494. *A Study of the Adsorptive Properties of Firebrick in Relation to its Use as a Solid Support in Gas–Liquid Chromatography.*

By J. Bohemen, Stanley H. Langer, R. H. Perrett, and J. H. Purnell.

The adsorptive characteristics of Silocel firebrick have been studied in connexion with its use as a solid support in gas–liquid chromatography. Adsorption isotherms for two organic vapours have been determined by the technique of frontal development chromatography. These were found to be of the Langmuir type and yielded a value for the surface area of the brick of 2·9 m.^{2}/g. The isotherms have been correlated with chromatographic data obtained by the elution method using columns containing dry firebrick.

The adsorptive capacity of the brick has been shown to be very considerably reduced after reaction with hexamethyldisilazane and any remaining adsorption could then be virtually completely suppressed by adding trace quantities of polyethylene glycol (*M*, 400). The possibilities of treatment of other conventional solid supports by hexamethyldisilazane are discussed, and it is suggested that gas–solid chromatographic adsorbents of any desired activity may be prepared by controlled treatment.

The solid particles normally used in gas–liquid chromatographic columns should, ideally, serve only as a support for the chosen involatile solvent; but this is often not the case, and if the weight ratio of support to solvent is more than about 20 : 1, adsorption by the support particles may become significant even though such materials as firebrick are, in fact, only weak adsorbers of most substances. The consequence of this adsorption is that retention volumes are no longer directly proportional to the weight of solvent, and so specific retention volumes can only be reliably measured with columns containing a high proportion of solvent. The fact that these values cannot be extrapolated to lean columns is a considerable inconvenience since it has been shown [1,2] that both efficiency and speed are gained by the use of such columns. In certain circumstances adsorption by the solid support can interfere with analysis even when columns contain a high proportion of solvent. This is particularly the case when polar solutes are involved, as shown by the elution of acetone or methanol from columns containing as much as 20% by weight of squalane on firebrick. Band spreading of the solute is so great that squalane columns can hardly be used for the analysis of mixtures containing polar materials. Since firebrick possesses all the desirable attributes of a column support material, except that of adsorptive inertness, it is worthwhile to study means whereby its adsorptive capacity can be reduced to an acceptable level.

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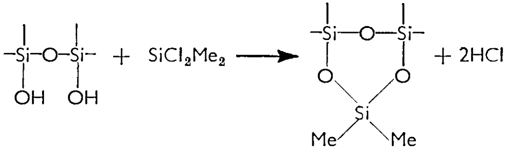
[1] Scott, "Gas Chromatography," 1958, Butterworths, ed. Desty, p. 36.

[2] Purnell, *Ann. N.Y. Acad. Sci.*, 1959, **72**, 592.

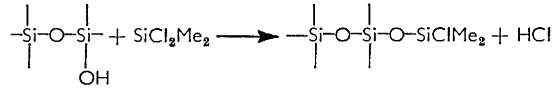
Several methods of pre-treatment of siliceous support materials have been described recently. Among these are acid- and alkali-washing,[3,4] metal deposition,[5] and polymer deposition.[5a] Knight [6] has described an alternative approach in the use of carrier gases saturated with water vapour. For use in gas–solid chromatography active carbon has been partially deactivated by incorporation of small amounts of squalane,[7] and alumina has been similarly treated with silicone oil.[8] None of these methods seems ideal, since, for example, the first two are claimed only to remove alumina and ferric oxide and do little to modify the characteristics of the silica. Metal deposition suffers the drawbacks of expense and, in addition, there is no guarantee that the metals will not react with, or serve as catalytic surfaces for, the reactions of solutes. Finally, saturation of a carrier gas with water or any other vapour calls for close experimental control and is in any case unlikely to be suitable in all systems and with all detectors.

Since the commencement of this work the use of dimethyldichlorosilane, which reacts with hydroxyl groups, has been briefly described.[9] This approach, which is similar to that adopted in this work, seems to be better than those described above, since it is widely assumed that the active adsorption sites in siliceous materials involve hydroxyl groups or electron-rich centres, and their elimination by chemical rather than physical means seems desirable.

