

Desorption of TEDA from Impregnated Respirator and Adsorber Charcoals*

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Rates of triethylenediamine (TEDA) desorption from five impregnated charcoals were measured to determine whether sufficient quantities might be released to pose a possible health hazard. Among four charcoals with nominally the same 5% TEDA impregnation, desorption rates varied over factors as great as ten in the range of 70-100°C. However, the highest rate extrapolated to only 0.12 mg/m³ at 25°C, well below the vapor pressure of TEDA (3500 mg/m³) and the Threshold Limit Values (TLV) for similar amines (4-40 mg/m³). At elevated temperatures TEDA desorption rates for one charcoal were high enough to affect methyl iodide trapping efficiencies and, possibly, charcoal ignition temperatures. Effects of varying flowrate, bed depth, humidity, and increasing the TEDA molecular weight were examined.

Introduction

Triethylenediamine (1,4-diazobicyclo[2.2.2]octane; N(CH₂CH₂)₃N; Dabco; TEDA), a catalyst used in making urethane foams, has also been recognized as an effective charcoal impregnant for the trapping of organic forms of radioiodine from air.⁽¹⁻³⁾ Its use as a replacement for the toxic metal salts in Whetlerized charcoal has also been suggested. For respirator cartridge, high volume air cleaning adsorber, and air sampler applications the low volatility of TEDA is as important as its reactivity with air contaminants.

This compound has a normal boiling point of 174°C but is known to sublime readily at room temperatures.⁽⁴⁾ The volatility of the pure crystals has brought up the question of the volatility of TEDA impregnated in activated charcoals. The reasons for the concern are 1) the possible release of significant amounts of this amine of unestablished toxicity from sorbents, especially in air-purifying cartridge applications; 2) the possible loss of TEDA from air cleaning adsorbers over long periods of use resulting in degraded performance; and 3) heating due to high loadings of fission products on adsorbers, resulting in TEDA desorption and possible ignition.

There are no toxicological data available for TEDA; however, TEDA belongs to the class of organic aliphatic

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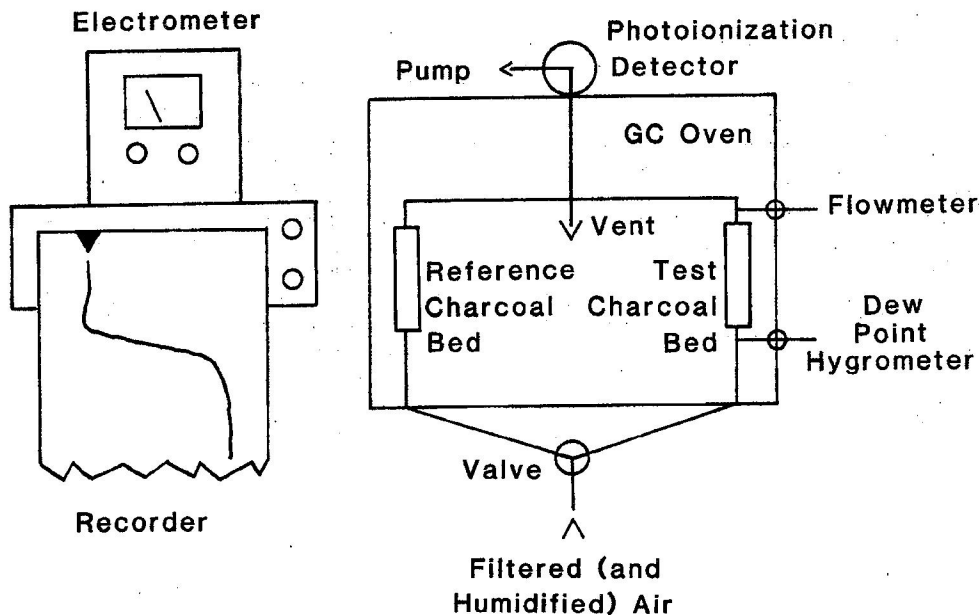


Figure 1 — The apparatus used for studies of TEDA desorption from charcoals.

amines, many of which have been shown to be toxic. Threshold Limit Values (1983)⁽⁵⁾ for similar amines are:

	mg/m ³	ppm
Ethylamine	18	10
Diethylamine	30	10
Triethylamine	40	10
Ethylenediamine	25	10
Diethylenetriamine	4	1

By structural and functional similarities, TEDA can be considered moderately toxic with a concern level of 1 ppm or greater. Vapor pressures measured over the range 50-110°C have been extrapolated to give 77 Pa (0.58 mm Hg) at 25°C (3500 mg/m³ at 1 atm).⁽⁶⁾ However, there was no information available on the volatility or desorption rate of TEDA impregnated on activated charcoal.

