Pakistan J. Sci. Ind. Res., Vol. 31, No. 3, March 1988

A METHOD FOR THE ANALYSIS OF SECONDARY CARBAMATE PESTICIDES

Mohammad Sharif Khan

Federal Pesticide Research Laboratory, PARC, Malir Halt, Karachi-27

(Received September 7, 1987; revised February 21, 1988)

A modified micro-kjeldahl distillation method has been successfully employed for the determination of secondary carbamates in technical material and in formulations. Methylamine, released on alkaline hydrolysis of sample, is steam distilled and absorbed in boric acid solution, which is titrated with hydrochloric acid using bromocresol green as indicator. The method has been used extensively with accurate and reproducible results for quality control of secondary carbamates. The method can determine these compounds down to a minimum of 0.02m mole of active ingredient.

Key words: Pesticide, Carbamate.

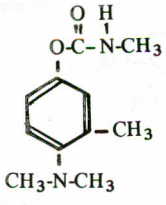
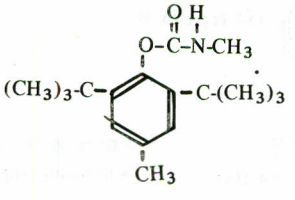
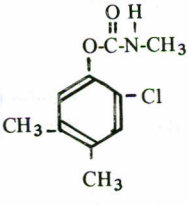
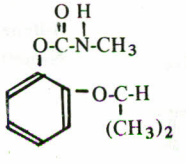
INTRODUCTION

N-methyl carbamates (insecticides) and N-phenyl carbamates (herbicides) are secondary carbamate pesticides represented by general formula $R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{N}\text{-}CH_3$ (R= aliphatic or aromatic group). Among this group of pesticides (Table-1) carbaryl (1-naphthyl-N-methyl carbamate), carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate) and aldicarb (2-methyl-2-(methylthio)-propanal-O-(methylamino) carbonyl) oxime, were available in this laboratory, and used to evaluate the adopted method of analysis.

Different products, released on alkaline hydrolysis, of secondary carbamate pesticides were used for their assay. It has been reported [1] that infrared absorption frequencies of carbamates containing N-H group shifted to higher frequencies in going from solid to a liquid phase due to the loss of hydrogen bonding, making the availability of H_2 $N\text{-}CH_3$ (methylamine) easier and rendering possible the analysis of these pesticides, as cases of carbaryl, aldicarb and carbofuran.

Assay of methylamine determines the active ingredients in these technical material and formulations of this group of pesticides. Carbaryl has been analysed by different method [2-7] which are time consuming and requires costly apparatus and large quantities of the sample. Aldicarb [8-11] and carbofuran [2-13] formulation products have been analysed by colorimetric or GLC methods using other hydrolytic products. The conditions of the experiment are very specific and the methods are time consuming and complicated. Thus assay of methylamine only seems the best possible common method for the analysis of such compounds. M. Akhtar *et. al* [14] modified the standard method [3] for the assay of carbaryl by using

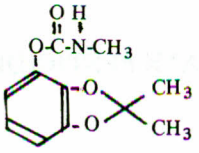
Table 1. List of secondary carbamates.

S. No.	Pesticides	Formula	Chemical name
1.	Aminocarb		4-(N, N-dimethylamino) – 3-methyl phenyl N-methylcarbamate
2.	Azak		2, 6-di-tert-butyl-4-methylphenyl N-methylcarbamate
3.	Banol		2-chloro-4, 5-dimethyl-phenyl N-methylcarbamate
4.	Baygon (Propoxur)		2-isopropoxyphenyl methyl carbamate

(Continued.....)

