CONF - 801038 - - 19

LA-UR - 80 - 3432

TITLE: DESORPTION OF TEDA FROM IMPREGNATED CHARCOALS

AUTHOR(S): Gerry Wood

MASTER

SUBMITTED TO: Presented at the 16th DOE Nuclear Air Cleaning Conference,
San Diego, CA, October 20-23, 1980. Proceedings to be
published at a later date. Unclassified.

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545
An Affirmative Action/Equal Opportunity Employer

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

DESORPTION OF TEDA FROM IMPREGNATED CHARCOALS*

Gerry Wood
Industrial Hygiene Group
Los Alamos Scientific Laboratory
University of California
Los Alamos, New Mexico 87545

Abstract

Triethylenediamine (TEDA) is one of the most effective charcoal impregnants for trapping organic forms of radioiodine from air. It is used in air cleaning adsorbers, air samplers, and air purifying respirator canisters and cartridges for airborne radioiodine. Volatility of the pure crystals suggested the possibility of significant TEDA desorption in these applications, resulting in toxic levels of amine and/or degradation of sorbent efficiency.

Measurements of TEDA desorption rates were made for four commercial charcoals. Temperatures of 70-120°C were used to give levels detectable with a photoionization detector. Extrapolations to temperatures nearer normal ambient were made by using Clapeyron equation plots.

Among three charcoals with the same 5% level of TEDA impregnation, desorption rates varied over factors as great as 10. Slopes of Clapeyron plots were similar, giving an average 25 kcal/mol heat of desorption. This corresponds to a doubling of the TEDA desorption rate with each 5°C (9°F) rise in temperature. Desorption rates were directly proportional to airflow rates or velocities through the test beds and independent of humidity. Desorption rates per unit weight of charcoal decreased exponentially with bed depth, presumably due to TEDA readsorption.

Calculations based on this data and the geometry of a standard adsorber cell showed that at normal ambient temperatures: (1) concentrations of TEDA in effluent air are well below expected toxic levels; and (2) losses of TEDA may be significant. At elevated temperatures TEDA desorption rates are high enough to affect methyl iodide trapping efficiencies and, possibly, charcoal ignition temperatures.

I. Introduction

Triethylenediamine (TEDA; 1,4-diazabicyclo[2.2.2] octane; $N(C_2H_4)_3N$) has long been recognized as an effective charcoal impregnant for the trapping from air of organic forms of radioiodine. TEDA-impregnated charcoals are used in air cleaning adsorbers, air purifying respirator canisters, and in air samplers. This compound has a normal boiling point of 174°C, but is known to sublime readily at room temperatures.

---

*Work supported by the Nuclear Regulatory Commission and performed at the Los Alamos Scientific Laboratory operated under the auspices of the U. S. Department of Energy, Contract No. W7405 ENG-36.

This volatility of the pure crystals has brought up the question of the volatility of TEDA impregnated in activated charcoals. The first reason for this concern is the possible release of significant amounts of this amine of unestablished toxicity from sorbents, especially in air purifying canister applications. A second reason for concern is the loss of TEDA from air cleaning adsorbers over long periods of use, resulting in degraded performance. Another concern for air cleaning adsorbers is heating due to high loading of radioactively decaying ^{131}I after an accidental release, resulting in TEDA desorption and possible ignition.

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

II. Experimental Details

Apparatus

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 cm^3/min. Detector response was amplified and attenuated with the electrometer component and recorded on a strip chart. The detector was calibrated by sublimation of TEDA crystals at 30.0°C into flowing air. Weight loss rate (4.80 µg/min) and diluent air flow rates (60-2000 cm^3/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. Temperature was monitored by a digital thermometer (±0.2°C). Charcoal samples of 1-4 cm^3 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 initially. For higher humidity studies a fraction or 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). Airflow rate (100-400 cm^3/min) through the test beds was adjusted using an electronic bubble flowmeter (Mast Development Co., Model 823-1). Linear flow velocities varied 2.35-9.40 cm/s; bed contact times varied 0.3-1.2 s.

Experimental Charcoals

Test charcoals were identified by their commercial sources as 8-16 mesh range with the impregnants given in Table I.

Table I. Experimental Charcoals

Source	Impregnants (Weight Percents)
Barnebey Cheney Co.	5% TEDA
Scott Health/Safety Products	5% TEDA
Norton Safety Products	5% TEDA
Mine Safety Appliances Co	2% TEDA + 5% KI$_3$
Mine Safety Appliances Co.	5% KI$_3$

Procedures

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 flowed through the former to the detector during oven equilibration. Upon reaching a steady detector baseline signal the airflow was switched to the test bed. An upscale signal shift occurred. When a constant level was attained, the airflow was switched back to the unimpregnated charcoal. 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 (μg/L). Desorption rates (μg/g-min) were then calculated from charcoal densities and airflow rates.