Dimethyldichlorosilane presumably reacts with hydroxyl groups located on the silica surface in the following way:



Evidently, two adjacent sites should carry hydroxyl groups for reaction to proceed to completion, and so it is unlikely that there will be complete removal of hydroxyl groups or reactive sites. In the presence of a single hydroxyl group reaction might proceed as follows:



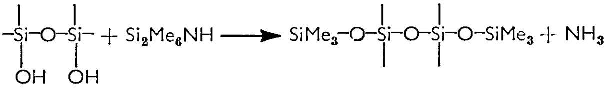
$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{\mathrm{OH}}{\mathrm{Si}}}- + \mathrm{SiCl_2Me_2} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{SiClMe_2} + \mathrm{HCl}$$

The remaining Si–Cl function is likely to confer undesirable properties such as reaction with solute. For example, with water, hydrogen chloride would be formed along with a hydroxylated surface similar to that of the original material.

The approach adopted in this work was suggested by the knowledge that hexamethyldisilazane reacts quantitatively with hydroxyl groups [10,11] according to the reaction

$$\mathrm{SiMe_3{\cdot}NH{\cdot}SiMe_3} + 2\mathrm{OH}^- \longrightarrow 2\mathrm{SiMe_3{\cdot}O}- + \mathrm{NH_3}$$

or, as envisaged on a silica surface



$$-\overset{|}{\underset{\mathrm{OH}}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{\mathrm{OH}}{\mathrm{Si}}}- + \mathrm{Si_2Me_6NH} \longrightarrow \mathrm{SiMe_3}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{SiMe_3} + \mathrm{NH_3}$$

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[3] James and Martin, *Biochem. J.*, 1952, **50**, 679.

[4] Liberti and Cartoni, " Gas Chromatography," 1958, Butterworths, ed. Desty, p. 248.

[5] Ormerod and Scott, *J. Chromatog.*, 1959, **2**, 65.

[5a] J. H. Knox, personal communication.

[6] Knight, *Analyt. Chem.*, 1958, **30**, 2030.

[7] Eggertson, Knight, and Groennings, *Analyt. Chem.*, 1956, **28**, 303.

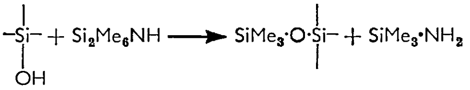
[8] Scott, *J. Inst. Pet.*, 1959, **45**, 424.

[9] Kwantes and Rijnders, " Gas Chromatography," 1958, Butterworths, ed. Desty, p. 63.

[10] Langer, Connell, and Wender, *J. Org. Chem.*, 1956, **23**, 50.

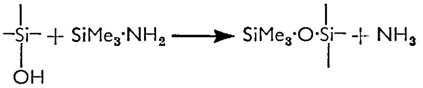
[11] Langer, Pantages, and Wender, *Chem. and Ind.*, 1958, 1664.

the reactive hydroxyl groups being quantitatively replaced by a group which may be expected to be very considerably less active as an adsorption site. Since the reaction probably proceeds in two stages with, in the first,



$$-\underset{\text{OH}}{\underset{|}{\overset{|}{\text{Si}}}}- + \text{Si}_2\text{Me}_6\text{NH} \longrightarrow \text{SiMe}_3\cdot\text{O}\cdot\underset{|}{\overset{|}{\text{Si}}}- + \text{SiMe}_3\cdot\text{NH}_2$$

followed either by



$$-\underset{\text{OH}}{\underset{|}{\overset{|}{\text{Si}}}}- + \text{SiMe}_3\cdot\text{NH}_2 \longrightarrow \text{SiMe}_3\cdot\text{O}\cdot\underset{|}{\overset{|}{\text{Si}}}- + \text{NH}_3$$

or by

$$2\text{SiMe}_3\cdot\text{NH}_2 \longrightarrow \text{Si}_2\text{Me}_6\text{NH} + \text{NH}_3$$

hydroxyl groups at adjacent sites are not necessary to the reaction, a fact borne out by the quantitative yield of ammonia obtained in reactions with known concentrations of hydroxylated materials. Water or hydroxyl groups on the surface of compounds of aluminium, iron, or other impurities will obviously also be removed by the silazane and their prior removal becomes unnecessary.

