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Charcoal Air Sampling Tube Storage Stability and Desorption Efficiencies of 1,2-dibromo-3-chloropropane (DBCP) and 1,3-dichloropropene (DCP)

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Many haloalkanes, haloalkenes, and organohalides in general are used in industry as feedstocks or products. Because of their widespread occurrence in occupational environments, and because these compounds exhibit sufficient untoward toxicity to warrant worker monitoring, accurate sampling and analytical protocols are essential. DBCP in limited amounts, and DCP predominantly, are used as subsoil fumigants.

DBCP will no longer be used in this country once existing stocks on Maui are depleted. Other countries including Israel, Mexico, and the Federal Republic of Germany continue to manufacture DBCP (Babich et al. 1981).

Telone II is a Dow Chemical Company registered tradename for a (Z) or cis- and (E) or trans- mixture of 1,3-dichloropropene. Standard formulations contain 92% active agent with 3-5% 1,2-dichloropropane (Martin and Worthington 1974).

Recent events viz. the detection of DBCP, ethylene dibromide (EDB), and other haloalkane residues in potable water of some western states could eventually preclude all uses of persistent fumigants. Safer, more biodegradable materials already in use such as DCP may completely replace the aforementioned fumigants. This increased usage will of course involve a greater proportion of workers who will require personal monitoring. At present, there is no promulgated standard for DCP exposure.

In this context, and in the course of a health hazard evaluation of actual DBCP and DCP exposures, both fumigants were evaluated for their desorption efficiencies at several mass loadings onto charcoal sorbent tubes (CT). Also, their stability on the collection matrix over time under various storage conditions was determined. Three laboratories participated in the study. It is hoped that this preliminary data will be a step toward an accepted industrial hygiene sampling method.

MATERIALS AND METHODS.

All charcoal tubes used were two-section (100/50 mg) coconut charcoal Lot 107, purchased from SKC, Inc. (Eighty-Four, PA). Additionally, all tubes were spiked with known masses of pure reference materials obtained from the U.S. Environmental Protection Agency Pesticides and Industrial Chemicals Repository (Research Triangle Park, NC). After fortification, approximately 1 liter (1) of air was drawn through the tube prior to capping and storage. Three desorption solvents were used: benzene, 1% v/v methanol-benzene, and 1% v/v methanol-toluene. All tubes were desorbed for 30 minutes prior to analysis. Blanks of the same lot tubes were run during every analytical series. All working standards were chosen to fall within a maximum of one order of magnitude of the samples being analyzed.

Gas chromatographic conditions for analysis with the particular desorption system were as follows: Maui Pineapple Company; benzene; Hewlett-Packard 5840 with 63Ni electron-capture detector; column was 1.8 m X 4mm i.d. glass with Supelco GP 4% SE-30 and 6% SP-2401 on 100/120 mesh Supelcoport and operated at 120°C. INALAB; 1% methanol-benzene; Hewlett-Packard 5830-A interfaced with a Tracor Model 700-A electrolytic conductivity detector operated in the halogen-specific mode; column was 1.5 m X 6 mm o.d. X 2 mm i.d. glass packed with 3% SP-2100 on 100/120 Supelcoport (AWS) operated by temperature program from 60 to 110°C for both compounds. NIOSH; 1% methanol-toluene; Hewlett-Packard 5830 with flame ionization detector in the splitless mode; column was DB-1 fused silica capillary operated at 80°C.

RESULTS AND DISCUSSION.

Desorption efficiency for DBCP from charcoal tubes was determined at four mass loadings as seen in Table 1. Spiking levels of 1, 10, and 20 micrograms (ug) per tube showed no particular differences in desorption efficiency after being stored in a freezer at -14°C (6.8°F) for 3 and 11 days. A spike of 5.4 ug/tube, followed by immediate desorption gave comparable desorption efficiency. The mean range of desorption efficiencies was 87.7 - 93.9% with a mean value of 91.2 ± 2.6%. The optimum loading level of the four levels examined was observed to be 10 ug DBCP per tube. DBCP showed only minor loss of material from

