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Study of Adsorption-Desorption of Contaminants on Single Soil Particles Using the Electrodynamic Thermogravimetric Analyzer

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■ The isothermal adsorption and desorption of organic vapors on a single soil particle was studied with the aid of the electrodynamic thermogravimetric analyzer (EDTGA). Toluene and carbon tetrachloride were tested at room temperature during their adsorption on Sphero-carb, montmorillonite, and Carbopack particles. The maximum amount of either organic compound adsorbed was comparable to that required for one monolayer coverage of the particle surface area. Significant differences among various pairs of solid-organic vapor examined were identified and correlated to differences in solid pore structure and chemical affinity between the organic compound and the solid.

Introduction

The increasing public and scientific concern with the problem of hazardous waste disposal has initiated and promoted the study of fundamentals associated with such waste treatment processes (1-3). At present, the dominant way of handling hazardous chemicals is disposal to a landfill site. Nevertheless, studies over the recent years have shown that in many cases such a solution may be detrimental to the environment. Organic compounds, such

as low molecular weight halocarbons, can be released from waste landfills and contaminate groundwater, soil, and air, posing an immediate threat to human health (3-7). The transport of contaminants in the environment is a complex process, and among other factors, it involves the adsorption and desorption of these compounds by soil particles (3).

With landfill costs increasing and regulations on land-filling becoming more strict, a search for alternatives to conventional hazardous waste treatment has become a necessity. Incineration is currently a proven solution for treating most organic contaminants, and well-designed incineration systems provide the highest overall degree of destruction of hazardous waste streams (8). Hence, although a costly treatment, significant growth is anticipated in the use of incineration and other thermal destruction methods (8, 9). In addition to these, the future will see development of several thermal and nonthermal (10-15) soil decontamination techniques including use of microorganisms, electrokinetic methods, vacuum extraction and volatilization, and soil aeration. Most of these treatment methods involve contaminant desorption.

Recent studies have pointed out the importance of adsorption and desorption of contaminants in the soil particles during incineration (1, 2). Pershing and co-workers suggested contaminant desorption as the probable rate-limiting step at long times in the evolution of the contaminant from soil particles, which necessitated heating

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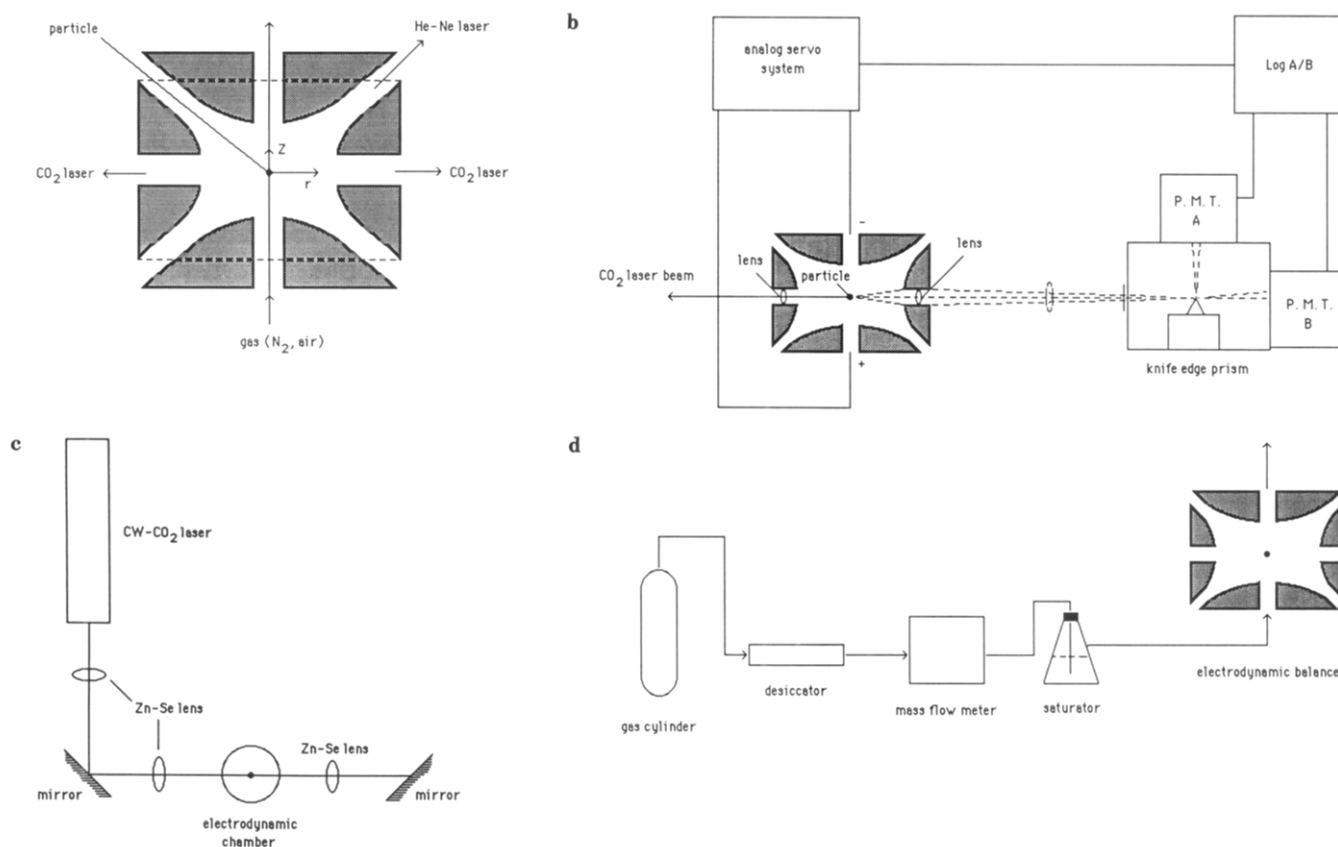