It is not to be expected that this treatment of siliceous or other support materials will entirely eliminate their adsorptive properties but, as is shown later, the small amount of residual adsorption can be suppressed to an acceptable level by the additions of extremely small quantities of polar liquids with good spreading properties such as the polyethylene glycols.

EXPERIMENTAL

Treatment of the Support.—All the work described here was carried out with Silocel firebrick. This was sieved dry and then wet and residual fines were removed by sedimentation. The material was then dried under vacuum at 150°.

25 g. of this sample, while still warm, were covered with a mixture of 80 ml. of light petroleum (b. p. 60—80°) and 15 ml. of hexamethyldisilazane. The mixture was heated on a steam-bath and refluxed for 1 hr. A drying tube of calcium sulphate was used at the condenser exit. After refluxing, 2 ml. of n-propanol were added. This helps materially by wetting the firebrick, and although it reacts with unchanged hexamethyldisilazane to form $\text{SiMe}_3\cdot\text{OPr}$, this in turn reacts with hydroxyl groups in the same way as the parent silazane. After 30 hr. the mixture was again refluxed for several hours. The firebrick was then washed with light petroleum (2 × 50 ml.), then n-propanol (1 × 50 ml.), and then again with light petroleum (2 × 50 ml.). Finally, it was filtered off and dried for 2 hr. on a steam-bath in an atmosphere of nitrogen.

Preparation of Columns.—Columns were prepared in stainless-steel tubes, and the method of packing and the chromatographic apparatus were those already described elsewhere.[2]

The elution chromatographic apparatus was operated with a double-channel thermal conductivity cell. One arm of this cell was sited at the outlet end of the column, and the other was situated at the inlet end between the point of sample injection and the column head and as near to the latter as possible. In consequence of this arrangement, an " injection peak " appeared on every chromatogram, its size and width being a measure of the reproducibility of the injection. These injection peaks appear on the " negative " side in the chromatograms shown later, being followed when vapour samples were used by an air peak, also negative, and finally by the peak of the solute under study. The distance between the air peak and the solute peak is clearly a measure of the retention of the solute. If they were superimposed the retention would be zero. Improved performance of the firebrick *i.e.*, reduced adsorption, is therefore indicated by closer correspondence of the air and solute peaks in the chromatograms obtained with columns containing only packing and no solvent, *i.e.*, the extent of solute adsorption becomes comparable to that of an inert gas.

Determination of Adsorption Isotherms.—To assist in the evaluation of the chromatographic results, attempts were made to determine adsorption isotherms of certain solutes on the various supports by conventional B.E.T. and gravimetric methods. The adsorption was in each case, however, so feeble that useful data could not be obtained. The chromatographic technique of frontal development is capable of yielding data from which adsorption isotherms may be constructed and the method has been applied by Phillips and his collaborators [12] in studies of adsorption of vapours by charcoal. In consequence, this method was adopted in this work; it gave reasonably consistent results.

The apparatus consisted of a pre-mixing system for introducing streams of nitrogen and vapour of known composition into a column of the material under study. Detection of eluted material was made by a thermal conductivity cell, the signal being fed to a Foxboro e.m.f. Dynalogue recorder. The chromatograms obtained were the usual step-type diagrams. It is hoped to describe this apparatus and further results in greater detail later.

RESULTS AND DISCUSSION

Fig. 1 illustrates chromatograms obtained in the elution by nitrogen, at constant flow rate, of cyclohexane, acetone, and benzene from each of four columns. These columns, which were as nearly as possible identical in length, diameter, and packing density, contained: (*A*) Johns-Manville Silocel firebrick (C.22) untreated in any way. (*B*) Firebrick which had been treated with hexamethyldisilazane. (*C*) Untreated firebrick to each 1 g. of which had been added 0·001 g. of polyethylene glycol 400. (*D*) Hexamethyldisilazane-treated brick to which had been added polyethylene glycol as in (*C*).

