A Method for Sampling and Analysis of Propoxur in Air

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The insecticide propoxur (o-isopropoxyphenyl-N-methyl-carbamate) is a proven insecticide for the intradomiciliary control of various mosquito species (1,2,3,4). In addition to contact toxicity the insecticide has been shown to have an effective fumigant action (5,6,7). Little information is presently available regarding how long, and at what concentrations, the compound will persist in the air following single and repeated monthly applications or of the significance of this persistence in respect to mosquito control.

Methods for the collection and determination of trace quantities of pesticides in air have recently been reviewed by Miles, et. al., (8). These authors have shown that pesticide dusts and vapors are more efficiently trapped from air in Greenburg-Smith impingers than by filters alone. As a trapping medium, ethylene glycol was found superior to water and various hydrocarbon solvents. The trapped insecticides, primarily chlorinated hydrocarbons and organophosphates, could easily be extracted from the ethylene glycol with benzene and further cleaned up or concentrated, as desired, prior to gas chromatographic analysis.

Analytical methods for carbamate insecticides include direct gas chromatographic techniques in which a specific element in the intact compound is detected with a selective detector (9,10). Alternatively, indirect methods involving conversion of the carbamate to a suitable derivative which in turn is determined by EC or FPD can be employed (11,12,13,14).

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1/ This Program is supported by the Agency for International Development, U. S. Department of State.

Bulletin of Environmental Contamination & Toxicology, Vol. 8, No. 6, 1972 © by Springer-Verlag New York Inc.

As propoxur is presently being evaluated as a possible substitute for DDT in various Central America malaria programs, the following investigation was made to develop a simple method of sampling and analysis which would better elucidate the role of the fumigant properties of the compound as a factor in vector control.

MATERIALS AND METHODS

Apparatus [1/]: Air samples were collected in Greenburg-Smith midget impingers (Unico Model 1200-10, Unico Environmental Instruments Inc., Fall River, Mass. 02722) positioned in a Unico Telematic Air Sampler, Model 150. The sampler was calibrated to draw 2.8 L/min free air through the impinger when charged with a trapping solution. Verification of the exact flow rate was made using a Rockwell gas meter previously calibrated against a wet test meter.

Gas chromatographic analyses were made on a Varian model 1700 equipped with a tritium foil electron capture detector. A glass column, 180 cm x 0.4 cm i.d., packed with 3% OV-1 on 60/80 mesh Gas Chrom Q was used. Operating parameters were: injector 190°C; oven 135°C; detector 190°C; nitrogen flow rate 60 ml/min; attenuation 2 x 10^{-10}.

Mass spectral analyses were made by employing both direct probe introduction and combined gas chromatographic mass spectrometric (GC-MS) techniques on a Perkin Elmer 270 combined GC-MS double focusing low resolution mass spectrometer.

All solvents used were redistilled prior to use and all chemicals were reagent grade. Dimineralized, glass distilled water, washed with benzene, was used throughout the analytical procedures.

Chemical analysis: A standard curve was made by preparing a stock solution of o-isopropoxyphenol in benzene. Aliquots representing 0, 120, 240 and 480 ng were transferred to 60 ml separatory funnels and sufficient benzene added to make a total volume of 10 ml. Two ml of a 2% solution of chloroacetic anhydride in benzene and 0.2 ml of pyridine were added to each, the solutions swirled and allowed to stand for 10 minutes. The solutions were then washed with two separate 5 ml portions of water and given a final washing with 5 ml of 3% Na_2SO_4. The washings were discarded each time. The benzene fractions were then transferred to a 15 ml centrifuge tube and centrifuged at 3,000 r.p.m. for 5 minutes. Separated water was removed from the bottom of the centrifuge tube by use of disposable glass pipettes. A 5 µl sample of each concentration (equivalent to 0-200 pg) was then injected into the gas

1/ Use of trade names is for identification purposes only, and does not constitute endorsement by the U. S. Department of Health, Education and Welfare.

chromatograph to establish a standard curve of peak height versus concentration.

A stock solution of propoxur was prepared in acetone. Aliquots of this stock, equivalent to the o-isopropoxyphenol concentrations previously mentioned, were added to 15 ml of 0.05 N NaOH in 60 ml separatory funnels and allowed to stand for 15 minutes. The solutions were then made acidic by addition of 1 ml conc. HCl and allowed to stand for an additional 10 minutes. The solutions were extracted with two separate 5 ml portions of benzene, the benzene fractions combined, centrifuged to remove excess water and transferred to a clean 60 ml separatory funnel. These fractions were then treated in the manner as outlined in preparation of the standard curve.

The results obtained using both standard materials should be the same. The carbamate pesticidal compound or the corresponding phenolic hydrolysis product may be used as a standard in this analytical procedure. The selection is dependent on the specific determination to be made.

Experimental design: Six Greenburg-Smith impingers were charged with 15 ml of 0.05 N NaOH and each fortified with 12 ng of propoxur. Air was drawn through the impingers at a flow rate of 2.8 L/min. for periods of 0, 15, 30, 60, 90 and 120 minutes. At the end of each designated time period, the solution was transferred to a 60 ml separatory funnel and extracted and analyzed as previously described.

