Similarly after different intervals the residue amount increased at higher concentration but the percentage recovery had little variation. In the 2nd set both the percentage loss and the quantitative loss increased with the increase of volumetric spraying dose. In the first set, percentage recovery had little variation, although the amount increased with the increase of spraying dose. However, these data clearly indicate a short residual effect of Petkolin.

In the present method an attempt has been made to determine the residual effect and the quantity of the residue of Petkolin on cotton leaves by an indirect colorimetric method. In comparison to the bioassay method for residues, the present colorimetric method is better because, here we can actually determine the quantity of the insecticide present on the leaves. This determination was easily possible in the case of Petkolin due to its light petroleum nature.

TABLE 1.—PETKOLIN RECOVERED AFTER GIVEN TIME ON THE BASIS OF TRANSMITTANCE AT 520 mμ. (SAME QUANTITY AND DIFFERENT CONCENTRATION).

Quantity and concentration of the samples		Patkolin applied mg	0 hr		24 hr		48 hr		72 hr		96 hr		120 hr		144 hr		168 hr	
%	ml		mg	%	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%
0.5	5	90	49.50	55	6.80	7.6	5.00	5.5	2.80	3.1	Nil	6.0	Nil	6.0	Nil	6.0	Nil	0.0
1	5	180	99.36	55.2	13.80	7.6	9.40	5.2	7.80	4.3	4.80	2.6	2.00	1.1	Nil	0.0	Nil	0.0
2	5	360	196.48	54.8	17.80	5.0	15.00	4.3	11.40	3.2	8.00	2.3	4.00	1.1	1.00	0.8	1.00	0.3
3	5	540	280.80	52	22.00	4.2	19.00	3.8	14.00	2.6	10.40	2.0	6.80	1.2	3.00	0.7	3.00	0.5

TABLE 2.—PETKOLIN RECOVERED AFTER GIVEN TIME ON THE BASIS OF TRANSMITTANCE AT 520 mμ. (DIFFERENT QUANTITIES BUT SAME CONCENTRATION).

Quantity and concentration of the samples		Petkolin applied mg	0 hr		24 hr		48 hr		72 hr		96 hr		120 hr	
%	ml		mg	%	mg	%	mg	%	mg	%	mg	%	mg	%
1	5	180	90.00	50	3.00	1.6	0.80	0.45	0.800	0.45	Nil	6.00	0.00	0.0
1	10	360	158.40	44	9.00	2.6	1.10	0.30	1.100	0.30	0.800	6.23	0.00	0.0
1	15	540	194.40	36	26.40	5.0	2.20	0.41	2.20	0.41	1.00	6.20	0.00	0.0

References

1. S. Siddiqui, S.A. Qureshi and S.H. Ashrafi, Pakistan Patent 113,190 (1963).
2. S.H. Ashrafi, S.M. Murtuza and D. A Asmatullah, Pakistan J. Sci. Ind. Res., **7,** 211 (1964).
3. S.H. Ashrafi, S.M. Murtuza and D. Asmatullah, Scientific Researches, **3,** 186 (1966).
4. M. Anwarullah and T. Akhtar, Pakistan J. Sci. Ind. Res., **10,** 251 (1966)
5. M. Anwarullah, S.S. Qureshi and S.H. Ashrafi, Pakistan J. Sci. Ind. Res., **10,** 251 (1967).
6. S.A. Qureshi and S. Raza, Pakistan J. Sci. Ind. Res., **7,** 192 (1964).
7. S.H. Ashrafi, M. Tasnif and R.I. Zuberi, Pakistan J. Sci. Ind. Res., **8,** 265 (1965).
8. S.H. Ashrafi, S.A. Muzaffar and M. Anwarullah, Sci. Indy., **4,** 312 (1966).
9. G.W. Pearce, A.W. Avens and P.J. Chapman, J. Econ. Entomol., **34,** 202 (1941).
10. G.W. Pearce, P. J. Chapman and D.E.H. Frear, Ind. Eng. Chem., **40,** 284 (1948).
11. L.A. Richl, F.A. Gunther and R.L. Beier, J. Econ. Entomol., **46,** 743 (1953).
12. A.W. Avens, S.D. Gibbs and P. J. Chapman, J. Econ. Entomol., **55,** 819 (1962).
13. W.O. Negherbon, *Handbook of Toxicology Vol. III. Insecticides* (W.B. Saunders Company, Philadelphia and London, 1959), p. 451.