Pakistan J. Sci. Ind. Res., Vol. 26, No. 3, June 1983

ARGENTIMETRIC METHOD FOR THE DETERMINATION OF AZINPHOS METHYL USING DICHLOROFLUORESCEIN AS INDICATOR

Muhammad Mumtaz, Miss Nusrat Nasir and M.M.H. Baig

Federal Pesticide Laboratory, Pakistan Agricultural Research Council, Malir Halt, Karachi-27, Pakistan

(Received April 26, 1982)

Azinphos methyl is a non-systemic insecticide and acaricide of long persistence, chiefly effective against biting and sucking pests. It is mainly used in Pakistan on top fruit, cotton and citrus etc.

A method for the determination of Azinphos methyl has been developed. The method consists in hydrolysing azinphos dissolved in methanol at room temperature by sodium hydro-xide in the presence of phenol and estimating 0, 0, dimethyl hydrogen phosphorodithioate with silver nitrate, using dichlorofluorescein as the indicator.

INTRODUCTION

There are many methods for the quantitative analysis of Azinphos methyl in pure or formulated technical grade products [1–5]. The recommended method is based on the alkaline hydrolysis of Azinphos methyl to give dialkyl phosphorodithioic acid which is complexed with copper ions and, after extraction, measured spectrophotometrically at 420 nm.

Another method for the determination of Azinphos methyl is by hydrolysis with KOH in 2-propanol giving anthranilic acid, which is diazotised and coupled with N-(1-Napthyl) ethylene diamine to give red colour measured at 555 nm [6].

Miles *et al.* [7] reported an argentimetric method for the analysis of Malathion which, on hydrolysis, gives dimethyl phosphorodithioate (which is also obtained from Azinphos methyl on hydrolysis). The dimethyl phosphorodithioate reacts with silver nitrate and forms an insoluble precipitate; the end point is determined potentiometrically.

Hill *et al.* [8] reported an iodometric method for the analysis of Azinphos methyl which, after hydrolysis, is buffered to pH 3–9 by addition of sodium acetate/acetic acid buffer solution. Dilute aqueous cupric sulphate solution is added and the cupric salt of 0, 0-dimethyl phosphorodithioic acid which forms, is extracted with chloroform. The cupric salt remaining in the aqueous layer is determined iodometircally using sodium thio-sulphate.

In the present paper, a simple volumetric method, based on argentimetric titration of dimethyl phosphorodithioate, is proposed for the determination of Azinphos methyl. (Potential interferences, if any, in liquid formulations are removed by passing the sample through Florisil column chromatography before the determinative step).

METHOD

Reagents:

i) *Preparation of Indicator:* Take 0.1 g of 2.7 dichlorofluorescein in 100 ml volumetric flask and make up to the mark with Methyl alcohol.

ii) *Silver Nitrate Solution, 0.1N:* Dissolve 16.99 g of pure $AgNO_3$ in distilled water, add a few drops of con. HNO_3 and make up to 1 litre in a measuring flask.

iii) *Phenol Solution,* 30 % w/v in methanol.

iv) *Sodium Hydroxide* (Carbonate free) 3N.

v) *Dilute Nitric Acid* – General-purpose.

Procedure

Accurately weigh amount equivalent to 0.80 – 1.00 g pure Azinphos methyl (Analytical Standard purity 88 %), and dissolve in methanol in 50 ml volumetric flask. Transfer 10 ml aliquot to 250 ml erlenmeyer flask with 2 ml, 3N NaOH and 2 ml 30 % phenol solution in methanol. Shake gently and let stand 20 min. Neutralize with dilute HNO_3 to pH 6.5 – 8.0. Add 15 drops of indicator solution (0.1 % 2.7 dichlorofluorescein in methanol) and dilute to approximately 100 ml with distilled water. Titrate with 0.1N $AgNO_3$ solution, to point at which precipitate formed coagulates and red colour developes on surface.

$$\% \text{ Azinphos Methyl (w/w)} = \frac{VxNx\ 158.55}{\text{g sample}}$$

Where V = ml Silver nitrate solution
N = Normality of silver nitrate
158.55 = One half the molecular weight of Azinphos methyl

Table 1. Check on assay using Azinphos methyl solution in methanol.

No. of Detn.	Azinphos methyl solution conc. g/50 ml	Vol test solution assay (ml)	Titre 0.1N $AgNO_3$ (ml)	Azinphos methyl recovered (%)
1	0.8120	10	4.52	88.31
2	0.8120	10	4.51	88.25
3.	0.8120	10	4.50	88.09
4	0.9180	10	5.10	88.28
5	0.9180	10	5.08	88.13
6	0.9180	10	5.12	88.49
Average				88.225
Standard Deviation				± 0.145

Liquid Formulation with Anionic and Nonionic Surfactants

Fill 300–22 mm glass column with about 10 cm florisil 60–100 mesh, then add 1.0 cm anhydrous sodium sulfate. Moisten column with 40 ml petroleum ether. Add liquid sample equivalent to 0.8–1.0 g active ingredient to column and eluate with 100 ml ethyl ether – petroleum ether eluate at the rate of 50 drops/minute. Dilute the eluate to 50 ml with methanol in volumetric flask. Take 10 ml aliquot and proceed as above.

RESULT AND DISCUSSION

A sample of analytical grade Azinphos methyl, 88 % purity (received from Bayer A.G.) was used to standardize the method by preparing solutions containing Azinphos methyl, accurately weighed, in 50 ml methanol. 10 ml portions of the solution were assayed by the proposed method. The results are shown in Table 1.

In analysing a typical liquid formulation of Azinphos methyl 20 % emulsifiable concentrate, the end point was not hard to see. However, in order to avoid any potential interference from surfactants (anionic and nonionic) which may be present in liquid formulations, a florisil column was also successfully used before the determinative step.

The proposed method is feasible, since complex apparatus are not required and the reagents are relatively easy to prepare. Also the procedure is very simple and less time consuming as it is finished titrimetrically instead of colorimetrically.

Hence the method is very useful in routine analysis, and pesticide laboratories with only rudimentary facilities can adopt this method profitably for quality control of this product in Pakistan.

REFERENCES

1. M.V. Norris, *et al.*, J. Agr. Food. Chem., 2, 570 (1954).
2. CIPAC Hand Book, 1, 25 (1970).
3. *Analytical Methods for Pesticides and Plant Growth Regulators,* ed. Zweig. G (Academic Press, N.Y., 1972, 6, 397).
4. FAO Specifications (CP/41).
5. *Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives,* ed. Zweig, G. (Academic Press, N.Y., 1964, 2, 231).
6. W.R. Meagher, *et al.*, J. Agr. Food Chem., 3, 282 (1960).
7. J.W. Miles, M.B. Goette, G.O. Guerrant and F.C. Churchill, JAOAC 55, 1133 (1972).
8. A.C. Hill, M. Akhtar, M. Mumtaz. Plant Protection Mannual for Analysis and Testing of Pesticides Formulations. 1st ed. Ministry of Agriculture and Works, Malir Halt, Karachi, PPM 21-B, 73 (1965).