III. Results

Charcoal Variation

Desorption rates (D) at 4.7 cm/s airflow velocity and 90°C varied from 0.9 to 9 μg/g-min for the three 5% TEDA charcoals. The 2% TEDA, 5% KI_3 charcoal desorption rate was 1.2 μg/g-min at the same conditions. No iodine or other desorbing vapors were detected from the 5% KI_3 (only)-impregnated charcoal up to 120°C.

The differences in desorption rates for the three 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.). These differences, however, do not affect the efficiencies of these sorbents for methyl iodide trapping. We have measured essentially equal efficiencies for the highest and the lowest TEDA desorption rate charcoals in this test group.

Temperature Variation

Clapeyron (or Van't Hoff) equation plots (log D vs 1/T) for TEDA desorption rates at 4.7 cm/s are shown in Figure 1. These are linear plots, as expected from analogy with evaporation and sublimation processes. The slopes of these plots are similar, implying similar heats of desorption, ΔH_D. The range of ΔH_D values was 23 to 29 kcal/mol with an average of 25 kcal/mol. This is much higher than the 14 kcal/mol heat of TEDA sublimation from pure crystals. The difference is due to TEDA-charcoal interactions. The 25 kcal/mol corresponds to a doubling of the desorption 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 yielded desorption rates of 0.0009 to 0.008 μg/g-min for the three 5% TEDA charcoals and 0.002 μg/g-min for the 2% TEDA, 5% KI_3 charcoal at 25°C.

Airflow Velocity Variation

The 5% TEDA charcoal with the highest desorption rate was used to study effects of varying airflow velocity (2.35-9.40 cm/s). Results for two temperatures are shown in Figure 2. Desorption rate was directly proportional to airflow velocity. This implies that the limiting process in TEDA loss was removal of vapor by flowing air, rather than the volatilization step itself.

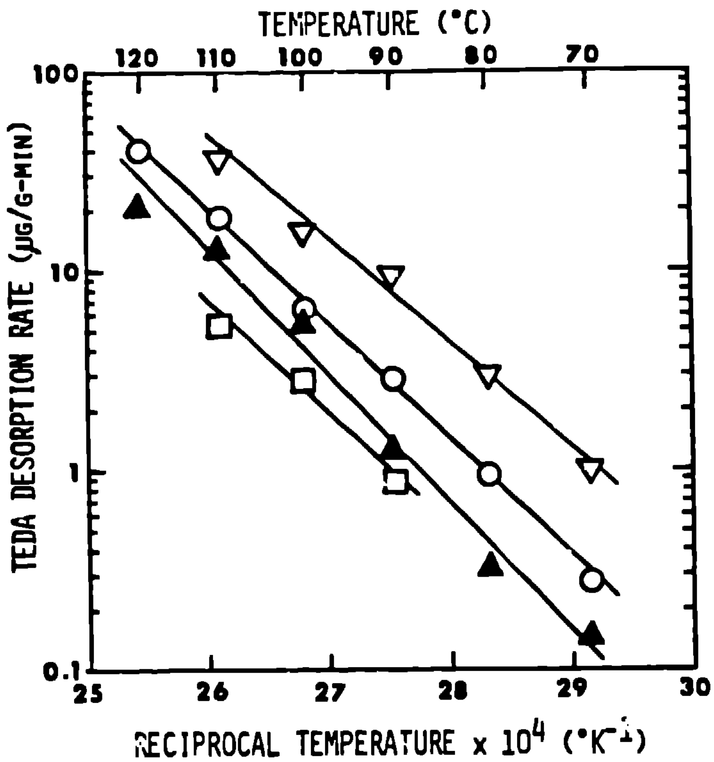

FIGURE 1

EFFECT OF TEMPERATURE ON TEDA DESORPTION RATE FROM THREE 5% TEDA CHARCOALS (▽,○,□) AND A 2% TEDA, 5% KI_3 CHARCOAL (▲)