FIG. 1. *Elution by nitrogen of* (1) *cyclohexane,* (2) *benzene, and* (3) *acetone at* 50° *from* 1·5 *m.* × 0·5 *cm. columns containing*: (A) *untreated firebrick*; (B) *firebrick treated with hexamethyldisilazane*; (C) *untreated firebrick* +0·1% *of polyethylene glycol* 400; (D) *treated firebrick* +0·1% *of polyethylene glycol* 400. (Sample injection at right of each chromatogram, " negative " peak is air.)

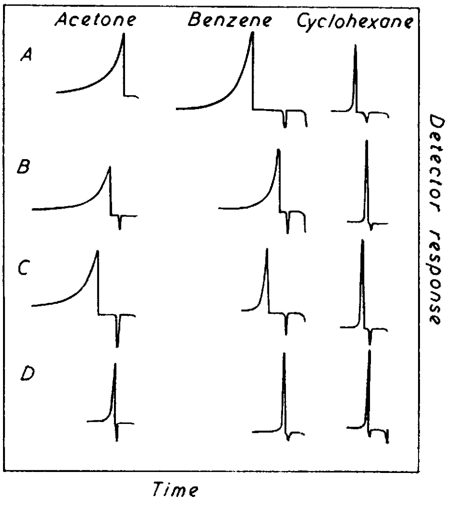
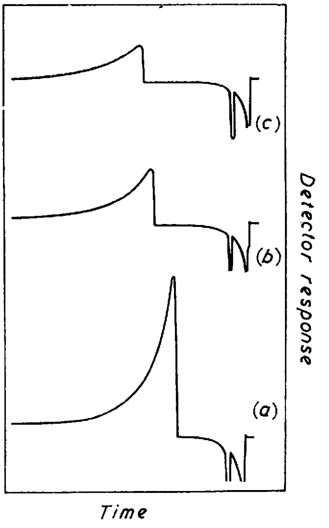


FIG. 2. *Effect of benzene sample size on peak position and shape.* Elution by nitrogen at 50° from 150 cm. × 0·5 cm. column of untreated firebrick. First " negative " peak is sample at column head, second is air emerging from column outlet. Sample sizes: (*a*) 0·5 ml.; (*b*) 1·0 ml.; (*c*) 2·0 ml. of vapour.



We consider first the chromatograms obtained with column *A*; cyclohexane is the solute least strongly retained by the natural brick, acetone being more strongly retained and showing, in addition, marked asymmetry of its peak. Benzene, the most strongly retained of the three solutes, like acetone, yields highly distorted peaks.

The extent of retention and the degree of asymmetry of the resulting peaks is to a large extent determined by sample size. Fig. 2 illustrates this for the elution of benzene from

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[12] James and Phillips, *J.*, 1954, 1066.

column *A*. With increasing benzene sample size the peak broadens, the front appearing earlier. It is noteworthy that the back of the peak hardly changes position with sample size and, in fact, if the various peaks are superimposed the tails merge and reach the base line at the same point. This behaviour, which was also observed for acetone, methanol, n-propanol, hex-1-ene, and acetaldehyde, would seem to imply an adsorption isotherm of the Langmuir type in which a saturation limit is reached.

Comparison of the curves obtained with column *B* (Fig. 1) with those from column *A* immediately shows the marked reduction of adsorption following from treatment of the firebrick with hexamethyldisilazane. Not only do the peaks emerge very much sooner, that is, closer to the air peak but they are narrower although still somewhat asymmetric for benzene and acetone. A similar improvement, though nothing like as great, is effected by addition of a trace of polyethylene glycol to untreated brick. This is evident from the curves for column *C* also shown in Fig. 1.

The result of combining the treatment of the brick with hexamethyldisilazane with the addition of the polyethylene glycol is shown in diagrams *D* of Fig. 1, and there is no doubt that adsorption has been effectively eliminated. For all three solutes the chromatographic and air peaks are virtually superimposed, the difference between them corresponding only to about 2 ml. of gas flow. This quantity is partly residual adsorption and partly retention by the very small amount of polyglycol. The latter is of no significance for the solutes studied, but for high molecular-weight solutes might result in an appreciable retention. However, this could be turned to good account, since the column might well be used as it stands for very rapid analysis of high-boiling mixtures at low temperatures.