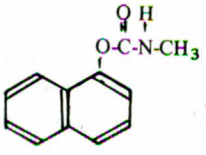
(Table 1, continued)

5. Bendiocarb



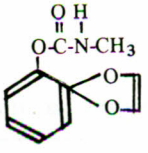
2, 3-isopropylidenedioxy-phenyl N-methylcarbamate

6. Carbaryl



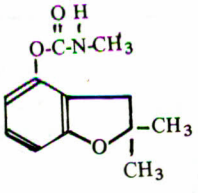
1-naphthyl N-methylcarbamate

7. Dioxacarb



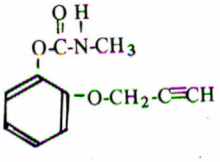
2-(1, 3-dialane-2-yl) phenyl N-methylcarbamate

8. Carbofuran (Furadan)



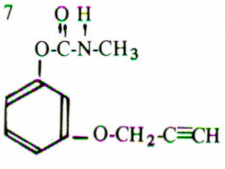
2, 3-dihydro-2,2-dimethyl-7-benzofuranyl N-methylcarbamate

9. Hercules 9699



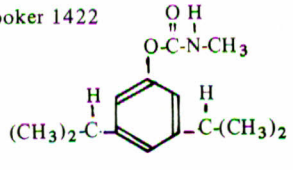
2-propargyloxyphenyl N-methylcarbamate

10. Hercules 8717



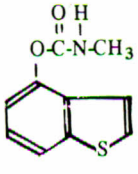
3-propargyloxyphenyl N-methylcarbamate

11. Hooker 1422



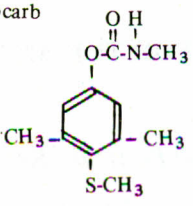
3, 5-di-iso-propylphenyl N-methylcarbamate

12. MCA-600



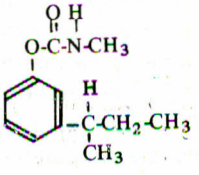
4-Benzothionyl N-methylcarbamate

13. Methiocarb



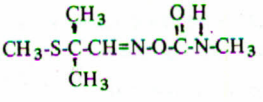
4-methylthio-3, 5-xylyl N-methylcarbamate

14. RE-5305



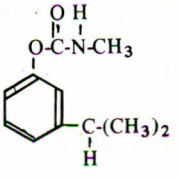
3-sec-butylphenyl N-methylcarbamate

15. Aldicarb (Temik)



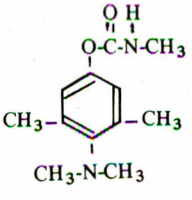
2-methyl-2-(methylthio–propanal O-[(methylamino) carbonyl] oxime

16. UC–10854



3-isopropylphenyl N-methylcarbamate

17. Zectran



4-(N, N-dimethylamino)-3, 5-dimethylphenyl N-methylcarbamate

micro-kjeldahl distillation apparatus as used for distillation of ammonia. This method is not only quick but requires smaller quantities of the sample. The present paper is an extension of its application to analyse other compounds of the same group producing methylamine on alkaline hydrolysis and their mixtures too. Thus providing an easy and general method of common use for a greater number of determinations at a time.

MATERIAL AND METHODS

Reagents. Boric acid-mixed indicator solution:

20ml of 0.1 % ethanolic bromocresol green was mixed with 4ml methyl red and added to 500ml of 2 % boric

acid solution in water. This solution was used to absorb methylamine distilled over.

Apparatus. Micro-distillation assembly:

Kjeldahl type used in these tests was similar to the quick-fit-quartz assembly cat. No. 21/100MC consisting essentially of a 100ml kjeldahl flask, a distillation head with steam inlet and a leibig condenser or equivalent which can ensure complete distillation of methyl amine without carry over of alkali.

Procedure. A minimum of 0.02m mole of the carbamate (or an equivalent quantity of formulation, was introduced into the distillation apparatus. Solid samples were weighed directly into the distillation flask while liquid samples were pipetted into the flask through the ground joint in the head and rinsed with about 1ml water. The flask was then fixed to the head of the apparatus. 2.5ml of 40 % sodium hydroxide was added through the joint in the head followed by a rinse with about 1ml water.

