A NEW GAS-LIQUID CHROMATOGRAPHIC PHASE

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This paper is a preliminary communication which describes the preparation of a new type of gas–liquid chromatographic phase where the stationary phase is chemically bonded and attached to the support phase.

The existence of silanol groups on various silica gels has been shown by thermal decomposition, lithium aluminium hydride reduction, and infra-red spectroscopy. WARTMANN AND DEUEL[1] have formed a number of organic derivatives of silica gels with Si–O–C bonds:

$e.g.$ Si—OH + SOCl$_2$ → SiCl + SO$_2$ + HCl

Si—Cl + ROH → Si—O—R + HCl
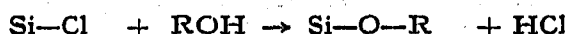
Although "R" groups containing up to 18 carbon atoms were attached to such silica gels, all were relatively easily hydrolysed. Derivatives of "silica chloride" having Si–C bonds were also prepared:

(a) Si—Cl + ClMgR → Si—R + MgCl$_2$

(b) Si—Cl + LiR → Si—R + LiCl

Similar reactions coupling organic groups to colloidal silicic acid, silica, and even quartz have been described by WEISS and co-workers[2-4].

EXPERIMENTAL

Preparation of the phase

Celite 545 (acid and alkali–methanol washed) was dried by heating at 600° for 10 h.

To this dry Celite 545 (39.70 g) was added pure redistilled n-hexadecyltrichlorosilane (11.40 g) and about 500 ml of sodium dried light petroleum spirit (b.p. 60–80°). The resultant mixture was then shaken for 5 h in a closed vessel, and the light petroleum was then removed under reduced pressure (0.1 mm). The powder
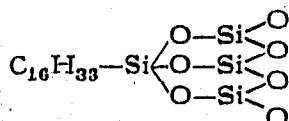
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so formed was then shaken vigorously in a flask fitted with a Dreschel head, through which was passed a continuous stream of warm air saturated with water vapour. Copious fumes of hydrogen chloride were evolved for some hours, and the air stream was stopped when no further hydrogen chloride could be detected in the exit stream – after about 12 h.

The resultant damp material was dried for about 12 h at 60°, 0.1 mm pressure. The dried material was then used for gas chromatography (Phase I).

Subsequently a batch of Phase I was treated with hexamethyldisilazane after the manner of PERRETT AND PURNELL[5], in order to remove any "active" centres.

Thermal analysis of the phase

On the assumption that the organic grouping n-$C_{16}H_{33}$ is attached to the Celite surface in the form of:

$$C_{16}H_{33}-Si \left< \begin{matrix} O-Si \left< \begin{matrix} O \\ O \end{matrix} \right. \\ O-Si \left< \begin{matrix} O \\ O \end{matrix} \right. \\ O-Si \left< \begin{matrix} O \\ O \end{matrix} \right. \end{matrix} \right.$$

then from the example of the preparation given above, the total organic content ($C_{16}H_{33}$) would be expected to be 14.5 % w/w of the whole material.

Thermal analysis of the final product gave an ash of 86.1 %, by weight, giving an indirectly analysed organic content of 13.9 %. This was thought to be in excellent agreement with the value predicted from the reactant quantities.

Chromatographic characteristics of hexadecyltrichlorosilane/Celite combined phase

Gas chromatography was carried out on a Griffin and George D. 6 Gas Density Balance chromatograph, using a 2 m, 0.6 cm O.D. stainless steel U column containing about 12 g of the combined phase/support. The column was operated at successively increasing temperatures up to 250°. At each stage, after a little initial bleed-off of volatile material, consistent retention and chromatographic characteristics were obtained over substantial operating periods. There was no evidence of any decomposition of the phase in continual operation at 250°.

The phase was compared under similar operating conditions with a freshly prepared phase of 15 % E. 301 Silicone Oil on 36–60 mesh acid and methanol washed Celite which gave closely similar retention times.

Examples of various classes of compound, and various mixtures were successfully chromatographed: benzene, acetone, neohexane, octene-1, heptyne-1, nonadiyne-1,8, n-pentyl acetate, tetrachloroethylene, n-pentanol, trimethyl-n-hexylsilane, trimethylethoxysilane, tri-n-propylsilane, trimethylstannane (thermal breakdown above 75°), petroleum ethers in ranges from 40–60° and 300–325°, methyl-n-butyldichlorosilane, tetraethylplumbane, essential oil extracts, and phosphonitrilic fluorides and chlorides.