To supply data to answer these concerns we have measured TEDA desorption from commercial impregnated charcoals.

Apparatus and Procedures

The apparatus used for measuring TEDA desorption is diagrammed in Figure 1. The detector for TEDA in air was a photoionization detector (HNU Systems, Inc., Model PI-52-02) through which air samples were drawn at 22 cm³/min. Detector response was amplified and attenuated with the electrometer component and recorded on a strip chart. The detector was calibrated by subliming TEDA crystals at 30.0°C into flowing air using a Calibration System (Analytical Instruments Division, Inc., Model 350). Weight loss rate (4.80 μg/min) and total air flow rates (60-2000 cm³/min) were measured and used to calculate calibration concentrations.

A gas chromatograph oven was used to control temperatures (70-120°C) of test beds, the air entering them, and the sampling lines. Temperatures were monitored with a digital thermometer (±0.2°C). Charcoal samples of 1-4 cm³ volume were packed into 0.95-cm-i.d. stainless steel tubes and held in place by glass wool. This resulted in bed depths of 1.4-5.6 cm.

Compressed air from cylinders was passed through a filter of activated charcoal before use. It was quite dry (4% RH) initially. For higher humidity studies a fraction of all of the airflow was passed through the headspace of a water reservoir. Resulting relative humidities were determined using a dew point hygrometer (General Eastern Model 1200). The average atmospheric pressure for these studies was 78 kPa (585 mm Hg).

Two charcoal beds were placed in the oven in such a way that the airflow could be switched by a valve to either. One bed contained unimpregnated activated charcoal and the other the test charcoal. Air flow through the former (100-400 cm³/min) was adjusted at ambient temperature (22 ± 2°C) using an electronic bubble flowmeter (Mast Development Co., Model 823-1). The system was then reconnected and heated to the desired temperature with air flowing through the unimpregnated charcoal bed. Upon reaching a steady detector baseline signal, the airflow was switched to the test

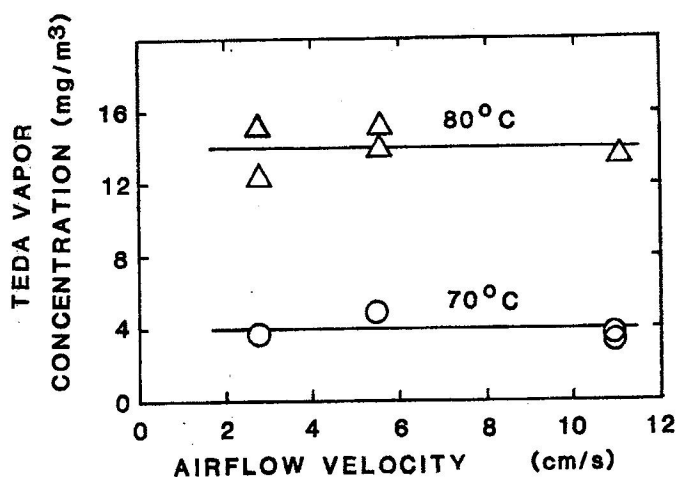


Figure 2 — Effect of airflow velocity on TEDA vapor desorption concentration at two temperatures.

bed. An upscale signal shift occurred. Such signal shift measurements were repeated at the same conditions, often using a fresh bed. At least three temperatures were used for each charcoal. Signal shifts recorded on the strip chart were measured with a ruler, multiplied by attenuation factors, and compared with calibration curves to get TEDA concentrations (mg/m³) and desorption rates (μg/g-min).

