Indian Journal of Chemical Technology
Vol. 10, January 2003, pp. 96-98

## Note

# A simple sensitive spectrophotometric method for determination of dichlorvos in environmental samples

Anupama Asthana[a], Ajai Pillai[a] & V K Gupta[b*]

[a]Chemistry Department, Govt. Arts and Science College, Durg 49 1001, India

[b]School of Studies in Chemistry
Pt. Ravishankar Shukla University, Raipur 492 010, India

*Received 23 October 2001; revised received 25 September 2002; accepted 20 November 2002*

**A sensitive method has been developed for spectrophotometric determination of an organophosphorous pesticide dichlorvos, also known as 2,2 dichlorovinyl methyl phosphate or dichlorophos. The method is based on hydrolysis of dichlorvos by sodium hydroxide to produce dichloroacetaldehyde, which on coupling with phloroglucinol in alkaline medium, gives orange colour. The orange dye shows absorption maxima at 475 nm and obeys Beer's law in the range of 10 -100µg/25 mL (0.4 to 4 ppm) of solution. The molar absorptivity and Sandell's sensitivity were found to be $4.53 \times 10^4$ l mol$^{-1}$ cm$^{-1}$ and 0.0048 µg cm$^{-2}$ respectively. The method has been successfully applied for the determination of dichlorvos in water, agricultural soil and vegetables.**

Dichlorvos also known as DDVP (2,2 dichlorovinyl methyl phosphate or dichlorophos) is highly toxic organophosphorus pesticide[1,2]. The common trade names of dichlorvos are Nuvan, Nogas, Vapona Phosvit, etc. It is a colourless to amber coloured oily liquid with mild aromatic odour, which readily decomposes in strong acids or alkalies. It is used as an insecticide in restaurants, hospitals and aircraft. It is liberated during application on vegetables, animals, agricultural premises and outdoor fogging. Toxic gases and vapours such as phosphorus, chlorinated oxides and carbon monoxide may be released in a fire involving dichlorvos. Dichlorvos is highly toxic by inhalation, dermal absorption and ingestion, it has also been reported to cause allergic contact dermatities[3,4]. The oral $LD_{50}$ for dichlorvos is 20 to 80mg/kg in rats[5]. The general instrumental methods used for the determination of organophosphorous pesticides are gas chromatography[6,7], gas liquid chromatography[8], infra red cavity technique[9], thin layer chromatography[10,11] polarography[12], solid phase extraction-high performance liquid chromatography[13], gas chromatography-solid phase micro extraction[14], spectrophotometry[15-18]. A few spectrophotometric methods have been reported for the determination of dichlorvos[19-23]. The methods described are generally based on alkaline hydrolysis of dichlorvos to produce dichloroacetaledyde followed by reaction with reagents like resorcinol[19], 2,4 dinitrophenyl hydrazine[20] and J acid[21]. Some of these methods have poor sensitivity and higher blank problem. The cholinesterase[22] methods are non selective as all organophosphorous pesticides interfere with the method.

In the present communication, a sensitive method based on the alkaline hydrolysis of dichlorvos to dichloroacetaldehyde as described by Hughes[20] has been developed. Dichloroacetaldehyde reacts with phloroglucinol in alkaline medium giving orange colour which exhibits maximum absorption at 475nm. The method has been successfully applied for the determination of dichlorvos in water, agricultural soil and vegetables. Other organophosphorous pesticides do not interfere with the proposed method.

## Experimental Procedure

### *Apparatus*

A Systronic spectrophotometer 106 with 1 cm silica cells and Systronic pH meter model 335 were used for spectral and pH measurements respectively.

### *Reagents*

All the reagents used were of AnalaR grade and double distilled deionised water was used throughout the experiment.

Dichlorvos (HCG, India 77%) — A stock solution (1mg/mL) was prepared by dissolving calculated amount of dichlorvos in ethanol, and working standard was prepared by appropriate dilution of the stock. 1% solution of phloroglucinol (Loba Chemie) and 0.01M sodium hydroxide were prepared in deionised water .

