

A METHOD OF COMPARING SOLID SORBENTS FOR SPECIFIC ADSORPTION  
OF VAPORS

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Objectives

The objectives of my talk this morning are fourfold: 1) to describe a test method which has been developed in our laboratory over the past few years; 2) to suggest an empirical classification of adsorptions that have been observed; 3) to present data for benzene and carbon tetrachloride on several batches of charcoal; and 4) to discuss some possible applications of the data from this test method.

The problem which we have attacked can be expressed by the questions, "Which of several materials is best for adsorbing vapors of a certain compound? What is a quantitative comparison?" The compound might be selected as representative of a certain class of compounds (for example, aniline for the aromatic amines), or it might be itself the one of interest.

Experimental

The test apparatus we used to explore these questions is shown in Figure 1. It is basically a gas chromatograph with some modifications. The sample is introduced by one of two methods: 1) a gas sampling valve may be used for gaseous samples of fixed volume; or 2) the injector of the gas chromatograph can be used for syringe injection of gases, liquids, or solutions. The liquids are vaporized in the hot injector.

For solutions, a chromatographic column can be used to retard the solvent and other unwanted compounds while allowing the test compound to elute. A valve is also included in the system for optional use of such a column, and to bypass the column before unwanted compounds elute. The carrier gas then transports the sample from the valve through the sorbent tube into the detector. Any detector that is linear in the range of interest is acceptable. The detector signal is recorded on a chart and, if possible, simultaneously integrated. An electronic digital integrator is very useful for this purpose.

The sorbent tubes are 6 mm O.D. by 60 millimeters long standard-wall Pyrex tubes. They are packed with a chosen volume of the sorbents to be tested, held in place with glass wool plugs. A constant volume is used instead of a constant weight, since densities may vary greatly among the sorbents. We usually use 25 cm<sup>3</sup>, which gives a 20-mm long section.

The first step for a test is to prepare a sorbent tube and equilibrate it in the apparatus at the test temperature. Air is purged with the carrier gas flow. The compound to be tested is then injected or sampled with the gas sampling valve. If necessary, the test compound is separated from other compounds present by column separation and by valve switching. The amount of sample injected must be sufficient to overload the sorbent. A sharp peak with tailing is usually observed when this is the case. When baseline is re-established, the injection of the same amount of the sample on the same sorbent section is repeated. With fresh sections of the same sorbent, additional pairs of injections are made with larger or smaller amounts of the compound.

#### Interpretation of Injection Data

The purpose of the duplicate injections on the same sorbent section is to determine the fraction of the first sample which was adsorbed and not subsequently desorbed. Let us call this process irreversible adsorption. The fraction irreversibly adsorbed is the difference of peak areas divided by the area of the second peak. This assumes that all irreversible sites (at the experimental temperature) were occupied during the first injection. Carrier gas flow rate may need to be adjusted to make this assumption valid.

An alternate treatment of the data is a graphical plot of peak area versus sample size. When this linear plot is extrapolated to zero area, the intercept corresponds to the amount of compound irreversibly adsorbed, and this calculation can be used to confirm results from the area difference calculation.

Adsorption isotherms for the reversible adsorption can be calculated from the shapes of the peaks (1,2). The reversible adsorption may be due to a second layer of molecules on the sorbent surface or to weaker adsorption sites. The total equilibrium adsorption isotherm is obtained by combining reversible and irreversible adsorption results. Also, from adsorption measurements and isotherms at two or more different temperatures, heats of adsorption can be calculated.

#### Adsorption of Benzene on Charcoal

As an example of the types of information which this test method will yield, let us consider some experiments with benzene on charcoal from an MSA Organic Vapor respirator cartridge. Figure 2 shows tracings of peaks from two consecutive 75- $\mu$ l injections of benzene on a 0.25-cm<sup>3</sup> section of charcoal at 25°C.