Figure 1. (a) Cross-sectional view of electrodes in electrodynamic balance. (b) Schematic of the position control system. (c) Schematic of the laser heating system. (d) Schematic view of the gas flow system.

well above the boiling point of the organic compound (1). They also suggested that with reactive, porous soils (e.g., clays), the last monolayer of contaminant molecules may be tightly bound to the soil, thus requiring temperatures significantly above the boiling point to ensure adequate cleanup (1).

It is clear that a fundamental study of the adsorption and desorption of contaminant organics on soil particles can contribute considerably to understanding the transport and diffusion of hazardous chemicals in soils and lead to optimization of the operation of incineration systems, such as rotary kilns. Transient phenomena involving rapid waste vapor release, called "puffs", are frequently encountered in rotary kilns and may cause failure of the incineration system (10, 11). Experimental evidence shows that puff magnitude increases with increasing temperature and kiln rotation speed and is also sensitive to the volatility of the waste (12). In the rotary kiln, the solids can be considered as a bed of many layers of particles that are being slowly stirred. Hence, contaminants may exist either adsorbed on the external surface of the particles or adsorbed on the internal pore structure of the particles or as a liquid phase within the bed. Clearly both intraparticle and interparticle effects contribute to the high complexity of the rotary kiln system.

It would be extremely helpful if the characteristics of a single-particle reactor were first investigated. To this end, we have used in our laboratory the electrodynamic thermogravimetric analyzer (EDTGA). The EDTGA is a device that consists of an electrodynamic balance modified to permit single-particle heating by a CO₂ laser, temperature measurement by a two-color infrared-pyrometer system, and continuous weighting by a position control system. The main advantages that the EDTGA has over the conventional TGA can be summarized as follows: (a)

higher accuracy in weight measurement and the fact that the TGA requires a large number of particles, i.e., average values are measured; (b) TGA data are often masked by external diffusion problems.

The fully instrumented EDTGA has been used successfully so far in a number of applications including measurement of temperature and weight of char particles undergoing oxidation (16, 17), measurement of heat capacities, and adsorptivities of single particles (18), calculation of water activities for single electrolyte solutions (19), and photophoretic force measurements on micron-size irradiated particles (20-23). Recently, the same apparatus has been used as a basic tool in developing a novel droplet imaging system that offers unique capabilities for characterizing size, mass, density, and composition of individual droplets (24).

In the present article we report our first results of the use of EDTGA in the study of adsorption and desorption of organic compounds on single particles of several porous soils.

Experimental Methods

Apparatus. The electrodynamic balance (EDB) consists of two endcap electrodes and a ring electrode. The basic characteristics and principles of operation have been described in detail in previous communications (25-28). A schematic of the electrodynamic balance is presented in Figure 1a. The chamber creates a dynamic electric field capable of suspending a single charged particle of sizes varying from 30 to 300 μm . The ac ring electrode provides lateral stability to the particle through an imposed ac field oscillating sinusoidally at 100 Hz and at an amplitude of ± 2000 V. The dc top and bottom electrodes provide vertical stability by cancelling out the gravity force and thus suspending stably the charged particle in the EDB.