No effective chromatography was possible for methanol, formic acid, n-butylamine, thiophene and silylamines, these either showing breakdown or greatly distorted peak shape. However, similar characteristics were observed on Silicone Oil for these compounds.

In general, peak symmetry and column efficiency was greater for the combined phase than for the silicone oil phase. The separation of a complex tretaalkylsilane mixture is shown in Fig. 1, using both phases, the boiling range being 26° to 280°. The much improved selectivity for close-boiling isomers is seen. A comparison of column efficiency estimated for the same component (*n*-propyltri-*n*-butylsilane) in each chromatogram, gave values for *n* (the number of theoretical plates) as $\simeq$ 1750 for the silicone oil column as against $\simeq$ 2300 for the combined phase.
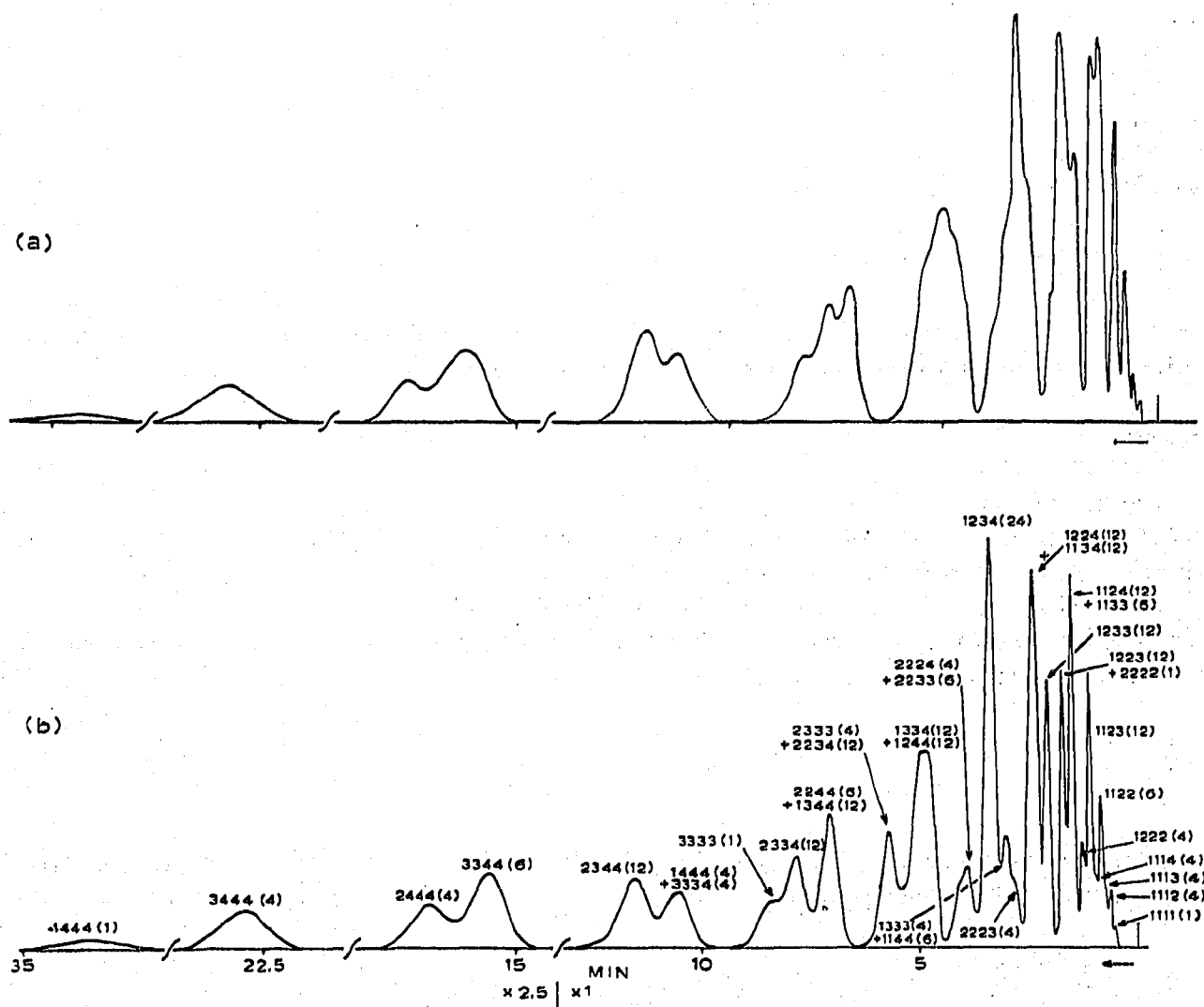