## Irreversible Adsorption

The difference in peak areas, which is shaded, represents the amount of benzene irreversibly adsorbed after the first injection. Subsequent injections would give us a repeat of this second peak to indicate that, indeed, we had occupied all irreversible sites.

Figure 3 shows peaks obtained from four injections of different volumes of benzene. Each injection was on a fresh section of charcoal. Note that the 20- $\mu$ l injection was completely adsorbed and there was no signal at the detector. Where the peaks overlap (on the tails), an equilibrium condition exists between adsorption and desorption.

In Figure 4 the areas of these peaks and others are plotted against the amount of benzene injected in microliters. Extrapolations of the data at 25°C. and 100°C. give intercepts of 25- $\mu$ l and 5.3- $\mu$ l, respectively, as the amounts of benzene irreversibly adsorbed. By calculation of the area difference, we get a slightly higher value of 27- $\mu$ l at 25°C.

## Equilibrium Isotherms

Equilibrium adsorption isotherms derived from peak shapes are shown in Figure 5. The nonzero intercepts are due to the irreversible adsorption. For air sampling of benzene, the range of interest is up to 50 parts per million, which is 5 times the Threshold Limit Value. For respirator cartridge work the range of interest is up to a thousand parts per million. If an equilibrium condition exists at these concentrations, the adsorption will be predominantly what I have been calling irreversible adsorption up to the point where all the irreversible adsorption sites are occupied. This may be considered a characteristic of a good sorbent.

## Heats of Adsorption

Heats of adsorption can be calculated from the difference in the adsorption isotherms at a given vapor concentration. In this case the heat of adsorption is 4.55 kcal/mole at zero parts per million, which would presumably correspond to the irreversible sites, and 3.15 kilocalories per mole at 1000 parts per million.

## Irreversible Adsorption Capacities of Various Charcoals

Irreversible adsorption capacities for benzene and carbon tetrachloride at 25°C. on 0.25-cm<sup>3</sup> of several batches of charcoal are given in Table I. The benzene results, and the carbon tetrachloride results in parentheses, were obtained by the area difference method. Most of the carbon tetrachloride data was obtained by area extrapolation. Note the agreements of the two methods for carbon tetrachloride, adsorption on

Charcoals 3 and 5. Also, note the wide ranges of capacities. Charcoal Number 5 (Barnebey Cheney petroleum charcoal) has the highest capacity for benzenes; Charcoal Number 2 (Barnebey Cheney coconut shell charcoal) has the highest capacity for carbon tetrachloride. However, for adsorption of both these compounds, Charcoal Number 3 (MSA coconut shell charcoal) is probably the best compromise.

Dr. Teass: What is the weight of the charcoal that corresponds to a quarter of a  $\text{cm}^3$ ?

Dr. Wood: Approximately 80 mg.

### Data Applications

#### Screening

Four applications of data from this test method are listed in Table II. Sorbent screening for adsorption capacity is illustrated by the data that have been shown for benzene and carbon tetrachloride on the charcoals. This is not limited to charcoals. At the present we are testing a variety of more than 50 sorbents for methylamine capacity. We have found that for such varied sorbents as silica gel, alumina, charcoal, and silicone OV-210 both irreversible and reversible adsorption have been observed for methylamine.

#### Desorption Efficiencies and Migration

The calculation of heats of adsorption has already been discussed. A possible application of this type of data is correlation with thermal or chemical desorption efficiencies. Also the problem of sample migration from a front to a back-up section of a sampling tube should also be related to the heat of adsorption of that vapor on the sorbent.

#### Specifications

The third suggested application is the establishment of specifications for sorbents. Breakthrough times of sampling tube or respirator cartridges should be very much dependent on adsorption capacities and heat of adsorption. One batch of sorbent could be selected as a standard. The adsorption capacity, heat of adsorption and breakthrough times for certain compounds on this standard sorbent would be measured. Then it could be assumed that any batch of the sorbent with the same or greater adsorption capacity and heat of adsorption would have the same or greater breakthrough times if tested. The advantage is that breakthrough times are often much more difficult and time-consuming to measure.

