DESORPTION OF ORGANIC VAPORS
FROM STORED C2A1 GAS MASK CANISTERS

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ABSTRACT

Activated carbon beds in gas mask and large filter configurations are designed for adsorbing toxic chemicals from breathed air. After such filters have been used, they are often sealed in plastic until they can be properly disposed of. Concerns for the health of those who must handle these packages have led us to measure vapor concentrations reached in plastic bags. Two model compounds, hexane and heptane, of differing volatility were loaded at various levels onto C2A1 canisters using a breathing simulator. The canisters were sealed in polyethylene zipper-lock bags; vapor concentrations in the bags were measured over periods of hours to weeks. Maximum concentrations reached within the first day of storage dropped to a constant level within a week. The final levels were determined by the average vapor loading on the carbon bed. Sealing a canister inlet and outlet with tape before placing it in polyethylene greatly reduced the maximum vapor concentrations in the bags.

INTRODUCTION

When used gas mask canisters, commercial organic vapor cartridges, or other activated carbon bed filters are sealed (e.g., in plastic) and stored for removal and disposal, vapors may desorb into the storage package dead volume. Concerns for the health of those who must handle these packages have led us to measure vapor concentrations reached in plastic bags. Hexane and heptane were selected as nonreactive model compounds.

EXPERIMENTAL

The tests described in this report were done with U.S. military gas mask canisters described as: Canister, Chemical-Biological, Mask, (ASZM-TEDA), C2A1. They contained an average of 113.7 g (0.4 g Standard Deviation) of triethylenediamine- and metal salts-impregnated activated carbon.

Fresh, weighed canisters were mounted in a manifold, in which cyclic, simulated-breathing, air flows were generated by a breathing simulator pump upstream of the canister mount. Average airflow volumes over experimental times (1/2 - 2 h) were measured with a calibrated dry-gas meter downstream of the canister. For hexane, the average airflow rates ranged 28 - 32 L/min; for heptane, 42 - 56 L/min.

Vapors of hexane or heptane were generated by injecting liquid from a syringe pump into a warmed "T" in the tubing between the pump and the canister. Differences in syringe volumes before and after an experiment, combined with total airflow volumes gave average challenge concentrations, which ranged 187 - 1149 ppm for hexane and 868 - 1184 ppm for heptane. Canisters were also weighed after an experiment to determine the amount adsorbed.

Commercial, polyethylene plastic (0.044-mm thick), one-gallon, zipper-lock food storage bags (Dow Chemical Co.) were used to stored loaded canisters. They were kept at normal room temperatures at usually dry (< 50% relative humidity) conditions. After taking two or three samplings after selected times, some canisters were placed in fresh bags for longer-term measurements. Canisters were reweighed to determine losses upon storage. Some canisters were sealed, inlet and/or outlet, with double layers of duct tape (Shurtape, Hickory, NC) before they were stored in bags.

Concentrations of vapor in the storage bags were measured using a photoacoustic infrared spectrometer (Type 1302 Multi-Gas Monitor from Bruel & Kjaer). Both hydrocarbon and water vapors were measured at 1-min intervals for samples drawn from a bag that was punctured with a syringe needle. The bags were then resealed with duct tape or replaced with fresh bags. Since the spectrometer was factory-calibrated for butane only, response factors were determined using saturated canister breakthrough levels of hexane or heptane generated by the syringe injection technique.

DATA ANALYSIS

The maximum of three or more vapor concentrations measured in each analysis was recorded. Background concentrations were subtracted. Calibration factors were applied. Response correction factors relative to the nominal butane readings averaged 0.83 ± 0.02 for hexane and 0.76 ± 0.04 for heptane. Loadings were determined by differences in canister weights. Vapor concentrations (parts-per-million, ppm, by volume at 0.77 atm pressure [Los Alamos]) were calculated from injection rates and airflow rates.

