Table VI. Calibration Data for Estimation of Low Concentrations of Diethyl Ether, Diisopropyl Alcohol, and Acetone

Conditions same as in Table III

Volume % isopropyl alcohol = diethyl ether = acetone = 1.00
Weight % isopropyl alcohol = acetone = 0.79 diethyl ether = 0.73

Peak Height Ratios

| | Column 1 | | | Column 2 | | |
	Isopropyl alcohol	Diethyl ether	Acetone	Isopropyl alcohol	Diethyl ether	Acetone
	0.755	2.45	1.37	0.714	2.56	1.39
	0.744	2.45	1.39	0.713	2.54	1.41
	0.741	2.56	1.41	0.726	2.38	1.40
Av.	0.747	2.49	1.39	0.718	2.49	1.40
Std. dev.	0.007	0.05	0.02	0.008	0.08	0.01

$$\text{Wt. \% (vol. \%) component} = \frac{\text{peak height component/peak height methyl ethyl ketone}}{M}$$

$$M = \frac{\text{peak height component in standard sample/peak height methyl ethyl ketone}}{\text{weight \% (or volume \%) component in standard sample}}$$

Table VII. Estimation of Acetone by Gas Liquid Partition Chromatography and Chemical Analyses

| | Acetone, Weight % | |
Sample	GLPC	Chemical[a]
T₁R	0.24	0.41
T₁OH	0.27	0.38
T 49	0.56	0.64
T 45	0.39	0.86
T 40	1.50	1.10
T 23	4.52	4.35
P	1.66	1.97
FI 40	1.67	1.93
WA	0.41	0.19

[a] Total carbonyl by hydroxylamine hydrochloride calculated as acetone.

mine low concentrations of isopropyl alcohol, diethyl ether, and acetone. It was found that either weight or volume per cent could be calculated directly, because at low concentrations the specific gravity of the samples was very close to 1.00. Table VII compares the results obtained by gas liquid partition chromatography and chemical method for acetone. The chemical method determines total carbonyl by hydroxylamine hydrochloride, which is calculated as acetone. It was known that some of these samples contained traces of numerous aldehydes and ke-

tones, but a specific acetone determination was desired in each case.

In addition to the routine applications, the dual chromatograph has been invaluable in trouble shooting large number of samples rapidly, special pilot plant studies, and "what is it?" samples.

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Determination of Surface Area

Adsorption Measurements by a Continuous Flow Method

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▶ A promising new approach to the measurement of surface area by the adsorption of nitrogen is presented. Nitrogen is adsorbed by the sample at liquid nitrogen temperature from a gas stream of nitrogen and helium and eluted upon warming the sample. The nitrogen liberated is measured by thermal conductivity. Good agreement was obtained with the conventional volumetric method. The new method does not involve vacuum techniques and is therefore free of concomitant maintenance problems, gives a permanent record automatically, is faster and simpler for routine application, and requires less skill. It can probably be extended to a lower range of areas, because of the high sensitivity of the thermal conductivity detection.

THE most widely used method for determining surface area involves measuring the amount of gas adsorbed on a solid surface at a temperature close to the boiling point of the gas. Nitrogen is most commonly used as the adsorbate. If the adsorption is measured at several gas pressures, the Brunauer-Emmett-Teller (BET) equation (1) can be used to calculate the amount of adsorbate required to form a monolayer. This value, multiplied by the proper factor for area covered per unit amount of nitrogen, gives the surface area. In this method the amount of adsorbed gas is usually determined by measuring pressure differences in a calibrated high-vacuum apparatus, which is fragile and complex. Recently, Loebenstein and Deitz (4) proposed a scheme for reducing the vacuum requirements by using a mixture of the adsorbate and an inert gas such as nitrogen with helium. However, they made no basic changes in the method of adsorption measurements.

The method described is also based on gas adsorption and use of the BET equation, but the adsorption measurements are entirely different. The amount of adsorbed gas is determined by concentration measurements in a continuous flow system rather than by pressure-volume measurements in a static system. The procedure is rapid and is applicable over a wide range of surface areas.

Results of some exploratory tests are given to demonstrate the feasibility of the method. More extensive studies are in progress to establish the scope and precision.