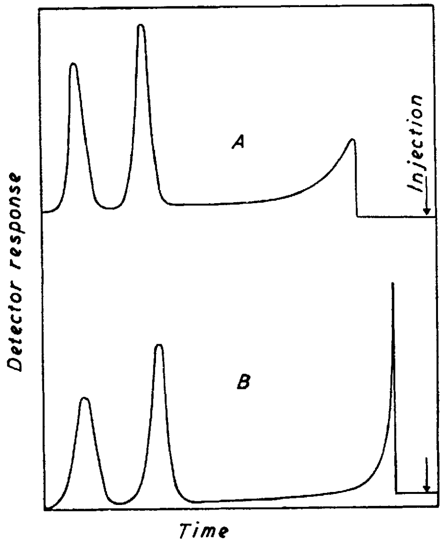


FIG. 3. *Chromatograms of mixture of cyclohexane, benzene, and acetone from columns* 120 *cm.* × 0·5 *cm. of* 20% *squalane on firebrick.* (*A*) *Untreated brick*; (*B*) *hexamethyldisilazane-treated brick.* Flow rates are the same and the carrier gas was nitrogen at 50°. Order of elution: acetone, benzene, and cyclohexane.

Fig. 3 shows a comparison of chromatograms of mixtures of cyclohexane, acetone, and benzene obtained with columns containing packings of 20% by weight of squalane on firebrick. The upper chromatogram was obtained with normal firebrick, while the lower was obtained with hexamethyldisilazane-treated brick. The acetone peak is highly distorted when untreated brick is used but when treated material is employed there is a considerable improvement. It is apparent that, after treatment, firebrick is more suitable as support for non-polar solvents in the analysis of polar materials. A point of importance brought out in Fig. 3 is that, even with a column containing as much as 20% by weight of squalane, the retention of acetone is, in large part, the result of adsorption by the support and not just due to solution in the squalane. Obviously, great care should be taken when specific retention volumes are measured in systems of this type. The fact that the retention volumes of the hydrocarbons are the same with both columns while those of acetone are different suggests that the adsorption sites for the different types of solute differ in some way, those operative in benzene adsorption being suppressed by the large amount of squalane present while those at which acetone is held are still available.

While the addition to a column of such a small quantity of polyglycol as 0·1% is of little consequence in terms of the added retention, for example, the retention of benzene by 20% squalane would be nearly 1000 times as great as that due to the polyglycol, it would be more satisfying in some respects if the solution to the adsorption problem could be found entirely through chemical means.

FIG. 4. *Adsorption isotherms for acetone vapour at* 50°. (1) Untreated brick; (2) hexamethyldisilazane-treated brick; (3) untreated brick with 0·1% of polyethylene glycol 400.