RESULTS

The effect of storage time on bag concentrations for canisters saturated at 964 - 1221 ppm hexane is shown in Figure 1. The range of loadings was 15.1 - 16.5 g. A maximum of

587 ppm was measured at 15.6 hours. A linear weight loss, observed over an 18-day period for one canister with 16.1 g initial loading, averaged 16 mg/day (Table 1).

Hexane/C2A1 Canisters
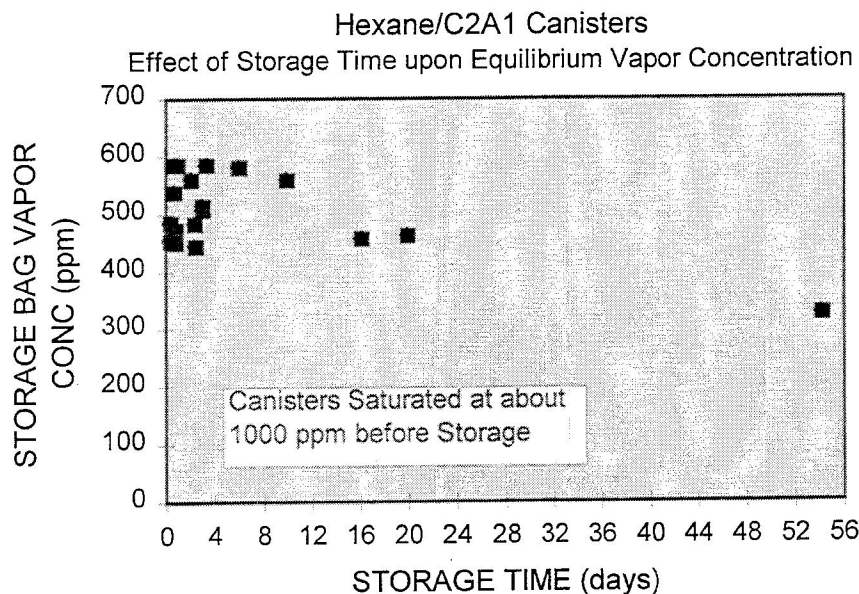### Effect of Storage Time upon Equilibrium Vapor Concentration

Figure 1. Hexane vapor concentrations in bags storing C2A1 canisters saturated at 964 - 1221 ppm.

Double bagging (quart/gallon) with one such canister reduced weight losses to 6 mg/day, while hexane concentrations in the outer bag reached 141 ppm at 5 hours, 183 ppm at 17 hours, and a maximum of 247 ppm at 10 days. Corresponding inner bag concentrations were 531 ppm, 463 ppm, and 526 ppm, respectively.

Similar decreases in bag concentrations with storage time were observed with heptane. For canisters saturated at 920 - 1026 ppm (20.5 ± 0.5 g), the maximum bag concentration observed was 468 ppm.

Partially loaded (10 g hexane at 938 - 1149 ppm or 9.5 g heptane at 868 - 1184 ppm) canisters showed similar effects of storage time (Figure 2). [Note that the time scale is logarithmic.] One-day and equilibrium concentrations were higher for the more volatile hexane. Equilibrium levels were also reached faster for hexane than for heptane.
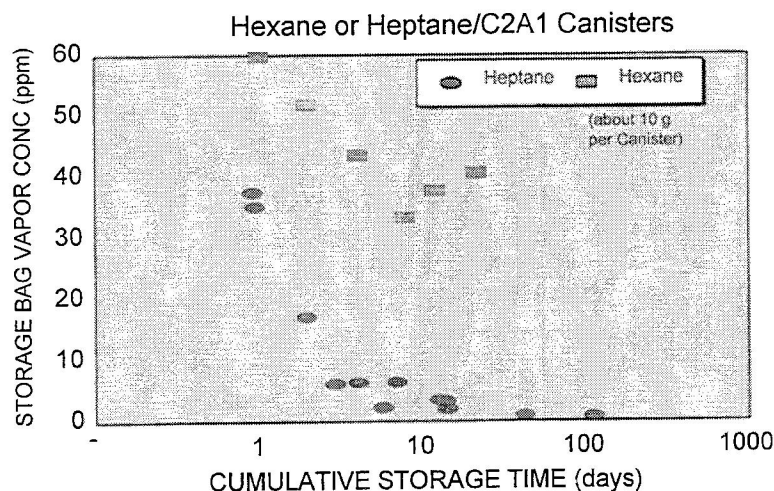
Hexane or Heptane/C2A1 Canisters