The present method for adsorption measurements is a modification of gas adsorption chromatography in which the column packing is the sample itself and the mobile gas phase is a known mixture of a suitable adsorbate and an inert gas. The primary purpose is to characterize various solid adsorbents, rather than to analyze gases or volatile liquids as in ordinary gas adsorption chromatography. This method of determining gas adsorption can be applied with many adsorbates and several available methods of detection. The authors chose nitrogen as the adsorbate and helium was employed as a diluent. A known mixture of nitrogen and helium is passed through the sample, the effluent being monitored by thermal conductivity measurements using a recording potentiometer. When the sample is cooled in liquid nitrogen, the absorption of nitrogen is indicated by a peak on the recorder chart. After adsorption equilibrium is established the recorder pen returns to its original position. The sample tube is allowed to warm by removing the liquid nitrogen coolant, causing desorption of nitrogen and producing a peak on the chart which is in the reverse direction of the adsorption peak. The potentiometer plots curves for both adsorption and desorption and the area under either one of these curves is a measure of the nitrogen adsorbed.

These peak areas can be calibrated for surface area measurements by either an absolute or a comparative method. In the absolute method, a known amount of nitrogen is added to the nitrogen-helium stream at the point normally occupied by the sample. From the resulting recorded curve, a factor is obtained for the amount of nitrogen per square centimeter of peak area. In the comparison method, this factor is obtained by calibration with a sample of known surface area.

APPARATUS

The apparatus is shown schematically in Figure 1.

Thermal conductivity detectors, one measuring and one reference cell, convection-diffusion type, containing approximately 15-ohm Gow-Mac elements (Gow-Mac Instrument Co., Madison, N. J.). The cell block is contained in a water bath at room temperature and is equipped with a copper coil, $^1/_8 \times 24$ inches to each cell to provide temperature equilibration for the incoming gas.

Recording potentiometer, 0 to 1 mv. A 0- to 10-mv. recorder is adequate for most work.

Electrical circuitry, for thermal conductivity detection as described by Dimbat, Porter, and Stross (2). A total bridge current of 110 ma. is supplied by a 6-volt storage battery.

Nitrogen (H.P. dry, Linde Co., New York, N. Y.), delivered at 2 p.s.i.g.

Helium (Air Reduction Co., Inc., New York, N. Y.), delivered at 5 to 10 p.s.i.g.

Nitrogen flow control unit, consisting of two capillary tubes in parallel, 0.25 mm. in inner diameter and 150 and 300 mm. long. The capillaries are used independently or together to give three nitrogen flow rates in the range from 5 to 20 ml. per minute with a pressure head of 2 p.s.i.g.

Helium flow-control needle valve.

Gas flowmeters, rotameter, and soap film meter (3), for the range from 10 to 75 ml. per minute.

Sample tubes, glass, U-shaped with tapered joints, 6 mm. in inner diameter and 300 mm. in total length. The sample bed in these tubes should produce no pressure gradient, and permit rapid heat transfer. With finely divided samples (Table II), the pressure drop was minimized with glass wool loosely threaded through the sample. Additional glass wool at each end of the bed held the sample in place. Tubes 6 mm. in diameter provided sufficiently rapid heat transfer, but much larger diameters were unsatisfactory.

Cold trap, glass, containing loosely packed glass wool, cooled to liquid nitrogen temperature, and located directly ahead of the sample tube to remove moisture and other condensable contaminants from the gas stream.

Sample bypass valve. This bypass permits reducing the flow through the sample bed. Adsorption equilibrium is assured, because with the lower flow rate in the sample tube, the gases and the sample itself are more readily cooled to liquid nitrogen temperature. The time of appearance of the desorption peak, which is used to determine surface area, can be controlled. The peak should be delayed for about 1 minute to allow the flow rate to become stabilized following the temporary upset caused by warming the sample tube. Peak areas are an accurate measure of adsorbed nitrogen only if measured at a constant and known flow rate. The bypass might be eliminated by suitable adjustment of flow rate and volume of exit lines.

Outgassing furnace, in which the sample, contained in a sample tube, can be heated to temperatures up to 500° C. in a flow of helium or nitrogen.

Connecting lines of flexible tubing, such as Tygon (U. S. Stoneware Co., Akron, Ohio). The line between the cold trap and the sample tube is clean, well dried glass tubing to protect the sample from contaminants.

PROCEDURE AND CALCULATIONS

In the procedure selected, the adsorption was measured at three nitrogen partial pressures. The peak area calibration was made using known amounts of nitrogen (absolute method).

