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Sampling of Airborne Dichlorvos and Fenitrothion by Using Octadecylsilane Cartridges

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Pest control operators (PCOs) usually spray insecticides in small areas such as kitchens or cabinets. They are exposed to various insecticides, especially, organophosphorus (OP) insecticides. To evaluate their occupational exposure, sampling of airborne insecticides at their breathing zone is important. There are many reports on sampling procedures for airborne pesticides (Wakimoto et al. 1974, van Dyk and Visweswariah 1975, Wright and Leidy 1978, Jackson and Lewis 1979, Draper et al. 1981, and Nishiyama 1981). Roper et al. (1984) compared the sampling efficiencies of five solid sorbents for trapping airborne pesticides and found polyurethane foam, Chromosorb 102, and C_{18} to have good sampling efficiencies. Thomas et al. (1985) also used Chromosorb 102 for sampling airborne pesticides. Hayes et al. (1980) used a commercial octadecylsilane (ODS, C_{18}) cartridge for collecting airborne OP pesticides because it was small and light weight, and did not disturb the worker's movements. Although these sorbents all collected sufficient amounts of pesticides, the pesticide eluate resulting from extraction of the sorbent had to be concentrated before quantification by gas chromatography.

In the present study, the sampling, retention, and extraction efficiency of ODS cartridges was investigated for determining airborne dichlorvos and fenitrothion. These insecticides were efficiently collected by ODS cartridges and were eluted with 3 mL of methanol. The eluate was directly determined by gas chromatography without concentration.

MATERIALS AND METHODS

Dichlorvos and fenitrothion were obtained from Wako Pure Chem. Ind., Osaka, Japan. A standard solution (100 μg/mL) was prepared with acetone. A 2% dichlorvos - 5% fenitrothion emulsifiable concentrate (EC) was used and was diluted 40-fold with water. The ODS column used was a Sep-Pak C_{18} cartridge (Waters Assoc. Milford, MA) which was washed with methanol and acetone and purged with nitrogen before use. The sampling pump used was a Roken Shiki-T.R. Personal Sampler (RM-2, Shibata Rika Chem. Ind., Tokyo, Japan) with a pumping rate 0.6 L/min. A Shimadzu GC 6A gas chromatograph (Kyoto, Japan) equipped with a flame photometric detector operated in the phosphorus

mode was used with a 2 m x 3 mm i.d. glass column packed with 2% OV-101 coated on 60-80 mesh Gas Chrom Q. The column temperature was 180 °C; injection port and detector temperatures were 220 °C; and the nitrogen carrier-gas had a flow rate of 50 mL/min. The concentration of pesticides was quantitated by using the peak height method.

The air sampling system consisted of a glass funnel (6 cm top i.d.) at the inlet, a ODS cartridge, and a personal air sampler connected with a polyethylene tube. Extraction efficiency for OP insecticides from the ODS cartridge was determined by applying 50 µg of each insecticide to the cartridge. The cartridge was purged of acetone by the use of a pump for 3 min. Adsorbed insecticides in the cartridge were eluted with methanol until the eluate amounted to 3 mL. A 2-uL aliquot of the eluate was injected directly into the gas chromatograph. Retention efficiency was determined by placing 50 µg of each insecticide on the cartridge and then pumping air through the cartridge for 5 hr at the rate of 0.6 L/min. The insecticides were eluted with methanol and analyzed by gas chromatography. Sampling efficiencies for OP insecticides were determined by means of closed chamber (110L) in which diluted EC solution was sprayed at the rate of 10 mL/min (Figure 1). The ODS cartridge was connected to a dual impinger (containing 30% aqueous acetone solution and with a collection efficiency as follows: fenitrothion 96%, dichlorvos 100%) and the air in the chamber was trapped for 10 min. The insecticides in the cartridge were eluted with methanol. The eluate from the cartridge and the aqueous acetone in the impinger were analyzed by gas chromatography.

RESULTS AND DISCUSSION

After collecting the OP insecticides in the cartridge, methanol was used as the eluent, because it is generally used to remove organic compound from the ODS cartridge. Fenitrothion was eluted up to 1 mL, and dichlorvos up to 2 mL with methanol. Therefore, 3 mL of the eluate from the ODS cartridge was fractionated and each eluate was injected directly into the gas chromatograph to avoid loss of dichlorvos, which is a volatile compound.