### *Method*

An aliquot of standard solution containing 10-100µg of dichlorvos was evaporated to 0.5mL in a water bath and kept in ice cold water. 0.5mL of 1M sodium hydroxide solution was added and left

*For correspondence (E-mail : anupamaproject@yahoo.com; Fax :0788- 436116)

Table 1 — Effect of various pesticides and copollutants (Concentration of dichlorvos 2 ppm)

| Foreign species | Tolerance limit ppm | Foreign species | Tolerance limit ppm* |
|---|---|---|---|
| BHC | 600 | Antimony arathion | 50 |
| Malathion | 500 | $Ca^{2+}$, $Mg^{2+}$, $Cd^{2+}$ | 30 |
| Cyanide | 200 | $K^{+}$, $Cl^{-}$ | 30 |
| Kelthane, fluoride | 100 | $Cu^{2+}$, $Pb^{2+}$ | 60 |

*The amount of foreign species causing an error of ±2%.

Table 2 — Determination of dichlorvos in water, soil and vegetables.

| Sample | dichlorvos found*µg | | dichlorvos added µg | Total dichlorvos found* | | % of Recovery | |
|---|---|---|---|---|---|---|---|
| | Present method | Reported method[21] | | Present method | Reported method | Present method | Reported method[21] |
| | $x$ | $x'$ | $z$ | $y$ | $Y'$ | $(y-x)x100$ z | $(y'-x')x100$ z |
| Agricultural | 5.98 | 5.98 | 10 | 15.82 | 15.79 | 98.40 | 98.10 |
| Waste water[a] | 3.02 | 2.99 | 20 | 22.72 | 22.64 | 98.50 | 98.20 |
| Soil[b] | 2.82 | 2.81 | 10 | 12.62 | 12.62 | 98.00 | 98.20 |
| | 4.86 | 4.84 | 20 | 24.30 | 24.28 | 97.20 | 97.20 |
| Cauliflower[c] | 3.28 | 3.25 | 10 | 13.05 | 13.01 | 97.70 | 97.60 |
| | 5.12 | 5.09 | 20 | 24.89 | 24.80 | 98.80 | 98.50 |
| Tomato[d] | 6.51 | 6.50 | 10 | 16.42 | 16.40 | 99.10 | 99.00 |
| | 3.58 | 3.54 | 20 | 23.41 | 23.32 | 99.15 | 98.90 |

*Mean of three replicate analysis.
a= 250mL, b, c and d = 50g.
Amount of water, soil and vegetable samples taken were 250mL and 50g respectively, calculations were done for 50mL and 10g samples respectively. Samples were collected from the fields where dichlorvos were sprayed.

for 15-20 min for complete hydrolysis. 1 mL of 1% phloroglucinol was added dropwise and kept in a boiling water bath for ~15 min. The solution was kept in ice cold water and made upto 25mL with 0.01M sodium hydroxide solution. The absorbance of dye was measured at 475nm(λmax) against a reagent blank. The pH of the final solution was 10.5-11.5.

## Results and Discussion

The effect of concentration of sodium hydroxide on hydrolysis of dichlorvos was studied. For complete hydrolysis, 0.5mL of 1M sodium hydroxide solution was required. 1mL of 1% phloroglucinol was required for maximum colour intensity.

### *Effect of temperature and time*

Hydrolysis of dichlorvos was quantitative at around 0°C. The hydrolysis of dichlorvos to dichloroacetaldehyde, is completed within 15 min. The heating for ~15 min after addition of phloroglucinol at 100°C was found necessary for obtaining optimum results.

Beer's law is obeyed in the range of 0.4 - 4ppm. Molar absorptivity and Sandell's sensitivity were found to be $4.53 \times 10^4$ l mol$^{-1}$ cm$^{-1}$ and 0.0048 µg cm$^{-2}$ respectively. The reproducibility of the method was checked by seven replicate analysis of standard dichlorvos solution containing 50µg/25mL over a period of seven days. The standard deviation and relative standard deviation were found to be 0.0141 and 3.44% respectively.

### *Effect of contaminants*

Effect of various pesticides and co-pollutants were studied by adding known amount of these impurities to a solution containing 50µg/25mL of dichlorvos. The tolerance limit in ppm of various foreign species associated with 2 ppm of dichlorvos are given in Table 1.