A quantity of sample, having preferably 5 to 25 square meters of surface area, is weighed into a sample tube, placed in the outgassing furnace at the desired temperature, and purged with helium at about 20 ml. per minute for 1 hour. The sample tube is cooled, purged with nitrogen, reweighed to determine the dry weight, and connected to the surface area apparatus (Figure 1). The nitrogen-helium total flow rate is adjusted to about 50 ml. per minute, using one of the three possible nitrogen flow rates obtainable from the nitrogen flow control unit. The nitrogen relative pressures, in the range from 0.05 to 0.3, are determined by flow rate measurements for helium alone and for nitrogen plus helium.

When the gas composition is constant throughout the system, as indicated by a constant base line on the recorder chart, the sample tube is immersed in liquid nitrogen to produce the adsorption peak. During the first part of the adsorption, the full flow of 50 ml. per minute is passed through the sample bed. The flow is then split about equally between the sample tube and the bypass line for the final equilibration. When equilibrium adsorption is established, as indicated by a constant recorder base line, the liquid nitrogen coolant is removed from the sample tube to produce the desorption peak.
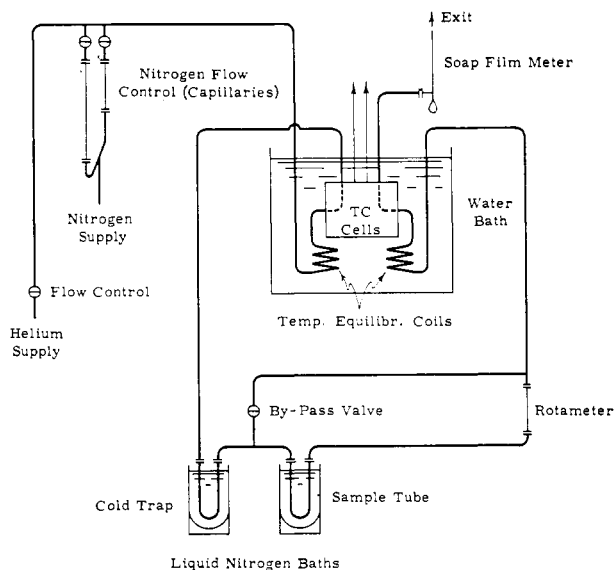

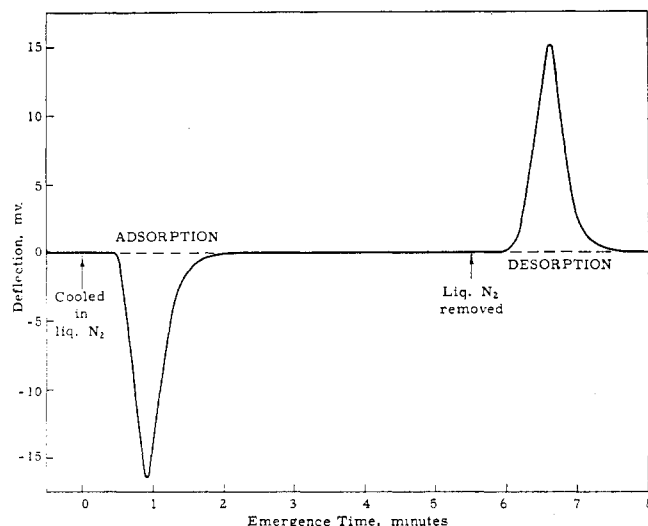Figure 1. Schematic diagram of surface area apparatus

Figure 2. Nitrogen adsorption and desorption curves

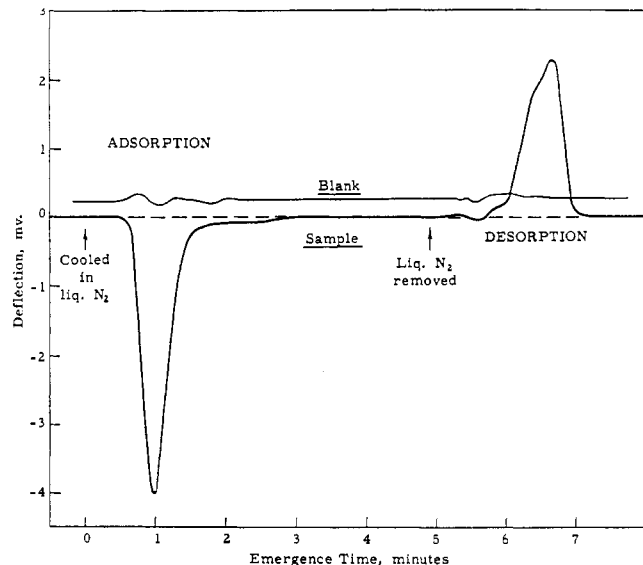Used cracking catalyst, 0.21 gram; surface area, 101 square meters per gram; p/p_0, 0.30

Figure 3. Nitrogen adsorption and desorption curves

Crushed firebrick, 0.75 gram; surface area, 3 square meters per gram; p/p_0, 0.25

Flow through the sample tube is maintained at roughly half the total flow rate. Similar adsorption-desorption chart recordings are obtained at the two other nitrogen partial pressures.