A position control system can be used, which automatically adjusts the electric field to keep the particle at the center of the chamber (Figure 1b). An optical microscope (Ealing) is used for viewing the particle and for manual control of the particle position. The microscope allows measurement of the particle size to $\pm 5 \mu\text{m}$.

A 20-W CO_2 laser supplies heat to the suspended particle (Figure 1c) and two-color infrared (2 and 4 μm) pyrometry is used for temperature measurement. A gas flow system allows exposure of the particle to the desired gaseous environment (Figure 1d). Additional information about the apparatus and its operation can be found elsewhere (25, 28).

Experimental Procedure. In the present study, the EDTGA was used to measure the relative variation of the weight of a suspended particle during adsorption and desorption of organic vapors at room temperature.

A single, dry particle was suspended in the chamber, through which a finite dry nitrogen flow rate was maintained. The particle was degassed before the adsorption runs by heating it with the laser. The voltage was then adjusted in order to balance the particle at its correct position. A nitrogen stream saturated with organic vapor was produced by bubbling the nitrogen through the liquid in a saturator and was then introduced in the balance. The voltage required to keep the particle at the same position was recorded as a function of time.

The desorption experiments followed the adsorption runs and started when the voltage reached a final, stable value. The saturator was switched off and dry nitrogen was introduced again. Saturation was achieved for flow rates of 14.3, 21.4, and 28 cm^3/min . The introduction of gases flowing upward past the suspended particle produces an aerodynamic drag force F_a , which affects the dc voltage required for balancing the particle. Hence, the force balance on a suspended particle in the EDTGA should be written as

$$mg = qE + F_a \quad (1)$$

where m is the particle mass (kg), g is the gravitational acceleration (m/s^2), q is the excess charge on the particle (C), and E is the electric field strength in the vertical direction (V/m).

The electrical field strength E is given by the equation

$$E = CV/Z_0 \quad (2)$$

where C is the chamber constant, V is the measured balancing voltage across the endcap electrodes and Z_0 is the characteristic length of the EDB chamber (0.004m).

Since low flow rates were used, i.e., the Reynolds numbers were less than 1, the aerodynamic drag on the particle is described by Stokes law:

$$F_a = 3\pi\mu vd \quad (3)$$

where μ is the gas viscosity, v is the gas velocity, and d is the particle diameter.

Combining eqs 1-3, one obtains

$$mg = qCV/Z_0 + 3\pi\mu vd \quad (4)$$

Due to the drag force effect, the voltage required to balance the particle was measured in the absence of gas flow at the beginning of each experiment. As shown in eq 4, the minimum mass variation detectable in the apparatus is given by the minimum voltage difference that can be measured. In the present configuration it was possible to measure $\Delta V/V_0$ as low as 10^{-4} where ΔV is the voltage change and V_0 is the initial voltage required to suspend the particle in the absence of organic vapor. In terms of weight, the above value means that a fractional change of

Table I. Physical Properties of Solid Materials

material	diam, μm	surface area, m^2/g	intrusion vol, ^a cm^3/g	bulk density, g/cm^3	porosity ^a
Spherocharb	125-150	860.0	0.83	0.63	0.525
montmorillonite	90-125	192.3	1.24	0.65	0.802
Carbopack	150-180	10.4	0.64	0.95	0.615

^aBased on mercury porosimetry.

10^{-4} in the particle weight is detectable with typical values of Δm in the range of 10^{-10} - 10^{12} g.

Materials. In order to determine potentially different solid-hydrocarbon affinities, three solids and two hydrocarbons have been examined in this work. Montmorillonite clay and Spherocharb and Carbopack particles were used. The physical properties of these materials are reported in Table I. The surface area was determined by the BET method and all the other properties reported in Table I were obtained by mercury porosimetry. Spherocharb and Carbopack are trade names of chars produced for chromatographic packing by Foxboro Analabs and Aldrich Chemical Co., respectively; they have been selected because of their spherical shape and because their characteristics do not differ significantly from particle to particle. Montmorillonite particles were not uniform in shape and only those with shape close to spherical were used in this study. Two hydrocarbons were examined, toluene and carbon tetrachloride.