Figure 2. Hexane and heptane vapor concentrations in bags storing partially loaded C2A1 canisters.

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Effects of amount of loading are shown in Figures 3 and 4. In Figure 3 immediate (1-day) and equilibrium (8-day) bag hexane concentrations both increased with loading (1 - 10 g loaded at 388 - 976 ppm). The equilibrium concentrations were lower at all loadings. Figure 4 shows more extensive equilibrium data (> 4 days storage after adsorption or ≥ 2 days storage after desorption in flowing air). This graph is similar to an adsorption isotherm that is usually plotted as capacity (e.g., g/g carbon) versus concentration (e.g., ppm). Two independently measured capacities, equivalent to 8 g/113.7 g carbon at 12.6 ppm and 15.8 g/113.7 g carbon at 445 ppm, were both in good agreement with the data in Figure 4.
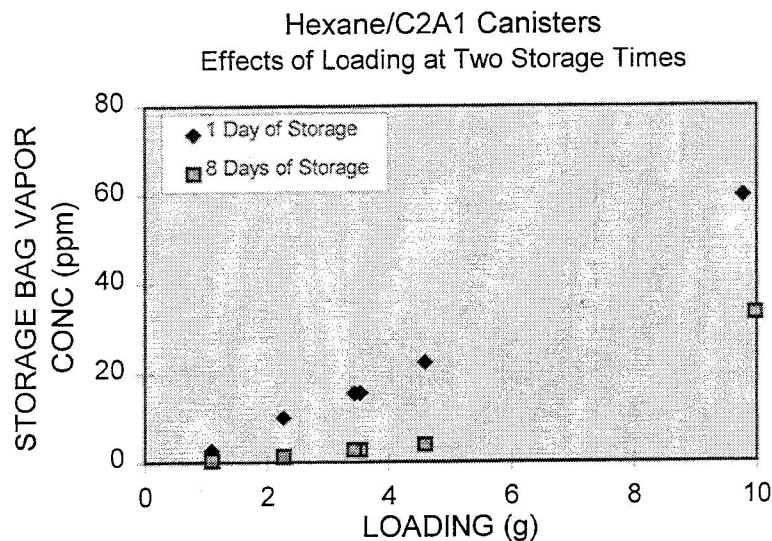
Hexane/C2A1 Canisters
Effects of Loading at Two Storage Times

Figure 3. Effects of hexane loading on storage-bag vapor concentrations at 1 and 8 days.

Hexane/C2A1 Canisters
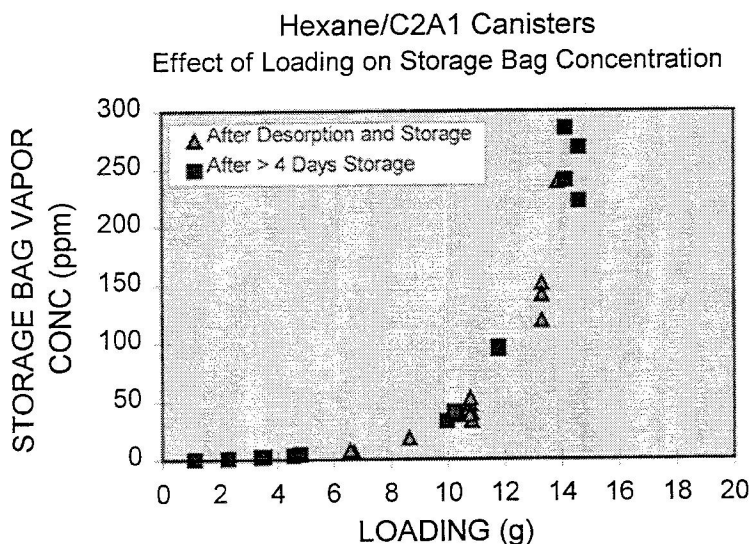#### Effect of Loading on Storage Bag Concentration