The areas of the desorption peaks are measured with a planimeter and normalized to a flow rate of 50 ml. per minute by multiplying them by the factor, observed flow rate/50. The desorption peaks were used for the determinations, because they were relatively free of tailing effects which were observed with some samples in the adsorption step and can be calibrated more conveniently. Known amounts of nitrogen, 2.33 and 4.45 ml. at standard conditions, were added to half the nitrogen-helium stream. The other half flowed through the bypass. The peak areas were measured and normalized to a total flow rate of 50 ml. per minute. The calibration factor for this study was based on an average of several results.

Data for a used cracking catalyst and the method of calculation are shown in Table I. The calculation is essentially the same as for the pressure-volume method (1), but it is much simpler. No corrections are required for sample cell volume (free space correction). The amount of nitrogen adsorbed, V_a, is obtained by multiplying the peak area, normalized to a flow rate of 50 ml. per minute, by the calibration factor. The relative nitrogen pressures, p/p_0 (x values in Table I) are computed from the ratios of nitrogen flow rates to total flow rates, the barometric pressure, and the saturation pressure of nitrogen (p_0) as determined with a nitrogen vapor pressure thermometer immersed in the liquid nitrogen coolant. The saturation pressure was not determined for each test; 835 mm. was employed for all calculations. This value was representative of the liquid nitrogen coolant.

After computing the amounts of nitrogen adsorbed and the corresponding relative pressures, the amount of nitrogen for a monolayer, V_m, is determined

by a plot of the BET equation (1). The surface area in square meters per gram is calculated as shown in Table I from V_m, the sample weight, and the factor for the area covered by nitrogen, 4.39 square meters per ml. This figure corresponds to a cross sectional area of the adsorbed nitrogen molecule of 16.3 A^2.

RESULTS AND DISCUSSION

Tests were made using between 750 and 70 mg. of five different adsorbents having surface areas in the range from 3 to 500 square meters per gram. Comparative results by this method and by the conventional pressure-volume method are given in Table II. The agreement was rather good. The determinations were made using a single sample of each adsorbent, so that the data do not afford an estimate of the precision. In a few tests the adsorption-desorption cycle was repeated two or more times to verify the desorption peak area; these areas agreed within

the precision of the planimeter measurements, which was about ±2%. Determination of the over-all precision obtainable by the method is in progress.

A typical chart recording, obtained with the sample of used cracking catalyst, is shown in Figure 2. The base line is arbitrarily assigned a value of zero millivolt. The adsorption-desorption cycle is completed in less than 10 minutes. Figure 3 is a similar chart recording for crushed firebrick which has a relatively low surface area, 3 square meters per gram. Tests with this sample were made with 0.75 gram of material and the recorder was operated at full scale, 10 mv. Also shown in Figure 3 is a tracing for a blank test, with the base line slightly raised for clarity, in which the sample tube contained only glass wool in an amount ordinarily used to confine the samples. The area for the blank desorption peak is very small compared with that for the corresponding peak for the

Table I. Data Sheet and Calculations on Used Cracking Catalyst

w	Sample weight after outgassing, gram	0.2096		
	Outgassing temperature, °C.	150		
f	Calibration factor, ml. N_2 per sq. cm. peak area	0.266		
p_b	Barometric pressure, mm.	765		
p_0	Saturation pressure of nitrogen	835		
R_T	Total flow rate, ml. per minute	45.6	51.3	57.4
R_{He}	Helium flow rate, ml. per minute	38.8	38.8	38.8
R_N	Nitrogen flow rate, ml. per minute = $R_T - R_{He}$	6.8	12.5	18.6
A_{obsd}	Observed peak area, sq. cm.	22.6	23.3	22.0
A_{norm}	Normalized peak area, sq. cm. = $A_{obsd} \times R_T/50$	20.6	23.9	25.3
V_a	Volume of nitrogen adsorbed, ml. = $A_{norm} \times f$	5.48	6.36	6.73
p	Partial pressure of nitrogen, mm. = $(R_N/R_T) \times p_b$	114	186	248
x	Relative pressure of nitrogen, p/p_0	0.136	0.223	0.297

Volume of nitrogen for monolayer, V_m (from BET plot), ml. = 4.81.
Surface area, sq. m. per gram = $(V_m)(4.39)/w$ = 101, where 4.39 is sq. m. per ml. of surface covered by nitrogen monolayer.