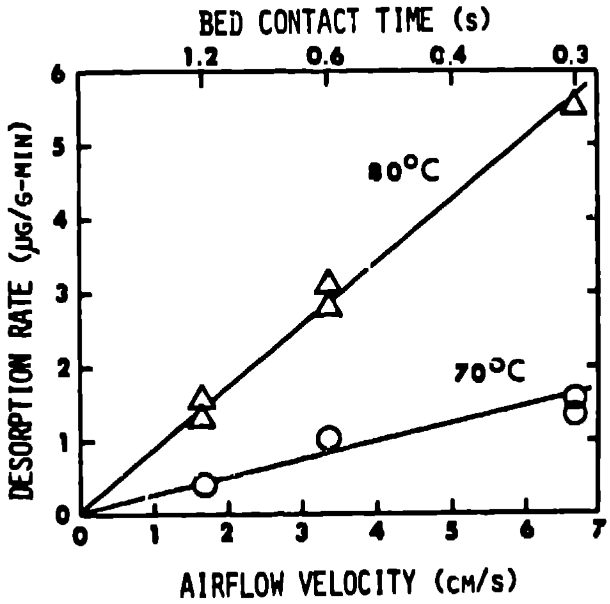

FIGURE 2

EFFECT OF AIRFLOW VELOCITY ON TEDA DESORPTION RATE

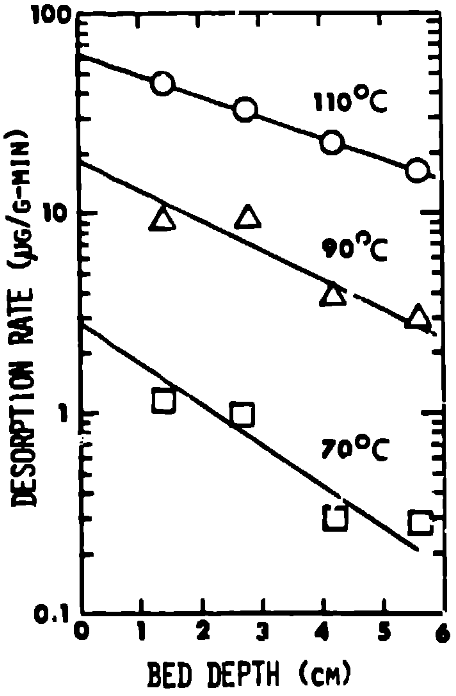

FIGURE 3

EFFECT OF BED DEPTH ON TEDA DESORPTION RATE

A general equation for desorption rate can be derived from the effects of temperature and flow velocity:

$$D = V \exp [a - \Delta H/RT]$$

Data from 21 measurements using this charcoal at 5 temperatures and 4 airflow velocities was fit to this equation to give a = 34.8 (std dev = 1.3) and ΔH = 24.9 kcal/mol (std dev = 0.9).

Humidity Variation

In one series of measurements with the highest desorption rate charcoal water vapor content of the air was varied. Dew points of -18 ± 4°C, 15.1 ± 1.4°C, and 24.8 ± 0.7°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 experimental parameters. Only dry air was used in other experiments.

Bed Depth Variation

In another series of measurements with the highest TEDA desorption rate charcoal, bed depths were varied 1.4-5.6 cm at an airflow rate of 200 cm^3/min. Desorption rates were again measured at 70°C, 90°C, and 110°C. Figure 3 shows an apparently linear decrease in the logarithms of the TEDA desorption rates (per gram charcoal) with bed depth. Within experimental uncertainties, which are greater for lower temperatures, the slopes of the semilog plots for the three temperatures are identical. The average slope for results normalized to 90°C was -0.32 (std dev = 0.04); i.e., $D = \exp [2.83 - 0.32d]$, with bed depth d in cm.

The decrease in desorption rates (per gram charcoal) with increasing bed depth is likely due to readsorption of TEDA desorbed nearer the front (inlet) of the bed. This is the reverse of the process of adsorption of a vapor from air onto activated charcoal.

IV. Conclusions

Calculated TEDA Losses from an Adsorber

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. 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 m^3/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. 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.

Table II. TEDA from an Adsorber

Temperature		Initial Desorption Rate		TEDA Concentrations	
(°C)	(°F)	(μg/g min)	(%/month)	(mg/m^3)	(ppm)
25	77	0.007	0.6	0.018	0.004
30	86	0.015	1.3	0.036	0.008
35	95	0.029	2.6	0.070	0.016
40	104	0.056	4.9	0.135	0.031
50	122	0.193	16.9	0.465	0.110

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 of 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 calculations was that for the "worst case" (highest desorbing rate) 5% TEDA charcoal. Use of one of the others should reduce TEDA loss below the significance level at normal ambient temperatures. And it should reduce the problem of TEDA loss and charcoal ignition in accident situations.

Calculated TEDA Concentrations from an Adsorber

Concentrations of TEDA in effluent air passing through the same adsorber are also given in Table II. There are no toxicological data available for TEDA; however, TEDA belongs to the class of organic aliphatic amines, some of which have established toxicity. Threshold Limit Values (1979) for similar amines are:

	mg/m^3	ppm
Ethylamine	18	10
Diethylamine	75	25
Triethylamine	100	25
Ethylenediamine	25	10
Diethylenetriamine	4	1

The obvious conclusion is that if TEDA toxicity is similar to the toxicity of these other amines, the TEDA releases from such adsorbers are well below the level of concern.

Correction to manuscript previously submitted entitled "Nonradiometric and Radiometric Testing of Radioiodine Sorbents Using Methyl Iodide"

Methyl iodide is more representative of reality than is carbon