Chromosorb 102, an Efficient Medium for Trapping Pesticides from Air

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Pesticides may enter and contaminate the air directly during spraying operations or gradually by volatilization or "mechanical removal" from soil, water, and plant surfaces (SPENCER 1970, FREED et al. 1972). Their presence in the air constitutes a possible exposure route for humans and wildlife, and may explain the worldwide distribution of the more stable chemicals.

Most of the existing methods for sampling pesticide vapors in air rely on a solvent-charged bubbler or impinger for collection (see, for example, MILES et al. 1970, STANLEY et al. 1970). The use of a solid sampling bed appears as an attractive alternative by allowing for increased flow rates and simpler collector design. Work along these lines has been reported for liquid-coated solids (RISEBROUGH et al. 1968, TESSARI and SPENCER 1971, SODERGREN 1972, COMPTON and BJORKLAND 1972), a support-bonded phase (AUE and TELI 1971), and inorganic adsorbents (for example, YULE et al. 1971). The former suffer the disadvantage of coextraction of the liquid phase with the chemicals of interest which may lead to problems of separation in the analytical scheme. This potential disadvantage is overcome through the use of support-bonded phases; however, these materials are not commercially available in sufficiently large particle sizes for high volume air sampling applications. While inorganic adsorbents possess high affinity towards most pesticides, their relatively high surface activity and hydrophilic nature may lead to hydrolytic and/or oxidative decomposition of the less stable chemicals (SEIBER et al. 1973).

DRAVNIEKS et al. (1971) and others (GELBIKOVA-RUZICKOVA et al. 1972, FRANKEL et al. 1972) have successfully used organic polymeric adsorbents for organic vapor collection. We report here that one such material, Chromosorb 102, has many characteristics

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which make it ideal for sampling pesticides from air. These include high sampling efficiency for pesticides of a wide range of volatilities and polarities, a hydrophobic nature to minimize the possibility of degradation of sampled chemicals, and ease of release of sampled compounds through solvent extraction for gas-liquid chromatographic (GLC) analysis.

MATERIALS AND METHODS

Chemicals

Chromosorb 102 (60/80 mesh), a crosslinked polystyrene resin having a surface area of 300-400 m^2/g, was obtained from the Johns Manville Corporation. It was purified before use by Soxhlet extraction with 1:1 hexane-acetone for 4 hrs followed by vacuum drying at 50°C. Drying or conditioning the adsorbent at higher temperatures led to unacceptable electron capture background, probably due to formation of aromatic carbonyl compounds (NEUMAN and MORALES 1972). Nanograde or equivalent solvents were used throughout. Pesticides were manufacturer's analytical standards except for the technical formulations used in the field studies.

GLC Analysis

Three GLC systems were employed: 1) MicroTek Model GC 2000R equipped with a tritium electron capture detector and 180 cm by 6.4 mm o.d. glass column containing 3% OV 1 on 80/100 Chrom W HP, operated at 190°C and nitrogen flow of 80 ml/min; 2) Varian Model 2100 equipped with a rubidium sulfate alkali flame ionization detector and 90 cm x 3.2 mm o.d. glass column containing 3% SE 30 on 80/100 Gas Chrom Q, operated at 170°C and nitrogen, air, and hydrogen flows of 35, 235, and 47 ml/min respectively; and 3) Varian Model 1200 equipped with a tritium electron capture detector and 90 cm x 3.2 mm o.d. glass column containing 11% QF-1/OV-17 mixed phase on 80/100 Gas Chrom Q, operated at 205°C and nitrogen flow of 40 ml/min.

Determination of Collection Efficiency

A glass testing apparatus equipped with 12/5 spherical joints, 0.6 cm o.d. connection tubing, 1 cm o.d. U tube, and 1.9 cm o.d. x 12.7 cm collection tubes was used (Fig. 1a). The air prefilter (2.5 cm x 3.7 cm) contained 1.5 g of 10/20 activated charcoal and each collection tube 4 g of Chromosorb 102 held in place with glass wool plugs. Pesticide standards were pipetted to the center of the U tube as dilute solutions in either hexane or acetone; the vacuum pump (Gelman Model 13152) was then turned on and the preheated (60-70°C) oil bath raised to cover the lower half of the U tube. Sampling was carried out at 8-10 lpm.