Table II. Comparison of Methods

Adsorbent	Outgassing Temp., °C.	Surface Area, Sq. M./Gram[a]	
		Continuous flow	Pressure-volume
Firebrick (20 to 30 mesh)	150	3.4	3.1
Furnace black, Pelletex[b] (14 to 48 mesh)	150	25.7	24
Silica-alumina cracking catalyst, used (powder)	150	101	103[c]
Alumina (powder)	500	231	237[c]
Silica-alumina cracking catalyst, fresh (powder)	150	455	438[c]

[a] Single determination.
[b] Godfrey L. Cabot, Inc., Boston, Mass.
[c] Averages of four or more measurements.

sample. With the other samples tested, which have higher surface areas (Table II), the blank is even less of a consideration; in these cases the recorder was operated at full scale, 25 mv., and the blank test gave no observable change in base line.

The large peak areas obtained with the firebrick sample, relative to the blank, indicate that still lower surface areas could be measured readily, perhaps well below 1 square meter per gram. This would be below the limit normally expected of the conventional pressure-volume method.

For greatest accuracy, the flow rate measurements should be corrected for changes in ambient pressure and temperature, which were not taken into account in this study. Also the saturation pressure of nitrogen, p_0, should be measured routinely in each test. Improvements in the apparatus can increase the speed and accuracy. Thus, the gases can perhaps be metered more precisely so that the relative pressures of nitrogen are exactly reproduced from one run to the next. With the apparatus used in these initial tests the flow rates were somewhat variable and had to be checked frequently. An automatic integrator for measuring peak areas would of course save time.

The thermal conductivity response of nitrogen in helium should be investigated. The authors assumed complete linearity over the concentration range employed, which may not be strictly valid. Also an evaluation should be made of the effects of possible impurities in the helium and nitrogen. It may be desirable to purify these gases beyond removal of condensables with a liquid nitrogen trap, as done in this study.

The system nitrogen-helium was selected for exploring the potentialities of the method; however, surface areas could be measured with hydrogen as the diluent. As with the conventional method, it is applicable with various adsorbates (which do not react chemically) at temperatures close to their boiling points. The diluent should not be adsorbed at the temperature employed. Other adsorbate diluent mixtures which may be useful are carbon dioxide at −79° C. or butane at 0° C. in helium, hydrogen, or nitrogen. Other detectors could be used in place of thermal conductivity such as those based on gas density, β-ray ionization, and heat of combustion.

By extending the adsorption measurement to higher relative pressures of nitrogen (p/p_0 from 0.4 to 0.95), information on pore diameter and pore volume could be obtained. The technique described is not restricted to determination of surface area and may prove useful for adsorption studies in general. It would provide a convenient means of comparing adsorption capacities and possibly adsorption rates of various solids.

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Gas-Liquid Chromatographic Analysis Applied to Air Pollution

Sampling

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▶ Probably the greatest need in the study of air pollution is methods for collecting, detecting, and determining trace amounts of organic pollutants. Methods are now proposed by which such pollutants can be collected on cold activated charcoal, transferred to gas-liquid chromatographic columns, and analyzed. The method applies to the range of 1 to 50 p.p.m. when 20-liter samples of air are taken. The efficiency of the combined operations of sampling, handling, and analysis is of the order of 80%. This general method permits detection, determination, and isolation of individual organic compounds.

THE present studies form part of a program undertaken to provide improved analytical methods for air pollution studies. Although reasonably acceptable methods have been available for most inorganic pollutants, no generally valid methods have been developed for organic substances. Chromatographic procedures are now recommended for such studies.

Major problems connected with air pollution have been those of sampling and identifying trace amounts of organic pollutants. The present paper describes the development of a method for the trapping of these traces in a manner suitable for transference to a gas-liquid chromatographic (GLC) column.

The problem of studying gaseous air pollutants resolves itself into three principal steps: sampling, identification, and determination. For sampling, various types of sampling bottles, or

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