Steam was bubbled through the apparatus and 10 ml distillate was collected in a 25 ml conical flask containing 2 ml boric acid indicator mixture. The first distillate was titrated using 0.01N hydrochloric acid. Second distilled similiarily obtained (10 ml) indicated absence of methyl amine on titration. Blank determinations were also made using the same procedure but with no pesticide.

Calculations. As one mole pesticides liberated one mole of methylamine on hydrolysis thus the acid used for titration is equivalent to the pesticide hydrolysed. Hence X ml of 0.01 N HCl used for titration is equivalent to

$$\frac{X}{1000} \times \frac{1}{100} \text{ moles of pesticide}$$

$$\text{or } \frac{M \times X}{1000 \times 100} \text{ gm of pesticide (M = Molecular Weight)}$$

$$\text{or } \frac{M \times X}{100} \text{ mg of pesticide}$$

$$\text{Therefore percentage (\%) active ingredient} = \frac{M \times X}{W}$$

(W = weight of sample in mg).

RESULTS AND DISCUSSIONS

Replicates of each pesticide have been analysed using dust or granular formulations available for agricultural purposes. Results given in Table 2 are well within the required accuracy. The method has been applied in the analysis of formulations without cleanup of the active ingredient and thus is quick and easy allowing more analyses at a time. The validity of the method has been demonstrated with both technical and formulated samples. The results range from 95.9 % to 105.3 % which are very close to the declared values.

Table 2. Results obtained in the analysis of carbaryl, carbofuran and aldicarb.

S. No.	Pesticide	Added mg	Found mg	% Recovery
1.	Carbaryl – Formulation	10	9.88	98.8
		10	9.88	98.8
		10	9.88	98.8
		10	9.88	98.8
		10	9.88	98.8
		10	10.28	102.8
		8*	8.13	101.6
	– Technical	85	85.43	100.5
2.	Carbofuran – Formulation	10	9.85	98.5
		10	9.85	98.5
		10	9.85	98.5
		10	9.62	96.2
		10	10.34	103.4
		10	9.59	95.9
		3	3.16	105.3
		3	3.04	101.3
		3	3.09	103.0
	– Technical	95	95	100
		95	93.03	97.9
3.	Aldicarb- – Formulation	10	9.96	99.6
		10	10.17	101.7
		10	9.96	99.6
		10	10.17	101.7
		10	9.96	99.7
		10	10.17	101.7

*A sample of Sevidol (8:8) containing 8 % carbaryl was analysed in the presence of 8 % BHC.

Acknowledgements. The assistance of Mr. Hameeduddin Syed during the conduction of these studies is acknowledged.

REFERENCES

1. T. Jo-Yen Chen and R. Walter Bensen, J. A.O.A.C., **49**, 412 (1966).
2. F. Martin, Kovacs Jr, J. A.O.A.C., **50**, 566 (1967).
3. W.E. Whitehurst and J.B. Johnson, Research and Development Department, Union Carbide Co., South Charleston, West Virginia (1958).
4. CIPAC Hand Book, **1**, 185 (1970).
   CIPAC Hand Book, **1A**, 185 (1979).

5. R. Miskus *et. al.*, J. Agri. F. Chem., **7**, 613 (1959).
6. F.A. Gunther, J. Agri. Food Chem., **10**, 222 (1962).
7. H.A. Stansbury Jr. and R. Miskus, "Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives", **2**, 437 (1964).
8. CIPAC Hand Book **IA**, 1094 (1980).
9. R.R. Romine, "Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives" **7**, 147, (1974).
10. J.C. Maitlan *et. al.* J. Agri. Fd. Chem., **16**, 549 (1968).
11. D.P. Johnson *et. al.* J. of A.O.A.C., **49**, 399 (1966).
12. R.F. Cook *et. al.*, J. Agri. Fd. Chem., **17**, 277 (1969).
13. R.F. Cook, "Analytical Methods for Pesticides, Plant Growth Regulators", **7**, 187 (1974).
14. M. Akhtar *et. al.*, Pakistan J. Sci. and. Res., **13**, 452 (1970).