### *Determination of dichlorvos in water and soil*

To check the validity of the method, synthetic samples were prepared by adding known amounts of dichlorvos to agriculture waste water and soil where it is used as fumigant. They were kept for ~12 h.

Dichlorvos is extracted by 2 × 25mL portions of diethyl ether. Ether solution was evaporated off and dichlorvos was determined by the proposed method. The recoveries are shown in Table 2.

### *Determination of dichlorvos in vegetables*

Various vegetable samples such as cauliflower and tomato from the agriculture field where dichlorvos was applied as a fumigant and insecticide, were weighed, crushed and fortified by adding known amount of dichlorvos. The crushed samples were kept for ~12 h. Dichlorvos was then extracted by 2 × 25mL portions of carbon tetrachloride. Carbon tetrachloride was then evaporated off and dichlorvos was determined by the proposed method (Table 2). Detection limit was found to be 10μg/spot.

## Conclusion

The present method is simple, sensitive and can be used satisfactorily for the determination of dichlorvos in environmental and vegetables samples.

## Acknowledgement

The authors are grateful to Pt. Ravishankar Shukla University, Raipur and Govt. Arts and Science College, Durg for providing laboratory facilities.

## References

1 Zweig G, *Analytical Methods for Pesticides Plant Growth Regulators* (Academic Press, NewYork), 2 (1964) 561.

2 Gruzdyev G S, *The Chemical Protection of Plants* (Mir Publishers, Moscow), 1983, 181.

3 Horn K H, Teichamann B, Schramn T & Nischan P, *Arch Gesch Wulstafarsch*, 58(1) (1988).

4 Maslinska D, Strosznajdar J, Zolewska T & Orlewski P, *Int J Tissue Rect*, 6(4) (1984) 314; *Chem Abstr*, 102 (1985) 73811z.

5 Kidd H & James D R, *The Agrochemicals Handbook*, Third Editionl (Royal Society of Chemistry Information Services, Cambridge, UK), 1991, 5.

6 Erney D, Gillespie, A Gilvydis D & Poole C F, *J Chromatogr*, 638 (1993) 57.

7 Sharp G J, Dilli S & Desmarchelier J M, *Analyst*, 113 (1988) 1493.

8 Holland P T & Machie J K, *Assoc Off Anal Chem*, 66 (4) (1983) 1003.

9 Konjevic N, Orlov M & Tritika M, *Spectrosc Lett*, 10(5) (1977) 311; *Anal Abstr*, 33 (1977) 6H(18).

10 Tewari S N & Harpalani S P, *Fresenius Z Anal Chem*, 285 (1)(1977) 48.

11 Patil V B & Shingare M S, *Talanta*, 41(3) (1994) 367.

12 Davidek J, Joseff S & Zolena D, *Milchwissenschaft*, 31 (5) (1976) 267; *Anal Abstr*, 32 (1977) 2F49.

13 Salleh S H, Saito Y, Kiso Y & Jinno K, *Anal Chim Acta*, 433(2) (2001) 207.

14 Lopez F J, Pitarch E, Egea S, Beltran J & Hernandez F, *Anal Chim Acta*, 433(2) (2001) 217.

15 Das J V, Agrawal O & Gupta V K, *Chem Anal*, 43 (6) (1998) 969.

16 Pillai A K, Agrawal O & Gupta V K, *Chem Environ Res*, 7(3&4) (1998) 173.

17 Namera A, Utsumi Y, Yashiki M, Ohtani M, Imamura T & Kojima T, *Clin Chim Acta*, 291(1) (2000) 9.

18 Jan M, Rasul Farah & Iffat Noor Ul Amin, *J Chem Soc Pak*, 19(4) (1997) 309.

19 Rangaswamy J R & Muthu M, *Microchim Acta*, 3 (1984) 433.

20 Hughes J T, *Analyst*, 88 (1963) 318.

21 Shivhare P & Gupta V K, *J Indian Chem Soc*, 68 (1991) 287.

22 Drevenkar V, Vasilic Z & Stefance Z, *Microchim Acta*, 2 (1981) 45.

23 Ali Syed, Shahid Haq Raiz, Ul Khaliq Mubasshirah & Shakoori AR, *J Zool*, 12 (1997) 31.