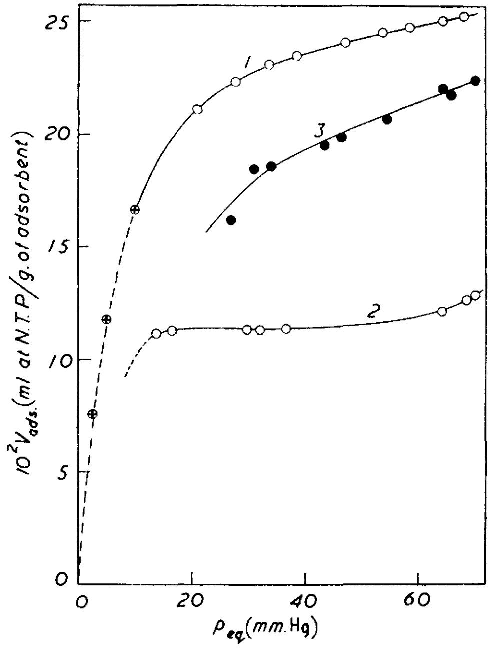
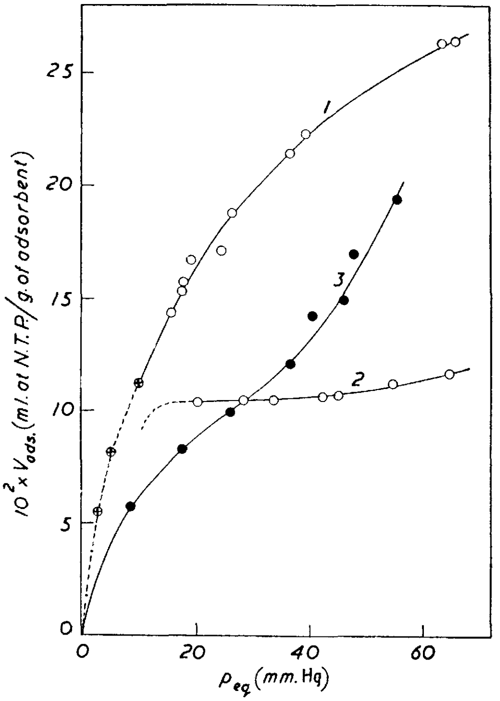


FIG. 5. *Adsorption isotherms for benzene vapour at* 50°. (1) Untreated brick; (2) hexamethyldisilazane-treated brick; (3) untreated brick with 0·1% of polyethylene glycol 400.



Adsorption Isotherms.—The adsorption isotherms for acetone and benzene on (1) untreated firebrick, (2) firebrick treated with hexamethyldisilazane, and (3) firebrick with 0·1% (w/w) of polyethylene glycol 400 are illustrated in Figs. 4 and 5. The curves obtained with untreated firebrick are very similar, although they cross at a partial pressure of adsorbate of 50 mm. The general form of these curves is consistent with Langmuir-type adsorption, as was suggested earlier on the basis of the observed chromatographic effects (see Fig. 2). Further confirmation of this view is obtained from Fig. 6, in which the data of Figs. 4 and 5 are replotted in the form $1/V_{ads.}$ against $1/p_{eq}$. The data for both acetone and benzene yield satisfactory straight-line plots, within the precision of the measurements. The area of the benzene molecule being assumed to be 31 Å^2,[13] the inter-

[13] McKee, *J. Phys. Chem.*, 1959, **63**, 1256.

cept on the $1/V_{\text{ads.}}$ axis yields a surface area of 2·9 m.^{2}/g., in excellent agreement with the value recently reported by Lee, Wall, and Baker,[14] who used nitrogen adsorption at low temperature. The points on curves (1) shown as crosses within circles and located on the broken lines, were calculated from Fig. 6. A further possible check on the surface area obtained in this work can be made by comparison with recent measurements for the adsorption of benzene vapour on silica gel reported by McKee.[13] The saturation value reported by him, about 80 c.c. of vapour at N.T.P., is close to 270 times that found in this work. By simple analogy, we would expect the silica gel used by McKee to have a surface area of about 780 m.^{2}/g., which may be compared with his reported values ranging from 500 to 600 m.^{2}/g.

The isotherms for the hexamethyldisilazane-treated firebrick are virtually identical for acetone and benzene. Owing to experimental difficulties, it was not possible to extend measurements to pressures as low as would have been wished. All of the points obtained fell on a plateau, and the form of the isotherm at lower pressures can only be supposed to be similar to that for untreated firebrick. However, it is clear from the diagrams that saturation of the treated firebrick is reached at about one tenth of the equilibrium pressure for saturated untreated firebrick. Further, the height of the plateau for the treated firebrick is, at most, one third of the value to be expected for the untreated material. Clearly, the treatment is very effective in suppressing the adsorptive characteristics of firebrick, and it should be borne in mind that the material used in the experiments cited had not received the most effective form of treatment. There is good reason to suppose that the chemical treatment can be used to reduce adsorption even more significantly.

Fig. 6. *Langmuir plots of adsorption isotherms* (Figs. 4 and 5).

