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Evaluation of XE-340 as a Trapping Medium for Airborne Organochlorine Pesticides

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Pesticides enter the air from a variety of sources, i.e., from direct contamination by spraying operations, from the gradual volatilization from soil, water, and plant surfaces, from manufacturing and formulation plants and from pesticide containers (Freed et al. 1972; Winnett and Siewierski 1975). Thus the need to evaluate the health effects of trace levels of these airborne pesticides has prompted the development of several sampling techniques.

The majority of the existing methods for sampling pesticide vapors in the air employ a system to concentrate the pesticides on one or more solid adsorbent polymers (Thomas and Seiber 1974; Frankel and Black 1978; Woodrow and Seiber 1978; Pellizzari et al. 1975; Fitch and Smith 1979; Seiber et al. 1980). The commercial types of these porous polymer sorbents include: the Parapak series (Waters Associates), the Amberlite XAD series (Rohn and Haas Chemical Co.), the Tenax-AC (Applied Science Laboratories Inc.), and the Chromosorb-Century series (Johns-Mansville Corp.). Relatively new to the commercial solid sorbent product lines are the Carbonaceous Ambersorb XE series (Rohn and Haas Chemical Co.). These resins (particularly XE-340 and XE-348) were introduced as possible alternatives to activated carbon and the polymeric adsorbents--their chemical nature having been described as an intermediate between the two (Hunt and Pangaro 1982).

The most commonly used solid sorbent in air monitoring programs today are the polymeric Amberlite XAD resins. This may be partly due to their availability in an inexpensive bead form, as compared to the more expensive chromatographic forms of the other porous polymers (Farwell et al. 1977). However, the necessary cleanup procedure prior to the actual use of the XAD resin is quite lengthy and time-consuming. There is also the disadvantage that the existing pre-sampling cleanup procedure, at best, only minimizes extractable materials in the XAD resin. Detectable quantities of various organic constituents are thus left which interfere in the identification and quantitation of environmental extracts by producing undesirable gas chromatography electron capture background.

The carbonaceous Ambersorb resins (particularly XE-340 and XE-348) have recently been shown to be substantially cleaner than the XAD resins, exhibiting little contamination in the boiling point range 100-300°C (Hunt and Pangaro 1982). This evidence influenced our decision to evaluate XE-340. Thus, in this paper we report the sampling efficiencies of selected organochlorine pesticides using XE-340 as the trapping medium.

MATERIALS AND METHODS

Unless otherwise stated, reagents and solvents were analytical reagent grade (Mallinckrodt, St. Louis, MO) and used as received. The selected organochlorine pesticides lindane (Chevron Chemical Co., Richmond, CA), dieldrin, aldrin (Shell Chemical Co., Houston, TX), heptachlor (Velsicol Chemical Co., Chicago, IL), O,P'-DDT, heptachlor epoxide (Chem Services, West Chester, PA), and α and γ-chlordane were prepared as 1 mg/mL stock solutions. Standard solutions for gas chromatography were prepared by diluting the stock solutions with hexane or ethyl acetate.

XE-340 resin was cleaned prior to use by the following procedure. The dry adsorbent (500 mL) was soaked in 1 L methanol for 10 min. The supernate was decanted, and the washing with methanol was repeated. The resin was then soxhlet extracted with 6% ethyl ether in hexane for 24 hr (48 cycles). The XE-340 resin dried at room temperature within 1 hr and was then stored in brown jars sealed with aluminum foil-lined caps.

XAD-4 resin was cleaned as follows. One L of the resin in a 2-L Erlenmeyer flask was wetted with 1 L distilled water. The supernate was decanted, and 1 L of 0.5 M HCl was added to the flask. The contents were swirled and stirred for 1 hr. The solution was decanted after the resin settled. The washing procedure was repeated with 1 L aliquots of distilled water till the pH of the supernate was that of the distilled water. The resin was then washed with methanol. This was followed by successive soxhlet extraction with methanol, ethyl acetate and ethyl ether, each for 24 hr (24 cycles). The resin was then dried under house vacuum in a flask that was in a water bath at 40°C and stored in aluminum foil-lined caps.

A Staplex model TFIA (The Staplex Co., New York) high volume air sampler was used in fortification experiments to test the trapping and retention efficiencies of XE-340 for the selected pesticide standards. A stainless steel screen covered the resin bed in each case while the air sampler ran. The air samples were collected at a rate of 60 m^3 of air/hr (Wehner 1982).