Three kinds of TEDA-impregnated charcoals (8-16 mesh) from 5 commercial sources were studied for TEDA desorption. The charcoals are not identified by source, since there is not enough information on them to assure lot-to-lot reproducibility of TEDA desorption behavior. Four of these charcoals contained a 5% by weight loading of TEDA. Another had a mixed impregnate — 2% TEDA and 5% KI₃. And one charcoal was impregnated 5% with a new compound called "C-Alykl TEDA" or "Heavy TEDA," which has an alkyl group, such as ethyl, added to one or more of the

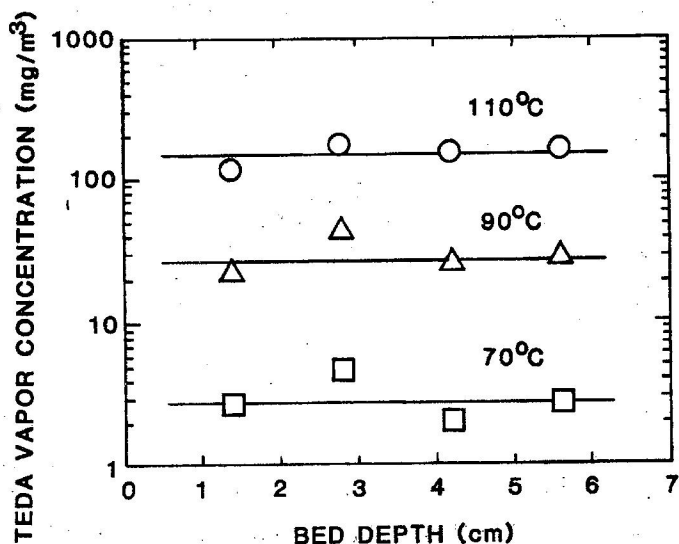


Figure 3 — Effect of bed depth on TEDA vapor desorption concentration at three temperatures.

ethylene bridges. The main objective is to make a higher molecular weight compound with lower volatility. The added alkyl group should not affect the reactive nitrogens. Another charcoal, impregnated with 5% KI₃ only, was also tested under the same conditions to provide a reference and to identify any iodine release upon heating.

Results and Conclusions

Since breathing through a respirator cartridge is not at a fixed, constant flow rate, we first studied the effect of airflow velocity. The results shown in Figure 2 for one of the 5% TEDA charcoals show the absence of effect of flow rate over the ranges 2.7-10.9 cm/s at 70°C and 2.8-11.3 cm/s at 80°C. Since bed depths also vary for different designs of cartridges and adsorbers, we also varied this parameter from 1.4 to 5.6 cm. Again, no effect on TEDA desorption concentration was observed (Figure 3). This result, combined with no velocity effect, implies that the TEDA was rapidly volatilized to an equilibrium distribution between the charcoal and the air passing through the charcoal.

Humidity was also varied over a range from 5% to 99% RH at 25°C. Dew points of $-18 \pm 4^\circ\text{C}$, $15.1 \pm 1.4^\circ\text{C}$, and $24.8 \pm 0.7^\circ\text{C}$ were measured at test conditions of 70°C, 90°C, and 110°C. At 25°C these dew points correspond to relative humidities of 4%, 54%, and 99%. Increasing water vapor concentrations decreased the response of the photoionization detector. When this response change was taken into account, no detectable changes in TEDA desorption rates were observed over these ranges of temperature and dew point. Only dry air was used in other experiments.

For the ordinary 5% TEDA charcoals, desorption concentrations varied widely (Figure 4). For example, at 90°C the range was 4 to 48 mg/m³. The mixed impregnant charcoal gave a value of 6 mg/m³, at the lower end of this range.