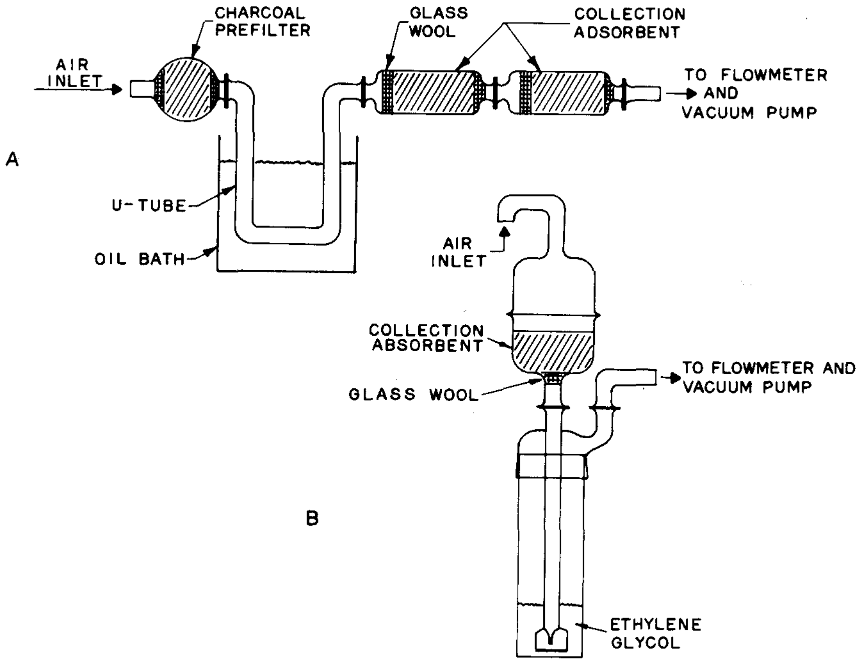

Figure 1. Apparatus for (a) determination of collection efficiency and (b) field studies.

At the end of each run the U tube was rinsed with 1:1 hexane-acetone and concentrated to an appropriate volume for GLC analysis. The adsorbent and glass wool plugs from each collection tube were placed in an alundum Soxhlet thimble and extracted with 1:1 hexane-acetone for 1 hr (50 exchanges). The extract was then concentrated to an appropriate volume for GLC analysis.

Field Studies

Studies already in progress in which animals were exposed at various distances to pesticide sprays afforded an opportunity to test the adsorbent under field conditions. In these experiments a single collection tube containing the adsorbent was connected to a backup Greenburg-Smith impinger (Ace Glass 7536-25) charged with 200 ml of ethylene glycol. The collection tube was of the same dimensions as those used in the collection efficiency experiments described above or consisted of an Ace Glass 7520 filter assembly containing the adsorbent (5 g) in the lower section (5 cm diameter) of the holder (Fig. 1b). Collectors were placed at varying distances downwind from the pesticide generator. For comparison of efficiency, 2 Greenburg-Smith impingers connected in series were placed alongside the adsorbent collectors at some of the stations. The pesticides were sprayed continuously over the period of sampling with a Micro-Gen ULV aerosol generator using the following formulations and rates: malathion, 95% technical grade sprayed at 3 oz/min; Baytex, 20% technical grade in cottonseed oil sprayed at 18 oz/min; and Dursban, 20% technical grade in cottonseed oil sprayed at 18 oz/min. Sampling was carried out at ca. 12-13 lpm for 5 mins.

Adsorbent samples were extracted as described in the preceding section. Ethylene glycol from the impingers was diluted with 100 ml of saturated sodium chloride solution and extracted with 3 50-ml portions of benzene. The combined benzene extracts were washed with 3 50-ml portions of water, dried over sodium sulfate, and concentrated to an appropriate volume for GLC analysis.

RESULTS AND DISCUSSION

Collection efficiencies for a variety of pesticides were determined at vapor concentrations corresponding approximately to 5 ng/m^3 to 25 μg/m^3. The former is in the pesticide concentration range often encountered in ambient air (YOBS et al. 1972). The first 4 g of adsorbent, in the upstream collection tube, trapped essentially all the pesticide vapor in each case (Table I). Thus little or no losses due to incomplete trapping, revolatilization, or incomplete extraction occurred. Absence of significant chemical degradation -- a key point in adsorbent trapping -- was inferred from close examination for minor peaks in the gas chromatograms; oxon and sulfoxide-sulfone peaks, for example, were not observed for any of the organophosphates studied. Since Kelthane was determined as its GLC decomposition product, p,p'-dichlorobenzophenone, any breakdown of Kelthane in the sampling process would not have been detected. Essentially the same high collection efficiencies were observed on 5 g of Chromosorb 102 held in a 5 cm diameter filter cup (Fig. 1b) through which the air was sampled at 20 lpm.