Figure 4. Effect of hexane loading on equilibrium storage-bag vapor concentrations.

Results of experiments done to determine the effects of sealing partially-loaded canister inlets and outlets are summarized in Table 1. Immediate (1-day) concentration levels and average weight losses over the first 18-60 days are listed.

TABLE 1. EFFECT OF CANISTER SEALING ON STORAGE-BAG CONCENTRATIONS
Canisters Loaded 1 Hour at about 1000 ppm Heptane and Bagged*

Treatment**	Bag Concentration at 1 day (ppm)	Average Weight Change (mg/day)
Unsealed	49.7	-16
Outlet only Sealed	46.6	-13
Inlet only Sealed	3.9	- 2.5
Inlet and Outlet Sealed	0.8	+ 0.7***

* Bagged in gallon-sized zipper-lock plastic bags of 0.044 mm thickness
** Sealing done with double layers of duct tape
*** Likely due to tape residue

DISCUSSION AND CONCLUSIONS

Maximum concentrations in storage bags were reached within one day. For saturated canisters (equilibrated in flow at a given concentration), the maximums were well below the challenge concentrations. They were higher for the more volatile hexane than for heptane. Storage-bag concentration decreases over time are attributed to hexane losses by permeation through the polyethylene bags. Since the experimental loadings fell on the plateau of the adsorption isotherm (see Figure 4), vapor concentration was very sensitive to small variations in loading. This explains the data scatter in Figure 1 and the relatively large concentration decreases with small weight losses. It could also explain the maximums being less than the loading concentrations, as vapor was lost during bagging.

For partially saturated canisters, the vapor concentration dropped more rapidly with time. This is attributed to migration of adsorbed vapors from the nearly saturated inlet to the less heavily-loaded remainder of the carbon bed.[1,2] This migration effect was faster for hexane than for the slower-diffusing heptane (Figure 2).

Vapor concentrations, immediate and at equilibrium, increased with loading (Figures 3 and 4). At equilibrium, before and after partial desorption, these concentrations and corresponding loadings reflected an inverted isotherm plot (Figure 4) Independent data agreed with these values. Therefore, concentrations from adsorption isotherm can be used to predict the equilibrium bag concentrations; however, they cannot be expected to predict immediate bag concentrations.

Sealing a canister outlet produced small decreases in bag concentration and weight loss rate (Table 1), since most of the loading was on the inlet. Sealing the inlet made big differences, as the tape was an effective barrier at the heavily loaded end. Upon sealing both the inlet and the outlet, releases to a storage bag, indicated by bag concentrations and weight changes, were virtually eliminated.

Based on these results and observations the following suggestions are made:

- Seal a used canister inlet with tape, preferably even before removing it from a gas mask.

- Also seal the canister outlet with tape.

- Allow at least a week for migration to evenly distribute the vapor on the carbon bed and for the vapor in the container (and bed) to reach a minimum before opening the storage container (or removing the tape). Allow this time especially if sealing with tape is not done before placing a used canister in a storage container.

REFERENCES

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(2) Wood, G.O., and R.J. Kissane, "Migration of Organic Vapors in Activated Carbon Beds between Periods of Airflow," published in the *Extended Abstracts and Programme of the EUROCARBON '98 Conference on the Science and Technology of Carbon*, Volume 1, pp. 271-272, Strasbourg, France (July 5-9, 1998).

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