Collection efficiency of the ODS cartridge was studied by collecting airborne fenitrothion and dichlorvos in the ODS cartridge connected to a double impinger. Collection efficiency of the ODS cartridge was quantitative: dichlorvos (100%) and fenitrothion (99.9%). When the sampling time changed from 1 to 7 min, the relationship of collected amounts of insecticides vs. sampling time was linear. ODS cartridges containing 50 µg fenitrothion and 50 µg dichlorvos were pumped continuously (0.6L/min) for 5 hr to determine the loss of collected insecticides. About 95% of adsorbed insecticides remained after pumping for 5 hr, and the flow rate was not changed for 5 hr.

ODS cartridges quantitatively adsorbed airborne OP insecticides. Adsorbed insecticides were eluted with a small amount of methanol and determined directly by gas chromatography without concentration. ODS cartridges could be used repeatedly after washing with acetone. Therefore, an ODS cartridge is suitable for routine analysis of

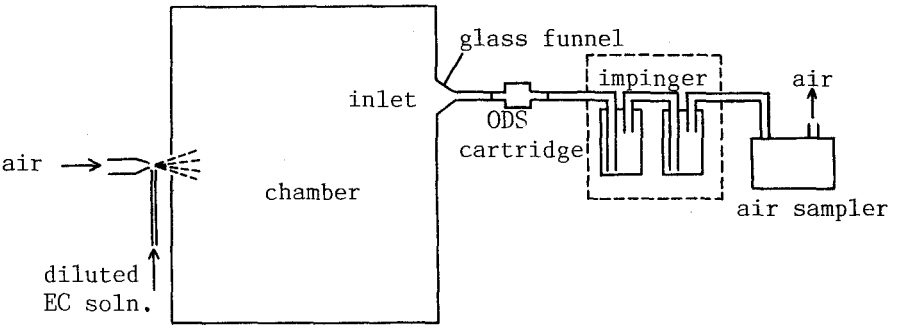

Figure 1. Apparatus for the determination of collection efficiencies of ODS cartridges

airborne OP insecticides.

Using an ODS cartridge the collection efficiency of commercial disposable masks (gauze mask containing charcoal; Kurare Co. Ltd., Osaka, Japan and micron filter pad; Koken Co. Ltd., Tokyo, Japan) for airborne OP insecticides was checked by the following method (Figure 1). A disposable mask was fitted to a glass funnel at the inlet and the air was pumped for 10 min while a diluted EC solution was sprayed into the chamber. Fresh air was then pumped for another 10 min. Adsorbed insecticides in each part of the mask were extracted with methanol or acetone. Table 1 shows the amount of insecticides adsorbed in each part of the mask. Seventy-one percent of the dichlorvos was adsorbed in the charcoal part of the mask, and 73% of the fenitrothion was adsorbed in the surface cotton of the mask and 10% of it was adsorbed in the ODS cartridge. Sixty-five percent of the dichlorvos was adsorbed in the filter pad and 35% of it passed through the filter pad. Fenitrothion was fully adsorbed in the filter pad. This difference of adsorption may be due to the fact that dichlorvos is highly volatile and exists in the vapor phase whereas fenitrothion was present mostly as an aerosol. Masks to protect workers from these insecticides must have both charcoal and filter pad.

The concentration of airborne fenitrothion and dichlorvos was estimated by the above method for two pest control operators who sprayed EC solutions of these insecticides in a restaurant kitchen for 27 min. Dichlorvos and fenitrothion in the air were 156 $\mu g/m^3$ and 19 $\mu g/m^3$, respectively. Airborne concentration of dichlorvos was higher than that of fenitrothion as compared with the ratio in the EC component used because dichlorvos was much more volatile than fenitrothion. These values, however, were below 1 mg/m^3 of dichlorvos (TLV, ACGIH) and 1 mg/m^3 of fenitrothion (MAC, Jpn. Assoc. Ind. Health). Urinary metabolites of OP insecticides, dimethyl phosphate (DMP) and dimethyl thiophosphate (DMTP), were analyzed according to the procedure of Daughton et al. (1979). The concentration of DMP and DMTP in the urine after work was as follows: for the sprayer, DMP 0.42 and DMTP 0.02 ppm; for the assistant worker, DMP 0.16 and DMTP 0.02 ppm. Although the concentration for the sprayer was higher

Table 1. Collection efficiency of commercial disposable masks and filter pads for airborne fenitrothion and dichlorvos

		Collection efficiency (%) fenitrothion	dichlorvos
Disposable gauze mask containing charcoal	surface (gauze)	73	28
	charcoal	8.5	71
	inside (gauze)	9.5	0.5
	ODS cartridge	9	0.5
Micron filter pad	filter pad	99.5	65
	ODS cartridge	0.5	35

than that for the assistant worker, even the later was revealed to have been exposed to these insecticides.

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