The air was fortified using a method developed by Ferreira (1979). A Pyrex glass tube (16 cm × 2 cm, o.d.) wrapped in a heating tape and connected to a variable autotransformer was used as the spiking vessel. The high volume air sampler was set up containing 100 mL each of XAD-4 or XE-340 resins, with the fortification tube mounted on a ring stand 5 cm in front of the sampling module at an

angle of 45°. The temperature inside the tube was monitored by mounting a thermometer on the ring stand.

The sampler containing the resin was turned on, and the air was fortified by slowly injecting 20 µL of a mixed standard solution of selected pesticides into the glass tube using a syringe. The air was sampled for 2 hr. A 2-hr control sample (no fortification of the air) was also taken. All the efficiency studies were done outdoors at ambient temperatures of 20-26°C. Once the air samples were taken, the resins were extracted as described below. The glass tube was rinsed with hexane (≈50 mL) after each run, into a 250 mL round-bottom flask and concentrated to a known volume for quantitation. The overall percentage recovery was defined by the equation

$$\% \text{ Recovery} = A/(B-C) \times 100$$

where A = amount in resin after sampling, B = amount added to the tube at the intake, and C = amount in the tube rinsings after volatilization.

Once the air samples were taken, the resin (XAD-4 or XE-340) was transferred to a 500 mL Erlenmeyer flask to which was added 150 mL n-hexane. The flask was stoppered with a foil-covered rubber stopper or a ground glass stopper and its contents swirled for 1 hr on a gyratory table shaker. After the resin had settled, the hexane was decanted through Whatman No. 1 filter paper into a 1 L round-bottom flask. The extraction with hexane was repeated with two 100 mL volumes, each time swirling the contents for 1 hr. After the last extraction, the resin with solvent was poured as a slurry into the filter papers. The flask, resin and filters were rinsed with several aliquots totalling 150 mL additional hexane for each sample. The filtered extracts were concentrated to ≈5 mL using a rotary evaporator at 40°C. The concentrated extract was transferred to 12 mL screw top (Teflon-lined) centrifuge tubes by means of disposable pipets. An additional 5-10 mL hexane was used to rinse the flask and complete the transfer to the tube. The extract was concentrated to 10 mL under a stream of nitrogen. A 1.0 mL aliquot of the extract was diluted to 10 mL for GC analysis.

A Varian 1200 gas chromatograph equipped with a tritium foil electron capture detector was used in these studies. A 1.8 m × 2 mm (i.d.) glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcon AW-DCMS was employed in the GC/ECD analyses. The operating conditions were: carrier gas (N_2) flow rate, 30 mL/min; injector temperature, 240°C; column temperature, 180°C; and detector temperature, 290°C. A detection limit for each of the test compounds was estimated from chromatograms of air blanks (unspiked air background collection) to be 200 pg/m^3, excluding O,P'-DDT (2 ng/m^3).

RESULTS AND DISCUSSION

Essentially, the preparation of the XE-340 resin prior to actual use in these studies involved a 24-hr soxhlet extraction with hexane while XAD-4 resin required several washings with acid and water followed by 3 to 4 days soxhlet extraction with several solvents. In spite of the shorter pre-sampling cleanup, extracts of XE-340 yielded comparatively negligible electron capture background (Fig 1A) when analyzed by GC/ECD. On the other hand, the XAD-4 resin still contained substantial interfering substances (Fig 1B). However, samples extracted from XAD-4 resin have recently been successfully analyzed on GC/ECD without the characteristic electron capture interfering background (Wehner 1982). Unfortunately, this procedure required an extra post-sampling workup involving fractionation through high pressure liquid chromatography (HPLC), thus prolonging further an already time-consuming procedure. This could pose a problem in any extensive field monitoring program involving large numbers of samples.

Recoveries of various chlorinated hydrocarbon insecticides from XE-340 resin are presented in Table 1. These results, ranging from 85-100%, compare favorably with those reported at similar fortification levels using XAD-4 (Seiber et al. 1980; Wehner 1982) and polyurethane foam (Lewis and MaLeod 1972) as the trapping media.