Results and Discussion

Typical adsorption-desorption results for toluene are shown in Figure 2a and b. Figure 2a shows the value of V/V_0 vs time for a Spherocharb particle of 170- μm diameter at room temperature. The total volumetric flow rate was maintained at 21.4 cm^3/min at all times. At $t = 0$ the voltage required to balance the particle in the presence of the gas flow is recorded as V_0 . The voltage V gradually increases during adsorption to reach a practically constant value recorded as V_a . The voltage required to balance the particle in the absence of gaseous flow (or equivalently in absence of a drag force) is also measured at the beginning of the experiment and recorded as V_{nf} . Using the above values, one can calculate weight changes using the equation

$$\frac{V - V_0}{V_{nf}} = \frac{m - m_0}{m_0} \quad (5)$$

and similarly the maximum amount of contaminant adsorbed per gram of solid particle X_a is given by

$$X_a = \frac{V_a - V_0}{V_{nf}} = \frac{m_a - m_0}{m_0} \quad (6)$$

where m_0 is the mass of dry solid and m_a is m_0 plus the mass of organic adsorbed. Note that the drag force contribution to both V and V_0 is identical since constant flow rate is maintained, and therefore, the difference $V - V_0$ in the numerator gives the net weight gain due to adsorption of the organic.

Figure 2b depicts the desorption profile of toluene at room temperature in dry nitrogen flowing into the EDTGA chamber at constant flow rate. An initial slow decrease in V/V_0 is observed, which probably corresponds to the slowly diminishing vapor pressure of toluene in the chamber. This is followed first by a sharp and then by a slow decrease in V/V_0 .

In order to be able to compare the rates of adsorption and desorption for various experiments the data are re-

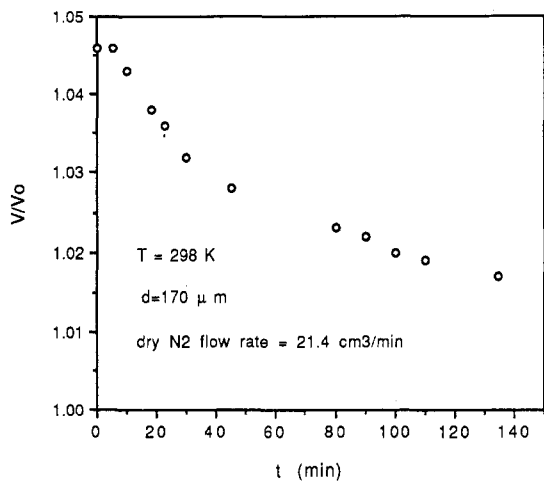
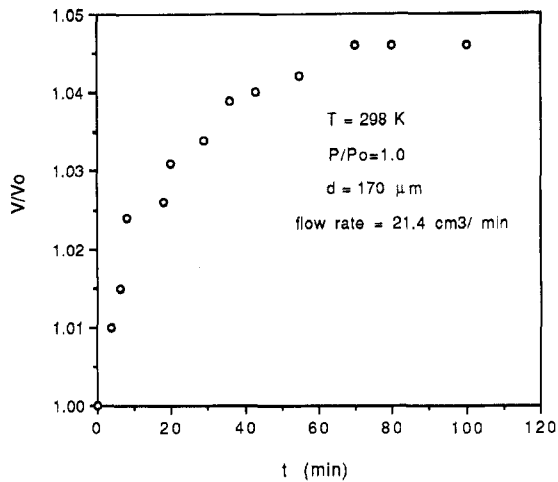


Figure 2. (a) Adsorption of toluene on Sphero carb particle. (b) Desorption of toluene from Sphero carb particle.

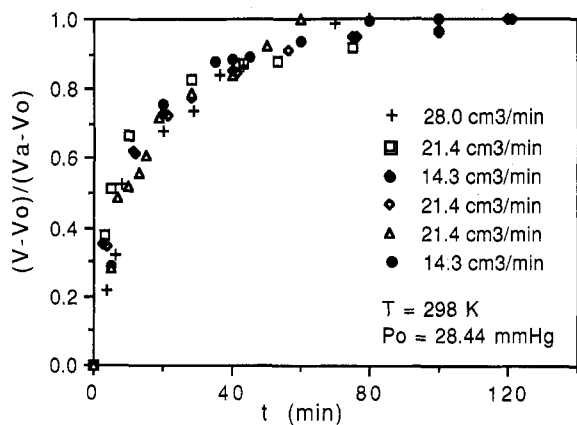


Figure 3. Sphero carb-toluene adsorption runs for different flow rates.