To further examine the retention of pesticides by the polymeric adsorbent, one gram segments were analyzed individually from a collection tube containing 4 grams of adsorbent (Table II). Only when an attempt was made to overload the adsorbent with a high level of Baytex was any appreciable penetration observed to the third 1 gram segment. In most cases the pesticides were quantitatively retained in the first segment at the flow rates employed.

TABLE 1

Collection Efficiencies for Pesticide Vapors on Chromosorb 102.

	Added to U Tube	Air Vol.	Left in U Tube	Collected (µg)		Recovery
				Tube 1	Tube 2	
Trifluralin	100 µg	1 m^3	0 µg	104	0	104 %
	10	1	0	10.4	0	104
	0.100	12	0	0.100	0	100
Lindane	8.0	4	0	7.6	0	97
	0.140	12	0	0.136	0	97
Kelthane	100	1	51	50	0	101
	10	1	1.2	8.8	0	100
	0.115	12	0	0.105	0	92
Dieldrin	100	1	7.0	93	0	100
	10	1	0	9.5	0	95
	0.091	12	0	0.091	0	100
o,p - DDT	100	1	17	79	0	96
	10	1	0	9.3	0	93
	0.180	12	0	0.177	0	98
Methoxychlor	100	1	84	17	0	101
	10	1	3.3	6.6	0	99
	0.294	12	0	0.268	0	92
Parathion	100	1	8	92	0	100
	10	1	0.7	8.6	0	93
	0.100	9	0.01	0.085	0	96
Diazinon	16.6	9	0.9	13.8	0	88
Malathion	31.5	9	3.5	28.5	0	102
Dursban	10	9	0	9.1	0	91

TABLE II

Penetration of Pesticide Vapors on 4 g of Chromosorb 102.

	Added to U Tube	Air Vol.	Left in U Tube	Collected in g Segments (µg)				Re-covery
				1st	2nd	3rd	4th	
Trifluralin	10.0µg	$4m^3$	0µg	9.6	0	0	0	96 %
Lindane	8.0	4	0	7.6	0	0	0	97
Kelthane	10.4	4	5.2	5.4	0	0	0	98
Dieldrin	10.0	4	0.2	9.5	0	0	0	97
o,p - DDT	10.1	4	0.6	9.6	0	0	0	99
Methoxychlor	9.8	4	4.1	4.9	0	0	0	92
Parathion	9.7	9	0	8.4	0	0	0	86
Baytex	34.8	9	0	32.5	1.6	0.3	0	98
	207.0	8	107	66.0	7.2	8.3	0	92
Dursban	10.0	9	0	9.1	0	0	0	91
Diazinon	16.6	9	0.9	13.5	0.2	0	0	88
Malathion	31.5	9	3.5	27.9	0.7	0	0	102

Prepurification of the adsorbent by solvent extraction served to lower the electron-capture and alkali flame ionization background such that quantities of most pesticides corresponding to 1-10 ng/m^3 would be easily observable above the reagent background (Fig. 2). Detectability limits for actual air samples will depend on the levels of organic interferences present and will vary from sample to sample. A chromatographic cleanup and fractionation step such as that described by SHERMA and SHAFIK (1972) should aid in lowering detectability limits to allow pesticide levels below 1 ng/m^3 to be determined in most cases.

Downwind trapping of three organophosphates introduced to the air by an aerosol generator was carried out to compare the Chromosorb 102 traps with ethylene glycol impingers (Table III). Baytex and Dursban were introduced as dilute formulations in cottonseed oil and Malathion directly as the technical (95%) material. Although only single runs were made in each case,