Table 1. Desorption Efficiency for DBCP From Charcoal Tubes

Mass applied	Mean % recovery after		
	1 day @ 23.8°C	3 days @ -14°C	11 days @ -14°C
1 ug[a] (n=6)	ND[c]	92.6±4.8	88.1±3.0
5.4 ug[b] (n=5)	87.7±2.5	ND	ND
10 ug[a] (n=6)	ND	93.9±1.4	92.0±0.9
20 ug[a] (n=6)	ND	93.9±3.2	90.2±3.4

a) after spiking, approximately 1 liter of air drawn through tubes; desorbed with 1 ml 1% v/v methanol-toluene for 30 min prior to analysis.
b) after spiking, approximately 1 liter of air drawn through tubes; desorbed with 1 ml 1% v/v methanol-benzene for 30 min prior to analysis.
c) not done.

the tube under these storage conditions over an 8 day period from day 3 to 11.

Similarly, DCP was applied to charcoal tubes at three levels and allowed to remain at room temperature for 1 hour prior to desorption, as shown in Table 2. The mean recovery was 85.3% over a mean range of 76.3 - 93.8%. The optimum loading level of the three masses applied was 5.8 ug DCP per tube. Table 3 summarizes the various analytical methods employed and the maximum desorption efficiency for each compound.

In Figure 1, the percent recovery (corrected for desorption efficiency) of DBCP and DCP from CT while stored at room temperature (23.8°C/75°F) is plotted against time. Recovery over time is indicative of the stability of the compound on the collection matrix. A least squares regression line of the data for DBCP recovery (n=14) gave a slope of -6.7 (r=.973), or in other words, a 6.7% loss per day when fortified at 10.5 ug of DBCP, stored at room temperature, and desorbed with 1% methanol-benzene. DCP recovery was stable over a 12 day period with a mean recovery of 88% (n=10) desorbing with 1% methanol-benzene.

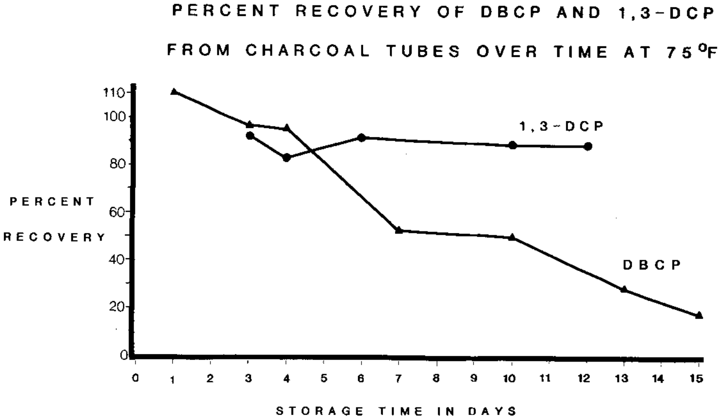

Figure 1. Percent recovery of DBCP and 1,3-DCP from charcoal tubes over time 75°F.

Adding a small amount of a polar solvent to a non-polar one will greatly change its desorption characteristics. For example, a mixture of 2% methanol in hexane is equivalent in solvating strength to acetonitrile. Using only benzene as a desorbing solvent gave a markedly lower recovery of DBCP. A typical 10.5 ug spike that was left on the bench for 1 hour and then desorbed, showed that the solubility of DBCP was substantially less with benzene alone than with the addition of 1% methanol to either benzene or toluene. An average recovery of 64.3% was maximum recovery for such a spike.

Table 2. Desorption Efficiency for DCP From Charcoal Tubes

Mass applied[a)]	mean percent recovery
0.49 ug	85.7±4.5
5.8 ug	93.8±3.4
54.0 ug	76.3±1.3

a) n=5 at each level; after spiking, approximately 1 liter of air drawn through tubes; desorbed with 1% v/v methanol-benzene for 30 min prior to analysis.