### *Interference Effects*

*The final application to be suggested is testing for interference effects, especially from water vapor. It would be necessary in this case to use a detector that will respond to the test compound but not to the interference compound. For example, a flame ionization detector will not respond significantly to water vapor. The interference compound could be introduced at a constant concentration in the carrier gas or as an injected amount following injection of the test compound. Effects of its presence, or amount of interference on adsorption capacity, retention, and heat of adsorption could be measured. It is our intention to continue to explore such applications of this test method at the Los Alamos Scientific Laboratory, as we develop methods for the sampling and analysis of toxic vapors in air.*

### *References*

- 1. Huber, J. F. K., and Keulemans, A. I. M., "Gas Chromatography 1962," M. van Swaay, ed., Butterworth's, London, 1962, p. 26.*
- 2. Gregg, S. J., and Stock, R., "Gas Chromatography 1958", D. H. Desty, ed., Butterworth's, London, 1958, p. 80.*

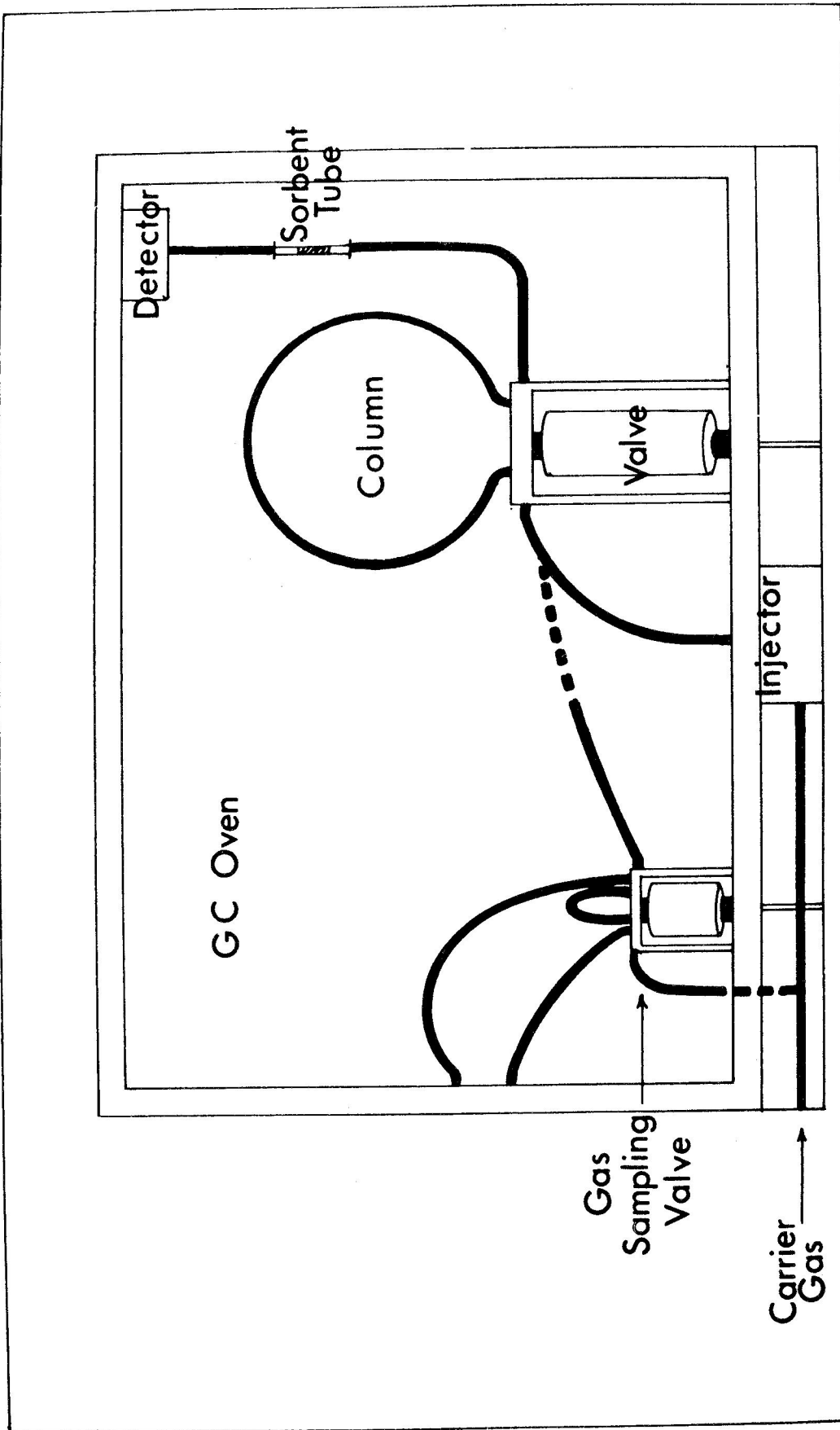


Figure 1. Apparatus for Testing and Comparing Solid Sorbents.

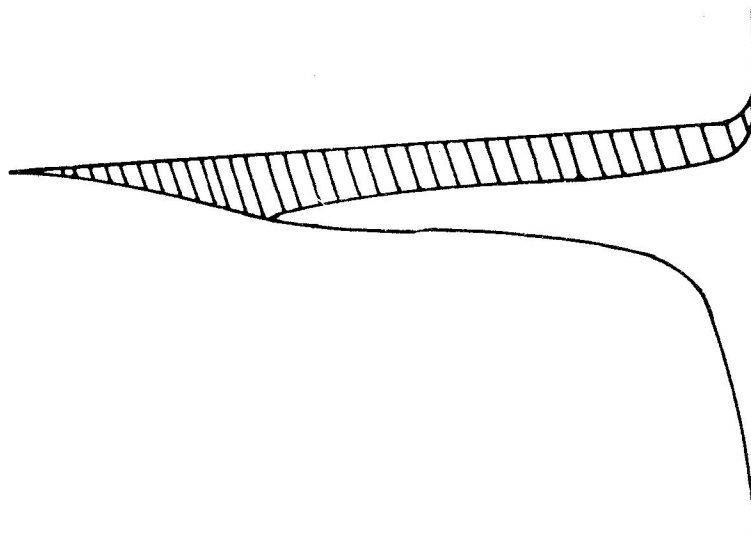


Figure 2. Peaks from Consecutive Injections of 75- $\mu$ l Benzene on 0.25  $\text{cm}^3$  Charcoal.