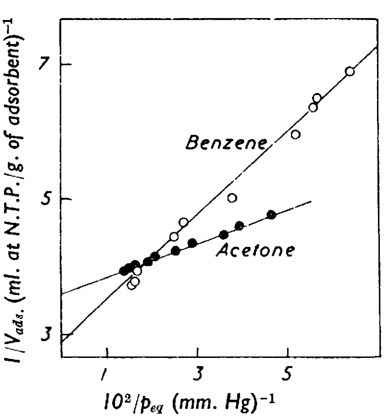
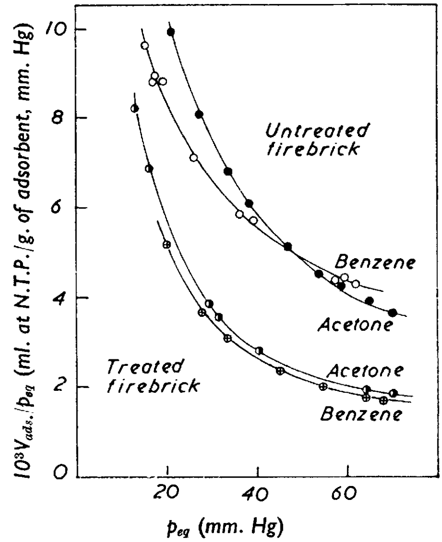


Fig. 7. *Plots of effective partition coefficient against partial pressure for benzene and acetone vapours with untreated and treated brick.*



The isotherms for firebrick with 0·1% of polyethylene glycol lie generally between those discussed above. In form, they are more similar to those for untreated firebrick than to those for the treated substance. This is particularly true for acetone adsorption, where the curve virtually parallels that for the untreated firebrick. No saturation limit was reached in the experiments, though these extended to 10% of vapour in nitrogen,

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[14] Baker, Lee, and Wall, 2nd Intern. Sympos. of I.S.A., Lansing, Michigan, June, 1959.

a value probably never attained in elution gas chromatography. Thus, while the polyglycol certainly reduces the amount of adsorption observed, the extent of this is not comparable with that resulting from chemical treatment.

Fig. 7 illustrates plots of effective partition coefficients against equilibrium pressures of adsorbate for acetone and benzene on untreated and hexamethyldisilazane-treated firebrick. From these it is evident that, with increasing size of sample of adsorbate, we may expect reduced retention times in a chromatographic column. Since the tail of a chromatographic elution peak is a region of very low concentration, we might expect that in experiments such as are illustrated in Fig. 3 the position of the tail of the peak for any given column would be reasonably constant. This was found. The effect of increased sample size in chromatographic experiments would, therefore, be most evident as a reduced retention of the high concentration region of the elution band, that is, in this instance, the front. The net result of these conclusions is that increasing sample size would lead to band-spreading in the forward direction, as observed.

More detailed consideration of the isotherms shown reveals certain discrepancies, particularly in the shape of the isotherms obtained with firebrick carrying polyglycol. While the acetone curve closely parallels that for untreated firebrick the corresponding curve for benzene shows a curious curvature at the high-pressure end. So far as can be ascertained, this curvature is real. The difference in the shape of the isotherms may again reflect a difference in the nature of the adsorption sites active towards benzene and acetone such as was suggested earlier in the light of the chromatographic data. It is clearly impossible, without detailed investigation, to clarify this point.

A further point of interest is the apparent increase, at high pressures, of the extent of adsorption by treated firebrick. Again, there seems no obvious reason why this should not be a real effect and, if so, it would seem to indicate the onset of significant capillary condensation. Since, however, the pressure region in which this is observed is so high, it is unlikely to be an important factor in gas–liquid chromatography, particularly since much of the porous structure will be filled with solvent.

In view of the improved characteristics of firebrick as a chromatographic support after treatment with hexamethyldisilazane, there seems little doubt that the treatment could be successfully applied to other materials such as Celite or Chromosorb, and even to conventional gas–solid adsorbents such as alumina or silica gel, which are known to have hydroxylated surfaces. The possibility exists that the latter might be modified in such a way as to produce adsorbents of any desired activity. Work along these lines is proceeding.

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