A comparison of percent recovery of DBCP over time at room temperature and under refrigeration (5.6°C/42°F) using 10.5 ug spikes and benzene as the desorbing solvent is illustrated in Figure 2. The data is

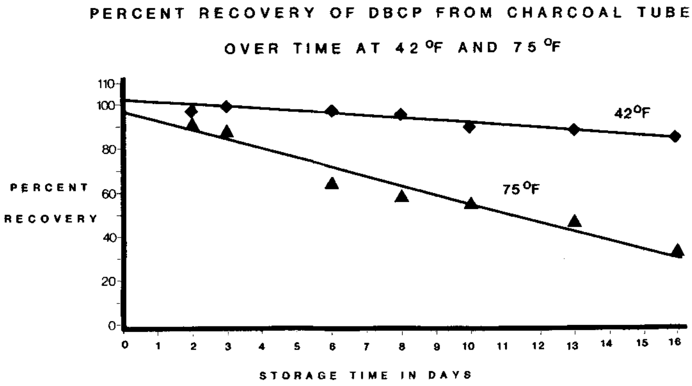

Figure 2. Percent recovery of DBCP from charcoal tubes over time at 42°F and 75°F.

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comparable to the trend shown in Figure 1, with a slope of -2.5% (n=10, r=.980). The stability of DBCP on CT is markedly enhanced upon refrigeration as evidenced by the diamond-symboled line in Figure 2 which gave a slope of -0.7% (n=10, r=.904).

The solubility of DBCP in benzene is greatly improved by the addition of 1% v/v methanol. The same is probably true for toluene, although this was not investigated in this evaluation. However, it was shown that the solubility of DBCP in 1% methanol-toluene is comparable to 1% methanol-benzene.

Since electron-capture detectors are easily damaged by methanol in the injection solution, it is imperative that very non-polar solvents be used for desorption when electron-capture is the detection system. A recovery of less than the NIOSH recommended 75% is the primary drawback to this method.

Of the three storage temperatures examined, freezing at -14°C is the most satisfactory for long-term (> 1 week) storage of DBCP samples on charcoal tubes. Percent recovery after 11 days at -14°C was negligibly less than that after 3 days. If freezing was not immediately available, cooling to 0°C would be acceptable for up to a week. After 2 days at room temperature, DBCP becomes quite labile, and the recovery declines precipitously.

On the other hand, DCP recovery was constant for 12 days. The inherently less-stable C-Br bonds of DBCP (as compared to the bond strength of a carbon-fluorine or carbon-chlorine bond) may react with the surface of the charcoal with dehalogenation of a vicinal dihalide

Table 3. *Analysis Summary*.

Lab	MPCo.	INALAB	NIOSH
Desorbing solvent	benzene	1% methanol-benzene	1% methanol-benzene
GC detector	electron capture	electrolytic conductivity	flame ionization
Limit of detection	mass/injection	mass/tube	mass/sample
DBCP	5 pg	22 ng	1 ug
DCP	100 pg	23 ng	ND
Maximum desorption efficiency (%)			
DBCP	64.3	90.1	93.9
DCP	----	85.3	----

as a result. The rate of reaction is greatly slowed at temperatures of 6°C and below, while at -14°C there is almost no appreciable reactivity. DCP remained stabile on charcoal at room temperature for at least 12 days.

During a field evaluation which included analyses for DBCP and DCP exposures (Albrecht 1983), it was observed that no breakthrough to the back-up section of the CT occurred for DBCP or DCP at sample volumes in the 50 liter range at a sampling rate of 100 cc/min. Maximum masses of fumigants found in the samples taken were 380 ug DBCP and 240 ug DCP. Finally, 46 field samples for DCP showed a ratio of the *cis*- to *trans*-isomer to be 1.345±.240.

REFERENCES.

Babich H, Davis DL, Stotzky, G (1981) Dibromomchloropropane (DBCP): A review. Sci Total Environ 17:207-221

Martin H, Worthington CR (eds) (1974) Pesticide Manual, 4th edn British Crop Protection Council, London

Albrecht WN, Coye MJ (1983) Health Hazard Evaluation HETA 81-236. National Institute for Occupational Safety and Health, Cincinnati, Ohio

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