

Determination of Specific Surface Area of PVC by a Gas-Chromatographic Technique

We will here report on a rapid method for determination, in the gas chromatograph, of the specific surface area of suspension and bulk PVC polymers. Since high polymers lie somewhat between conventional solids and ordinary liquids with respect to viscosity and the diffusivity of small molecules in the polymer phase, it is not immediately apparent which sorption mechanism will operate in the gas chromatograph with polymers as the stationary phase. We, therefore, have to consider two sorption mechanisms: (a) absorption of solutes in the bulk polymer phase and (b) adsorption of solutes on the polymer surface.

The basic equation in gas-liquid chromatography reads¹

$$V_R = \frac{RT}{\gamma_1 \cdot p_1^0 \cdot M_1} \cdot w \quad (1)$$

where V_R is the retention volume corrected for gas holdup in the column and for pressure drop from the inlet to the outlet of the column; T is the column temperature; γ_1 , p_1^0 , and M_1 are, respectively, the activity coefficient, the saturation vapor pressure, and the molecular weight of the injected substance (the probe molecules); and w is the weight of the stationary phase.

At a given set of experimental conditions (constant gas flow, column temperature etc.), eq. (1) may be written as

$$t_R = \text{const} \cdot w \quad (2)$$

where t_R is the retention time corrected for gas holdup in the column. It has been shown² that in gas-solid chromatography, the corresponding simple relation is

$$t_R = \text{const} \cdot w \cdot S_g \quad (3)$$

where S_g is the specific surface area of the solid. The constant contains in this case parameters describing the sorption on the surface of the stationary solid phase. A prerequisite for both eqs. (2) and (3) is that the probe molecules are injected in so low a quantity that absorption or adsorption takes place at concentrations corresponding to effectively infinite dilution or the linear part of the absorption or adsorption isotherms. These simple relations have been used, after calibration, to determine the weight of liquids coated on solid supports¹ and also to determine surface areas of solid catalysts.²

Smidsrød and Guillet³ observed a sharp minimum in the retention time at temperatures near the glass transition temperature T_g for poly(N-isopropylacrylamide) with *n*-hexadecane as the probe molecule. As an explanation for the phenomena, they proposed that adsorption on the polymer surface was the dominating sorption mechanism below T_g , whereas above T_g penetration of the probe molecule into the bulk of the polymer could take place causing the observed increase in retention volume. Although similar behavior has been found⁴ for poly(methyl methacrylate), poly(vinyl chloride), and polystyrene with long-chain hydrocarbons as the probe molecules, the possibility of utilizing eq. (3) for the determination of surface areas of polymers seems to be unexplored.

Experiments have now been carried out on PVC polymers, of both commercial and laboratory-scale origin, having different specific surface areas as determined in a BET apparatus. Samples from 0.4 to 3 g of the powder were filled into stainless steel columns. A glass wool stopper, 0.1 g, was used to keep the powder packed in one end of the column. The gas chromatograph was a Varian Aerograph 90 P with a thermal conductivity detector and equipped with a 10 ml bubble flowmeter and with extra accessories for temperature regulation of the column to $\pm 0.1^\circ\text{C}$. Hydrocarbons, 0.1 μl , and air, 0.8 μl , were injected, and the retention time was found from the distance between the air and the hydrocarbon peak. Helium was used as a carrier gas.

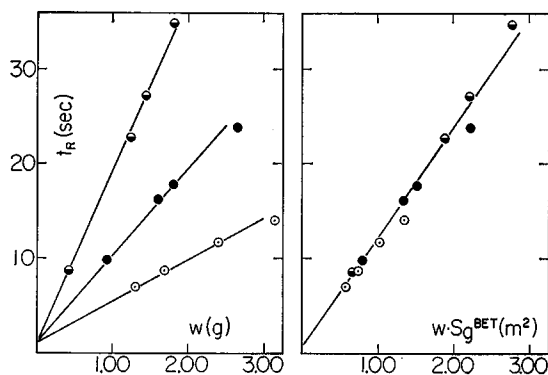


Fig. 1. Retention time t_R as a function of (a) weight w of PVC powders and (b) surface $S_g \cdot w$ of the powders. Gas flow, 40 ml/min; column temperature, 28°C; probe molecule, 0.1 μl n -octane; column diameter, 5 mm; column length 250 mm; (●) $S_g = 1.51 \text{ m}^2/\text{g}$; (●) $S_g = 0.84 \text{ m}^2/\text{g}$; (○) $S_g = 0.43 \text{ m}^2/\text{g}$.

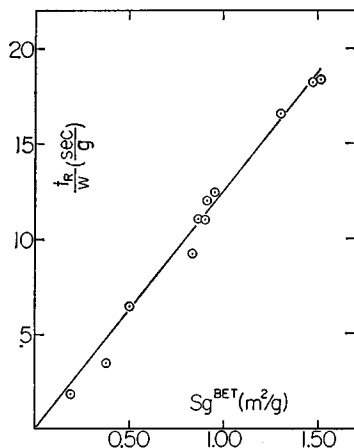


Fig. 2. Specific retention time t_R/w for PVC powders of different specific surface area S_g . Experimental conditions as in Fig. 1.

In Figure 1 are given results from runs with three PVC samples of different specific surface areas with n -octane as the probe molecule and the other experimental conditions as given in the legend. The plotting of the results is according to eqs. (2) and (3) in Figures 1a and b, respectively. The small intercept on the time axis, corresponding to a retention time of about 1 sec, was found to be due to adsorption on the glass wool stopper. When this is taken into account, the results in Figure 1b is a clear verification of the use of eq. (3) for the present system. In all the rest of the experiments, the retention time was corrected for the adsorption on the glass wool stopper.

A series of experiments at different temperatures between 23° and 35°C, at different gas flow between 33 and 50 ml/min, with columns of inner diameter between 3 and 12 mm, with different hydrocarbons from C_7 to C_{10} , and with badly and well-packed columns, revealed that eq. (3) in all cases could explain the results. Suitable experimental conditions were found to be a gas flow rate of 40 ml/min, a temperature of 28°C, and n -octane as the probe molecule. A series of PVC powders of different specific surface

areas were tested at these conditions. The specific retention time, t_R/w , as a function of the specific surface area is given in Figure 2. The result is a straight line, and from its slope the following relationship was found:

$$S_p \left(\frac{\text{m}^2}{\text{g}} \right) = 0.079 \left(\frac{\text{m}^2}{\text{sec}} \right) \cdot \frac{t_R}{w} \left(\frac{\text{sec}}{\text{g}} \right).$$

It is not clear if the scattering of the points in Figure 1 is due mainly to errors in the BET apparatus or in the gas chromatograph. An analysis of the sources of errors in the gas-chromatographic method will be given later when all the details of the present work are published. However, the speed with which the measurement could be carried out made it possible to carry out several measurements on each substance (5 to 10) which showed little spread. The total time needed for testing of a PVC sample with several injections was usually less than three quarters of an hour.

In conclusion, it may be said that, once calibrated, the gas-chromatographic technique seems to constitute a very rapid and accurate method for determining specific surface areas of PVC powders. The method may become valuable for studying morphology of PVC products as well as changes in morphology occurring during the polymerization process.

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