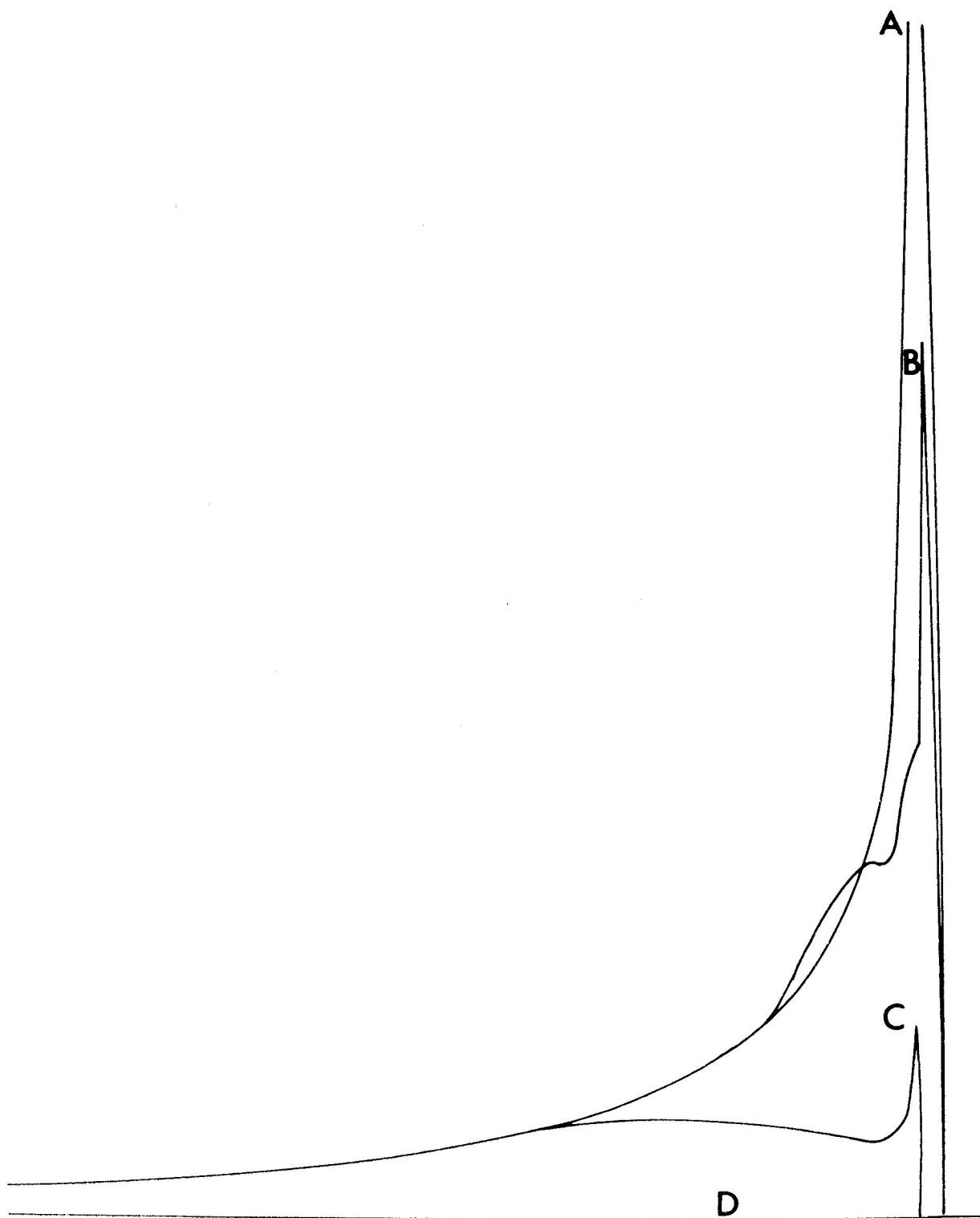


Figure 3. Peaks from Injections of Benzene onto  $0.25 \text{ cm}^3$  Charcoal from an MSA Organic Vapor Cartridge Respirator.