Recoveries of the various chlorinated hydrocarbon insecticides collected and extracted from XE-340 resin in a high volume air sampler are presented in Table 2. These results, with the exception of lindane, are within acceptable levels (70-98%). The low retention efficiency of XE 340 for lindane (45%) may not be due to losses via irreversible adsorption on the XE-340 resin, since resin fortified directly with a mixed standard solution of the pesticides gave recoveries of >90% (Table 1). Further, it could not be due to vaporization losses, since lindane has a lower vapor

Table 1. Hexane Desorption of Test Pesticides from XE-340.[a]

Compound	% Recovery[b]
α-Chlordane	100 ± 3
γ-Chlordane	100 ± 5
Lindane	95 ± 10
Heptachlor	101 ± 4
Heptachlor epoxide	96 ± 5
Aldrin	85 ± 3
Dieldrin	98 ± 4

(a) Fortified resin (7 µg) extracted without air sample collection. (b) Mean of triplicate ± S.D.

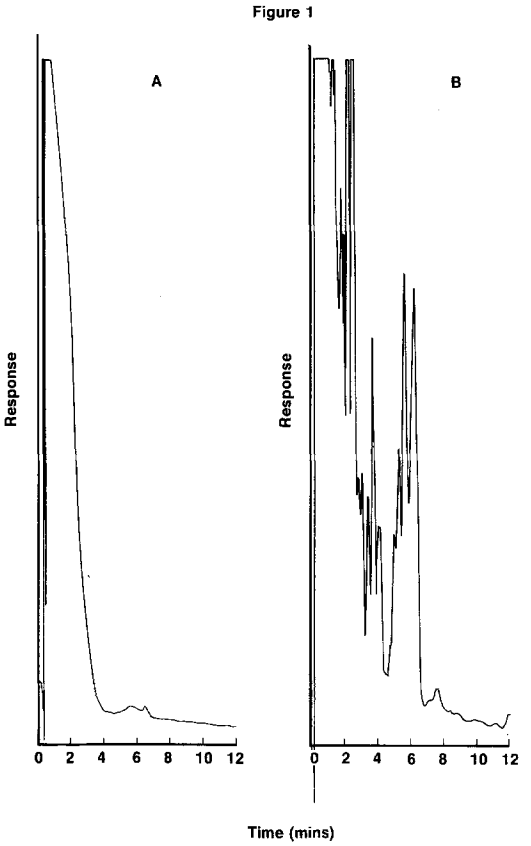

Figure 1. Gas chromatograms of air blank samples of (A) XE-340 and (B) XAD-4 resins. Five µL injections of each extract (1:10 dilution) were made on a glass column packed with 1.5% SP-2250/1.95% SP-2401 on 100/120 mesh Supelcon AW-DCMS (180°C) with ^{3}H foil electron capture detector.

Table 2. Recoveries from XE-340.[a]

Compound	Fortification Level (μg)[b]	% Recovery[c]	Vapor Pressure at 25°C (mm Hg)[d]
α-Chlordane	20 (6)	85 (8)	1×10^{-5}
γ-Chlordane	20 (6)	98 (4)	N/A[e]
Lindane	20 (3)	45 (3.5)	9.4×10^{-6}
Heptachlor	20 (3)	75 (5.4)	3.0×10^{-4}[f]
Heptachlor epoxide	20 (3)	70 (2.5)	N/A[e]
Aldrin	20 (3)	80 (3.6)	1.9×10^{-7}[f]
Dieldrin	20 (3)	77 (9.6)	5.4×10^{-6}

(a) Applied to air intake of high volume air sampler. (b) Number of trials in parentheses. (c) Mean with S.D. in parentheses. (d) Reference source (The Pesticide Manual 1977). (e) Data not available. (f) Vapor pressure at 20°C.

pressure than some of the other pesticides that were analyzed. A possible explanation might be the inability of lindane to partition from the air phase to the hydrophobic phase of the resin.

Possible losses due to storage of collecting bottles containing trapped pesticides on XE-340 were also investigated. However, no detectable losses of the pesticides were observed when the resin was refrigerated in brown bottles (stoppered with aluminum, foil-lined caps) for periods up to 7 days prior to extraction and analysis.

From this study, it is apparent that XE-340 resin can be used successfully as a trapping medium for most chlorinated hydrocarbon insecticides in air.

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