ported as a fractional attainment Y of the maximum adsorption, where

$$Y = \frac{V - V_0}{V_a - V_0} = \frac{m - m_0}{m_a - m_0} \quad (7)$$

Figures 3 and 4 contain normalized data for six Sphero carb particles during adsorption and desorption of toluene. Although the amount of hydrocarbon adsorbed is likely to vary from particle to particle, there is no appreciable variation in the rates of adsorption and desorption. Three different flow rates, 14.3, 21.4, and 28 cm³/min, were used in the experiments shown in Figures 3 and 4. It can be seen that the effect of gas flow rate on the rates of adsorption or desorption is insignificant. Certain scattering

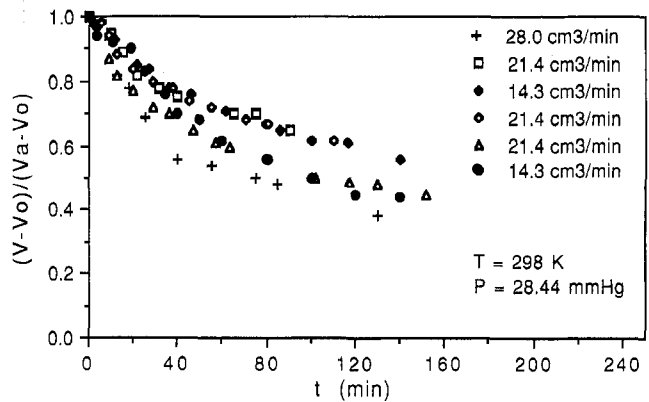


Figure 4. Sphero carb-toluene desorption runs for different flow rates.

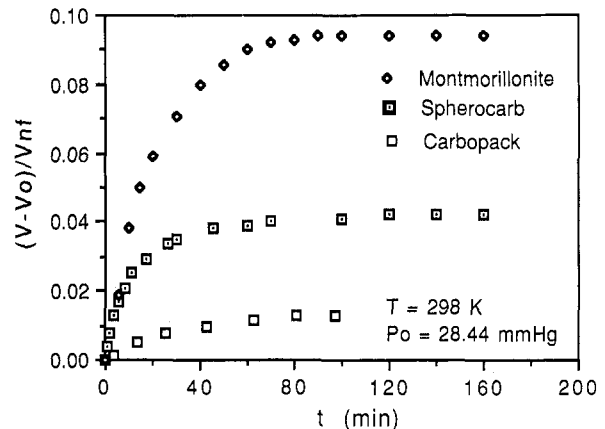


Figure 5. Average adsorption curves of toluene for different materials.

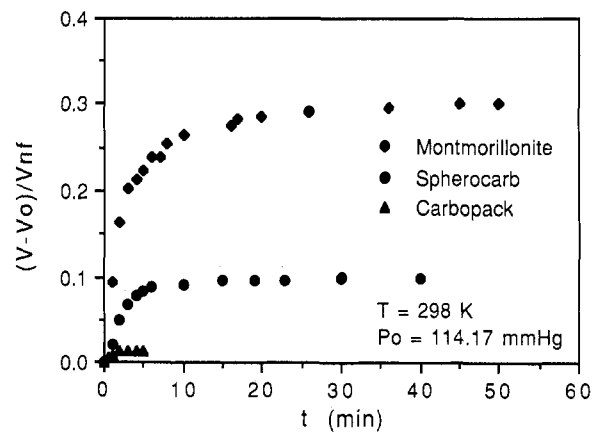


Figure 6. Average adsorption curves of carbon tetrachloride for different materials.

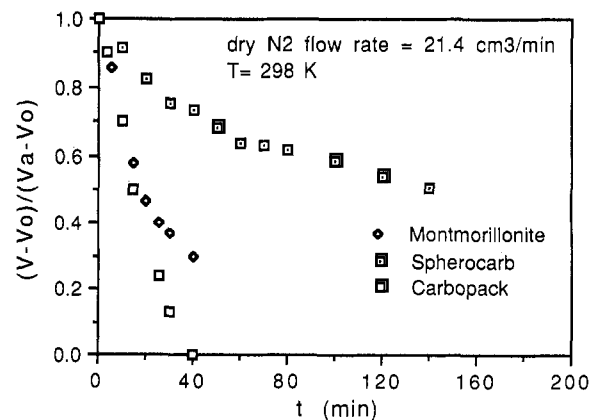


Figure 7. Average desorption curves of toluene for different materials.