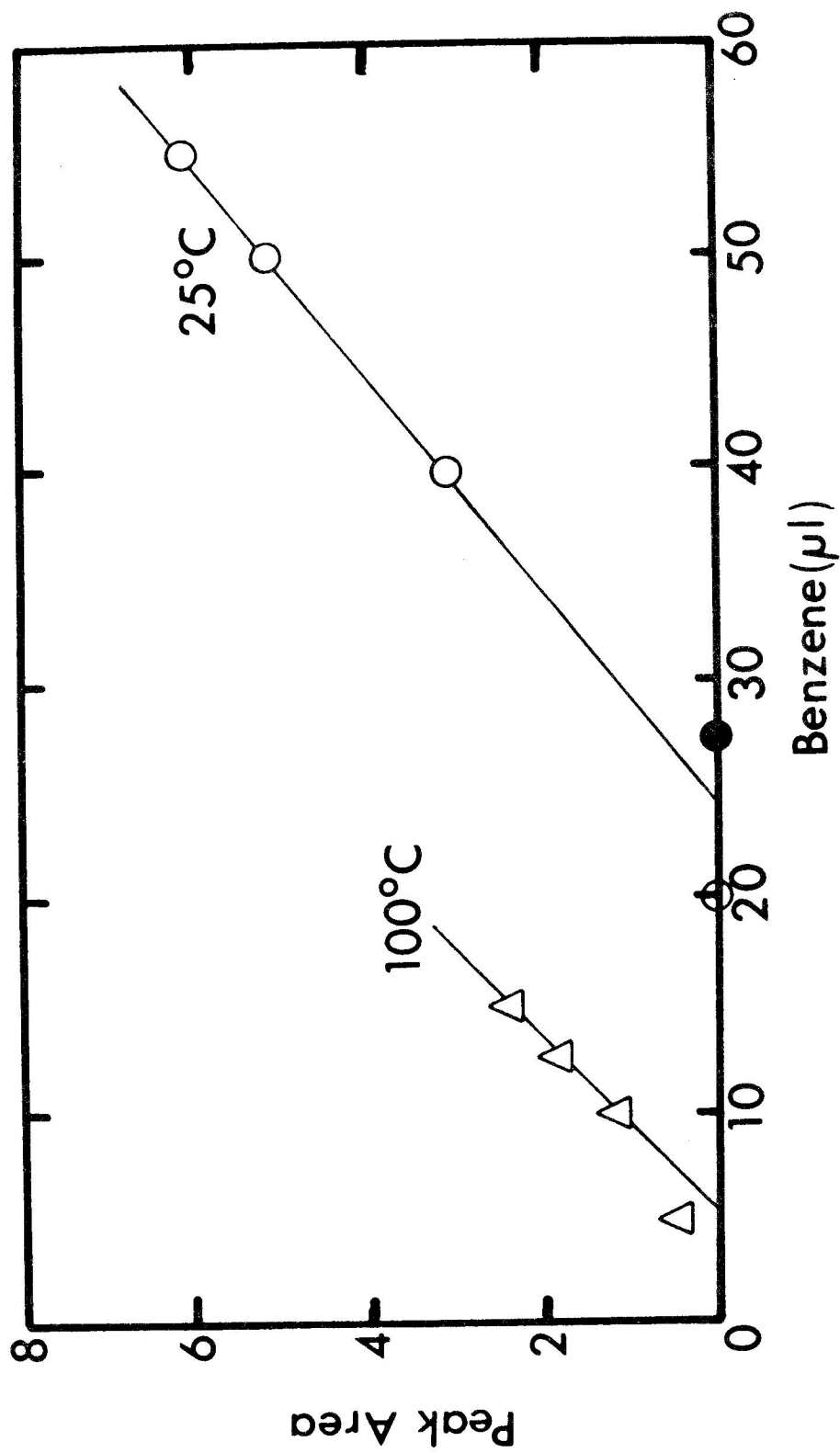


Figure 4. Plots and Extrapolations of Peak Areas from Benzene Injections onto Charcoal.