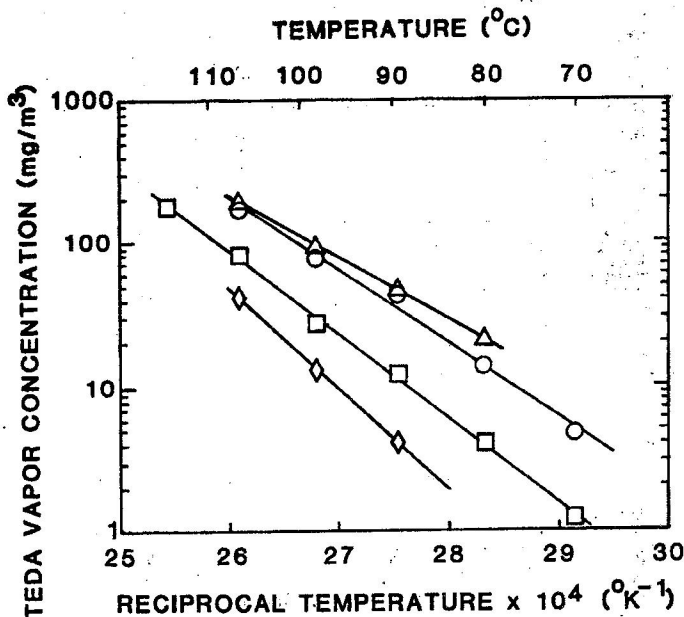


Figure 4 — Clapeyron plots for TEDA vapor desorbed from 5% TEDA charcoals into flowing air.

No iodine or other desorbing vapors were detected from the 5% KI₃ (only)-impregnated charcoal up to 120°C.

The differences in desorption rates for the four 5% TEDA charcoals are significant. They may be due to impregnation methods or due to the charcoal base characteristics (activity, surface area, pore structure, pore size, etc.).

Figure 5 shows a comparison of desorption concentrations of TEDA and Heavy TEDA. Both charcoals were from the same manufacturer, who said the same base charcoal was used. Note that the Heavy TEDA desorption was about 10 times lower than that for TEDA. This is what was expected. Efficiencies for trapping methyl iodide have been found to be similar for both impregnants.

As we have seen in Figures 4 and 5, Clapeyron equation plots (Log C versus 1/T) are linear. This was expected from analogy with evaporation and sublimation processes. The slopes of these plots are directly proportional to heats of desorption. The range of measured heats of desorption is shown in Table I. The average is 25 kcal/mol, much higher than the 14-kcal/mol heat of TEDA sublimation from pure crystals.⁽⁶⁾ The difference is due to TEDA-charcoal interactions. The 25-kcal/mol average corresponds to a doubling of desorption concentration and rate with every 5°C rise in temperature.

Another use of the Clapeyron equation plots is extrapolation to lower temperatures where TEDA desorption is too small to measure directly. Such extrapolations to 25°C yielded TEDA vapor concentrations shown in Table I.

The most important conclusion from these studies is shown in this table: the maximum desorbed TEDA vapor concentration at 25°C was calculated to be 0.12 mg/m³. No toxicological data are available for TEDA, but this is well below the TLV for similar amines, which range from 4 mg/m³ for diethylenetriamine to 40 mg/m³ for triethylamine.⁽⁵⁾

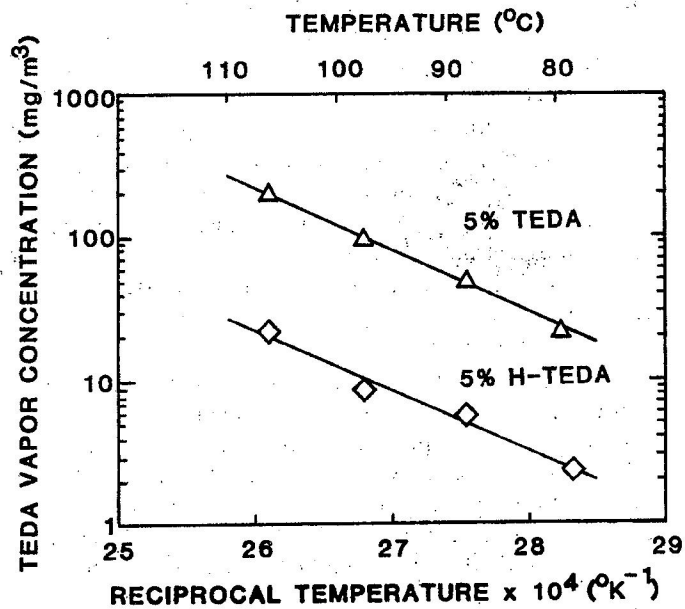


Figure 5 — Clapeyron plots for vapor desorbed from a "normal" TEDA charcoal and a "heavy" TEDA charcoal.