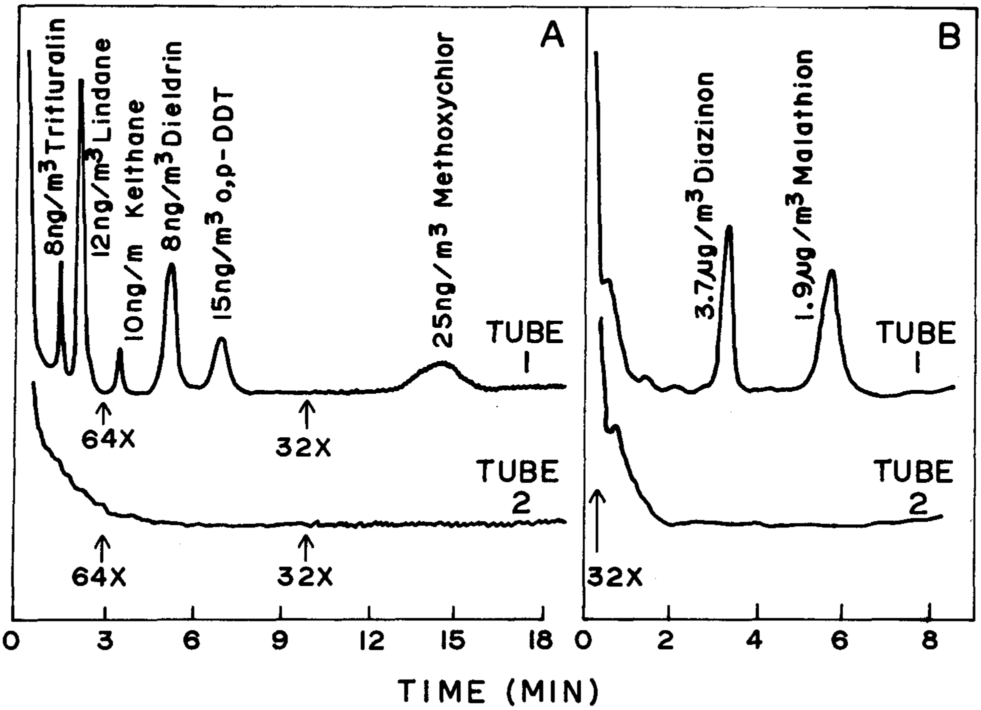

Figure 2. (a) Electron capture and (b) alkali flame ionization chromatograms of pesticides collected on 4 g of Chromosorb 102 (Tube 1). The reagent background was nearly identical with that of the backup trap (Tube 2). GLC conditions 1 and 2 were used for (a) and (b), respectively.

greater quantities of pesticides were trapped by the adsorbent than by the first comparison impinger at the three stations where the two types of collection devices were placed side by side. Relatively small quantities of pesticides escaped through the adsorbent and first impinger to the backup impingers at all the sampling sites. Thus while pesticides existed most likely as both vapors and aerosols and were present in relatively high

TABLE III

Collection of Baytex, Dursban, and Malathion During Field Spraying.

Distance from Spray Source	Collector	Amount Collected (μg) Baytex	Dursban	Malathion
15 ft	Chrom 102	--	45	--
	Backup Impinger	--	0.9	--
50	Chrom 102	--	77.4	--
	Backup Impinger	--	2.8	--
	1st Comparison Impinger	--	50.0	--
	Backup Comparison Impinger	--	2.0	--
100	Chrom 102	31.5	71	12.3
	Backup Impinger	0.3	0.3	<0.1
	1st Comparison Impinger	22.0	--	5.5
	Backup Comparison Impinger	0.3	--	0.3
150	Chrom 102	16.5	--	8.6
	Backup Impinger	<0.1	--	0.5
200	Chrom 102	12.5	--	--
	Backup Impinger	<0.1	--	--

concentrations in these experiments, the trapping results compare favorably with those in which vapors alone were introduced at lower rates to the adsorbent (Tables I and II).

Some flow rate limitations were noted with the 60/80 mesh adsorbent used in this study. For example, the maximum flow rate attainable through 5 g of adsorbent in the 1.9 cm diameter sampling tube was 11.2 lpm. This problem could be alleviated by use of the 5 cm diameter filter cup assembly; the maximum flow rate through 5 g of adsorbent in this assembly was 35 lpm, slightly higher than the rate (28.5 lpm) recommended for impingers used for pesticide analysis in ambient air (ENOS _et_ _al_. 1972). Extension of the concept of sampling through a solid bed to much higher air flows, such as those attainable by commercial high volume samplers, will require use of a larger adsorbent particle size or a sampler configuration in which the adsorbent is spread over a larger area than employed here.

The present study shows Chromosorb 102 to be an efficient trapping agent for both short and long term pesticide sampling applications. Experiments are presently in progress in which the sampling efficiencies of this adsorbent and two other solids, silica gel and paraffin oil on Chromosorb A (SEIBER et al. 1973), will be compared at higher flow rates.

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