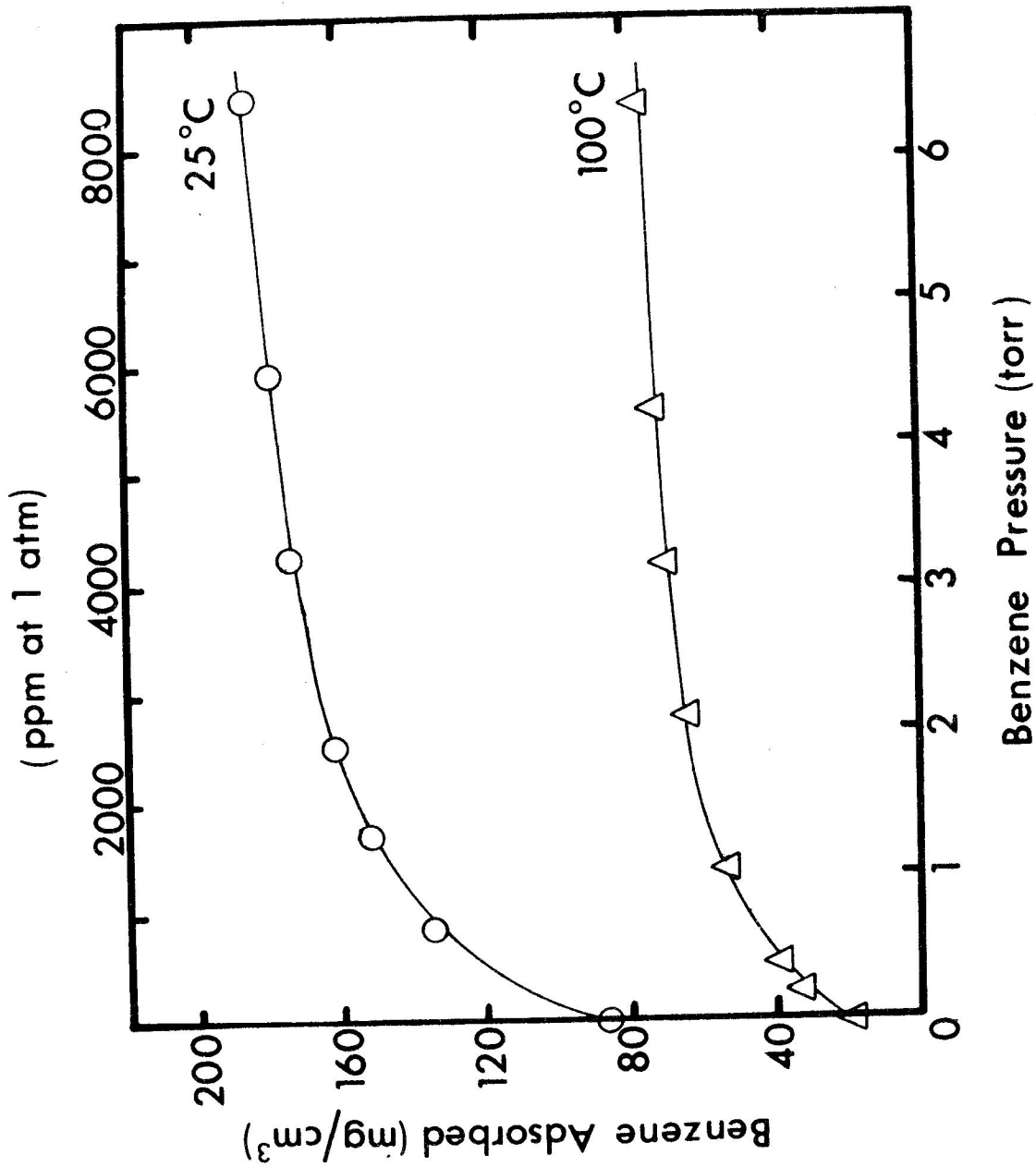


Figure 5. Equilibrium Adsorption Isotherms on Charcoal.

Table I. Irreversible Adsorption at 25°C.

<u>Charcoal*</u>	<u>Benzene (mg)</u>	<u>CCl<sub>4</sub> (mg)</u>
1	16.0 ± 0.5	46.9 ± 9.9
2	21.6 ± 1.2	64.9 ± 7.5
3	24.6 ± 0.3	54.2 ± 4.3
		(53.6 ± 1.4)
4	16.4 ± 0.8	45.9 ± 2.7
5	26.0 ± 2.6	35.1 ± 7.2
		(34.0 ± 0.5)
6	17.9 ± 0.8	33.8 ± 8.4

\*0.25 cm<sup>3</sup> per sample

Table II. Applications

1. Sorbent screening for adsorption capacity
2. Heats of adsorption
3. Specifications for sorbents
4. Testing for interference effects

*SECOND NIOSH SOLID SORBENTS ROUNDTABLE*

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