TABLE I
Triethylenediamine Desorption

Charcoal Impregnants	Heat of Desorption (kcal/mol)	Vapor Concentration at 25°C (mg/m ³)
5% TEDA	19.6	0.12
	23.2	0.032
	31.6	0.0003
	26.6	0.0036
2% TEDA	28.5	0.0011
+5% KI ₃		
5% H-TEDA	19.0	0.016

TABLE II
Maximum Adsorber TEDA Loss

Temperature (°C)	Temperature (°F)	Initial Desorption Rate (μg/g-min) ^A	(%/month)
25	77	0.007	0.6
30	86	0.015	1.3
35	95	0.029	2.6
40	104	0.056	4.9
50	122	0.193	16.9

^Aμg TEDA/g Charcoal/minute

Significant loss of TEDA from an air cleaning adsorber filled with TEDA-impregnated charcoal could result in degradation of efficiency for organic radioiodide removal. A standard (IES CS-8) Type II tray adsorber cell will be assumed for this calculation.⁽⁷⁾ It is designed with 5.08-cm (2-inch) deep beds containing approximately 22.7 kg (50 lbs) of charcoal. It is rated for a bed contact time of 0.25 s at 9.4 m³/min airflow (333 cfm), which corresponds to an airflow velocity of 20.3 cm/s. Initial desorption rates calculated at 1 atm are given in Table II for the charcoal with the highest TEDA desorption rates. Values at temperatures higher than 50°C can be estimated by doubling for each 5°C (9°F) rise. After significant TEDA loss, the absolute desorption rates (μg/g-min) will decrease with time, but the relative rates (%/month) may remain the same.

The desorption rates in Table II near normal ambient temperatures (25-35°C) may be significant for bed performance deterioration over 12-24 month use lifetimes of adsorber beds. However, other weathering and poisoning

processes are likely to be more significant. At higher temperatures, such as may result from high loading or radioactive nuclides, TEDA desorption becomes quite significant. This can result in rapid deterioration of efficiency for removal and retention of organic iodides. It may also contribute to ignition by providing TEDA vapor as fuel, which may explain why charcoal ignition temperatures are lowered by TEDA impregnation.

The data chosen for these adsorber calculations were those for the "worst case" (highest desorbing rate) 5% TEDA charcoal. Use of another could reduce TEDA loss below the significance level at normal ambient temperatures and could reduce the problem of TEDA loss and charcoal ignition in accident situations. However, it appears that measurements, such as described in this paper, will be required to identify the more stable TEDA-impregnated charcoals.

Acknowledgement

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References

1. Wood, G.O.: Respirator Canister Testing for Radioiodine. *Am. Ind. Hyg. Assoc. J.* 42:570-578 (1981).
2. Wood, G.O., G.J. Vogt, D.C. Gray and C.A. Kasunic: *Criteria and Test Methods for Certifying Air-Purifying Respirators Against Radioiodine*. Progress Report NUREG/CR-1055, LA-8029-PR. Los Alamos Scientific Laboratory, Los Alamos, NM (1979).
3. Wood, G.O., F.O. Valdez and V. Gutschick: *Criteria and Test Methods for Certifying Air-Purifying Respirator Cartridges and Canisters Against Radioiodine*. Progress Report NUREG/CR-3403, LA-9327-PR. Los Alamos National Laboratory, Los Alamos, NM (1983).
4. Windholz, M., ed.: *The Merck Index*, Ninth Edition, p. 1241. Merck & Co., Inc., Rahway, NJ (1976).
5. American Conference of Governmental Industrial Hygienists: *Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1983-1984*. ACGIH, Cincinnati, OH (1983).
6. Dietz, V.R.: Personal communication. Naval Research Laboratory, Washington, DC (1978).
7. Burchsted, C.A., J.E. Kahn and A.B. Fuller: *Nuclear Air Cleaning Handbook*, p. 58, ERDA 76-21. Oak Ridge National Laboratory, Oak Ridge, TN (1976).

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