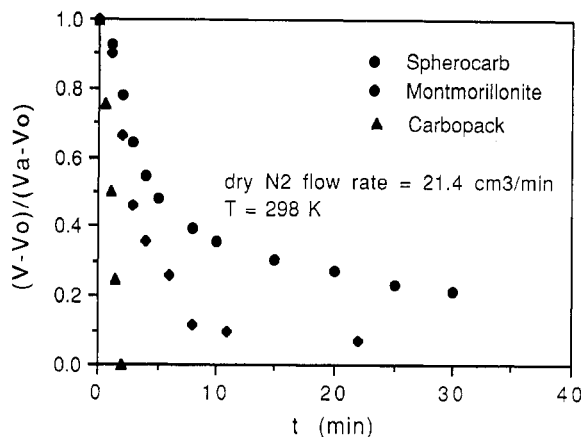


Figure 8. Average desorption curves of carbon tetrachloride for different materials.

Table II. Maximum Amount of Contaminants Adsorbed per Gram of Solid and Corresponding Characteristic Times for Adsorption and Desorption

materials	X_a , (g liquid/ g solid)	$\tau_{0.5a}$, min	$\tau_{0.9a}$, min	$\tau_{0.5d}$, min	$\tau_{0.5d}$, min
Sphero carb-C ₇ H ₈	0.029	8	45	140	>200
	0.061				
	0.048				
	0.045				
	0.025				
montmorillonite-C ₇ H ₈	0.045	13	47	17	>40
	0.130				
	0.070				
	0.100				
Carbopack-C ₇ H ₈	0.075	16	62	15	32
	0.009				
	0.017				
Sphero carb-CCl ₄	0.109	2	7	5	>30
	0.092				
	0.107				
	0.087				
montmorillonite-CCl ₄	0.292	2	17	3	11
	0.290				
	0.272				
	0.347				
	0.260				
	0.280				
Carbopack-CCl ₄	0.360	1	2	0.5	1.5-2.0
	0.012				
	0.012				
	0.012				

is observed in the desorption curves but there is no systematic trend of dependence of flow rate. This verifies the ability of the EDTGA to study weight changes on a single particle in the absence of external diffusional effects.

The transient adsorption behavior for all pairs of solid-organic vapor investigated is shown in Figures 5 and 6, while the corresponding desorption curves are shown in Figures 7 and 8. Each experimental point in Figures 5-8 corresponds to an average value of at least three particles examined. Each curve shown in Figure 3-8 can provide information about the characteristic time of either the adsorption or the desorption of the organic compound from the particle. The times required for the particles to adsorb 50% and 90% of the maximum amount that can be adsorbed under these conditions was defined as $t_{0.5a}$ and $t_{0.9a}$ respectively. Similarly, the times required to desorb 50% and 90% of the adsorbed compound were defined as $t_{0.5d}$ and $t_{0.9d}$ respectively. Table II contains X_a values for several experiments as well as average values of the above denoted characteristic times.

Table III. Comparison of X_a Values to Those Corresponding to One Monolayer Coverage of the Solid Surface

materials	X_m	X_a
Sphero carb-C ₇ H ₈	0.372	0.042
montmorillonite-C ₇ H ₈	0.081	0.094
Carbopack-C ₇ H ₈	0.004	0.013
Sphero carb-CCl ₄	0.678	0.098
montmorillonite-CCl ₄	0.148	0.300
Carbopack-CCl ₄	0.008	0.012

The above experimental results show clearly that considerable differences exist between montmorillonite, Sphero carb, and Carbopack as well as between toluene and carbon tetrachloride concerning adsorption and desorption characteristics. The amount of contaminant adsorbed can be correlated to certain properties of either the solid or the organic vapors. From the three solids examined, montmorillonite adsorbs the largest amount of C₇H₈ and CCl₄, and as shown in Table I, it has the largest intrusion volume. Sphero carb comes next, although it has the highest surface area. This can be explained by taking into account that Sphero carb consists mainly of micropores (<3 nm). Formation of liquid in pores of that size is highly likely and this could inhibit penetration of the organic compound inside the particle. In other words, the adsorbed compound has access to only a small fraction of the total internal surface area of the Sphero carb particle. Carbopack adsorbs the least amount of either organic compound and this is in agreement with its low surface area and large pores. In general, larger amounts of CCl₄ than C₇H₈ are adsorbed on all solids examined. This is mainly due to the higher vapor pressure, and consequently greater mole fraction of CCl₄ in the nitrogen stream, given the fact that all experiments were carried out at the same temperature (25 °C) and atmospheric total pressure.