Air samples were also collected in the field, in close proximity to spraymen, during application of the insecticide to a test house.

RESULTS AND DISCUSSION

The retention time of derivatized standard o-isopropoxyphenol and the derivatized compound resulting from the hydrolysis of propoxur were identical, suggesting the formation of the same derivative from both sources. Detector responses to the two derivatives were approximately equal and linear to 200 pg, indicating essentially equivalent conversion to the chloroacetate derivative was achieved (Figure 1).

Mass spectral analysis of the standard chloroacetate derivative of o-isopropoxyphenol employing direct probe introduction and combined gas chromatographic mass spectrometric (GC-MS) techniques revealed a molecular ion of m/e 228 with characteristic isotope intensity distribution for a species containing a single chlorine atom. Further fragmentation of the parent molecule resulted in major daughter ions of m/e 186, formed by loss of propylene; m/e 152, resulting from loss of COCHCl from m/e 228; m/e 137, arising from elimination of a methyl radical from the m/e 152 ion; and m/e 110 base peak ion of a catechol type structure; and finally, peaks at m/e 92 and m/e 81, characteristic of the fragmentation of the ionic species of m/e 110.

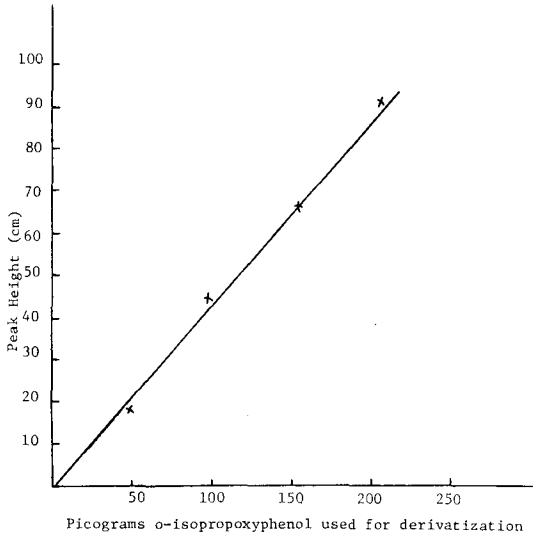

FIGURE 1. Detector response to picogram quantities of o-isopropoxyphenyl chloroacetate based on initial o-isopropoxyphenol concentration.

Confirmation of propoxur residue, obtained from an actual air sample and hydrolyzed and derivatized by means of the described experimental procedure, was accomplished by GC-MS analysis utilizing columns and GC operating parameters essentially similar to those given previously for the determinative analytical procedure. Observation of the molecular ion of m/e 228, and fragment peaks of m/e 186, m/e 152, and m/e 110 in the mass spectrum proved the presence of the o-isopropoxyphenyl chloroacetate. The source of propoxur in this instance was from an air sample collected in the field, in close proximity to spraymen, during application of the insecticide.

Although ethylene glycol has been shown to be an excellent trapping medium for a majority of pesticides (8), the utilization of this compound for trapping propoxur and its subsequent analysis would require the extraction of the insecticide from the medium with a solvent such as benzene, evaporation of the solvent and suspension of the residue in NaOH for hydrolysis to the phenol. The use of NaOH as a trapping medium eliminates the extraction and evaporation steps.

As indicated in Table 1, recoveries of more than 90% from fortified samples were obtained with air sampling periods up to 60 minutes. Increasing the sampling time resulted in increased loss of both the trapping medium and the insecticide, indicating extension of the periods of operation to be of limited value. Air was drawn through three separate fortified NaOH trapping solutions for 60 minutes and the samples stored in the cold for one week prior to analysis. Results showed no loss of the insecticide when compared to the values obtained from fortified samples treated similarly and analyzed immediately.

TABLE 1

Recovery of Propoxur from Fortified NaOH Trapping Solutions Following Operation of Air Sampling Units for Various Time Periods[1/]

Sampling Time (min)	Amount of NaOH Solution Lost (ml)	Amount of Insecticide Recovered (ng)	% Recovery
0	0	12.00	100
15	0	12.00	100
	0	12.00	100
	0	12.00	100
30	0.6	11.64	97
	0.7	11.88	99
	0.7	11.76	98
60	1.4	11.64	97
	1.6	11.40	95
	1.6	11.52	96
90	2.2	10.32	86
	2.7	10.08	84
	3.1	9.84	82
120	3.6	8.76	73
	4.1	8.52	71
	4.5	8.28	69

1/ All solutions fortified with 12 ng propoxur.

The results of this investigation show that the described analytical procedure provides a simple, rapid and sensitive determination for the insecticide propoxur, and demonstrates the feasibility of the method for monitoring this pesticide in air.

ACKNOWLEDGEMENTS

The work was supported, in part, by funds provided by the Agency for International Development. The authors wish to thank F. M. Funes A. for his technical assistance during the course of this investigation.

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