One interesting observation (Figures 7 and 8, Table II) during the desorption experiments is that mainly Sphero carb, and montmorillonite to a lesser extent, seem to retain an appreciable fraction of the adsorbed compound. In certain experiments, e.g., Sphero carb-toluene (Figure 7), the shape of the desorption curve indicates that a finite percentage of the adsorbed organic is irreversibly adsorbed in the porous solid at the temperature studied. A partial explanation of this phenomenon is given in Table III, which contains values determined experimentally for the six solid-vapor pair combinations. Both quantities X_m and X_a presented there are expressed in grams of organic per gram of solid. From mercury porosimetry measurements (29), it is possible to determine an average porosity for each solid. On the other hand, using the average surface area of each solid, which was calculated from N₂ desorption BET measurements (29), one can determine the mass of organic that will be required to cover 1 g of solid with one monolayer. This quantity is denoted as X_m in Table III. Also, an average value of X_a taken from Table II is included in the last column of Table III for comparison. The maximum amount of contaminant adsorbed is of the order of one monolayer for all the materials examined. It can also be seen from the tabulated values that in cases where part of the adsorbed organic is retained by the solid, the remaining quantity corresponds to a coverage of less than a monolayer. It is understood that a monolayer of adsorbate is more strongly bound to the solid surface and its desorption will be a longer process. This is mainly due to the fact that capillary condensation and intercalation of adsorbate molecules in micropores justify the long times that are observed during adsorption and desorption. For

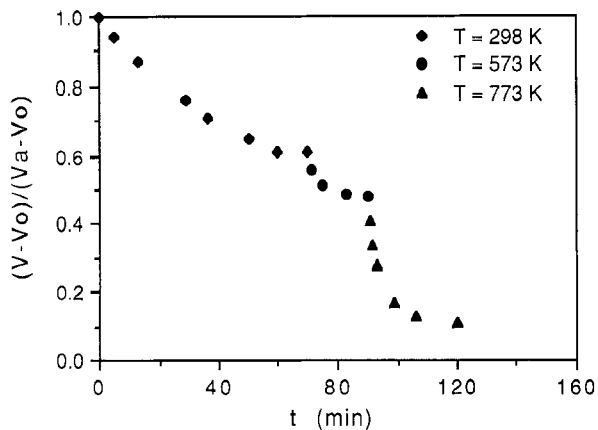


Figure 9. Sphero carb-toluene desorption run for different temperatures.

these times the diffusivity ranges from 10^{-7} to 10^{-9} cm^2/s (30).

As has already been mentioned, all the experiments shown in Figures 3-8 were obtained with both the saturator and the EDB chamber maintained at room temperature. Hence, the vapor-nitrogen stream introduced in the chamber is saturated with the organic vapor. Unsaturated mixtures can be introduced if the saturator temperature is lower. This would also result in a decrease in the partial pressure of the vapor around the soil particle. Experiments done under these conditions showed that complete recovery of the adsorbed compound can be achieved much faster upon decreasing the vapor partial pressure (29). An alternative in accelerating the desorption process is to heat the particle. Figure 9 shows transient desorption of toluene from a Sphero carb particle originally exposed to a nitrogen-toluene stream, saturated in toluene, at 25 °C. After 1-h exposure to a dry nitrogen stream at the same temperature, 60% of the amount originally adsorbed remains trapped in the porous solid. Laser heating of the particle to 300 °C results in a slight decrease of this amount to about 50%, and most of the organic finally desorbs only upon heating to 500 °C.

In summary, EDTGA has been shown to be a useful tool for studying the fundamentals of contamination and decontamination of porous soils. It can also be used for continuously measuring the temperature and weight of a heated particle during small intervals of time, as shown in Figure 9. Significant differences among various solids and contaminant compounds have been identified. The present study focuses primarily on showing the advantages of using EDTGA in related research. A systematic study of the adsorption-desorption characteristics and their dependence on the physical and chemical properties of the soil is necessary. Experimental work toward this goal is currently in progress.

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