Fig. 1 (a) Chromatogram of redistribution products from methylethyl-*n*-propyl-*n*-butylsilane on 15% (w/w) E.301 Silicone Oil on Celite at 150°. (b) Chromatogram of redistribution products from methylethyl-*n*-propyl-*n*-butylsilane on the "combined hexadecylsilane/Celite phase." 1 = methyl; 2 = ethyl; 3 = *n*-propyl; 4 = *n*-butyl. Theoretical proportions for random redistribution are shown in brackets.

It was noted that less tailing of peaks occurred on the combined phase for all the classes of compounds studied.

Although relative selectivity between different types of compound has not been extensively studied, appreciable selectivity is given in Table I.

Only in the case of chlorosilanes containing the highly active Si–Cl groups was any interaction with the phase found (presumably due to reaction with unblocked Si–OH groups). Small percentages of these materials present in mixtures were absorbed, even after treatment of the phase with hexamethyldisilazane, although only a small proportion of a complete chlorosilane sample was lost under similar conditions.

TABLE I

| Compound	t_R' (combined phase)* $\overline{t_R'\text{ E.301}}$
$(CH_3)_3SiC_6H_{13}{}^n$	1.15
$(C_3H_7{}^n)_3SiH$	1.26
$CH_3 \cdot C_4H_9Si^nCl_2$	1.24

* t_R' = adjusted retention time.

This effect has, in fact, proved useful in distinguishing small quantities of chlorosilane by-products produced in catalysed redistribution reactions of alkylsilanes.

DISCUSSION

Structure of the phase

If it is assumed that the Celite support material is a complex matrix, then two possibilities are open for the bonding of the hexadecylsilyl group to it; they are (1) by direct reaction, and (2) by adsorption and hydrolysis.

(1) Direct reaction. Assume initially that after initial drying the silicate structure is of the form:
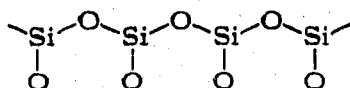

When this is perfectly dry, hexadecyltrichlorosilane will have no reaction with the chain, but by the passage of moist air, we can achieve structures as follows:
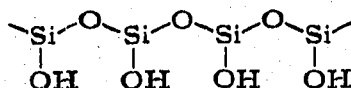
This may then react with the chloro-groups on the long chain silicon compound forming structures of the type:
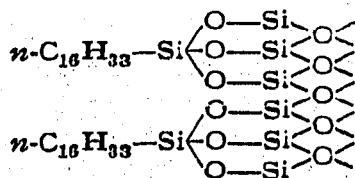
However, if some hydrolysis between chloro-groups also takes place, then the following type of structure is also feasible:

$$n\text{-}C_{16}H_{33}\text{-}Si\underset{\diagdown O\text{---}Si}{\overset{\diagup O\text{---}Si}{\diagup}}\cdots$$
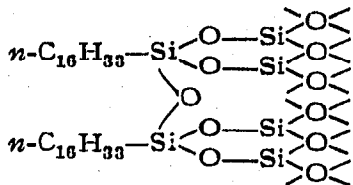
In this case the Celite surface would be covered by a "skin of combined polymer".

(2) *Adsorption and hydrolysis.* The alternative to (1) is to postulate that after the initial drying of the Celite, it adsorbs the *n*-hexadecyltrichlorosilane in the usual manner. When damp air is passed through the mixture, the chloro-groups hydrolyse and combine amongst themselves forming networks of polysiloxanes in three dimensions throughout the three-dimensional silicate network of the original Celite.

This type of reaction is naturally very difficult to differentiate from (1) but it is felt that if (2) does take place it is to a minor extent only. The reasons are as follows:

(a) With (2) we would expect to notice that different batches of the same material would show irreproducible retention data, due to inhomogeneity of the phase through inhomogeneous condensation reactions. This is not the case.

(b) When subjected to thermal pyrolysis there was no gradual loss in weight, as might be expected if low molecular weight polymers were present. The phase broke down sharply at around 320°, the region expected for C–Si bonds under the oxidising conditions of the thermobalance. Also treatment of the phase with a number of solvents in attempts to solvent extract low molecular weight polymers failed completely.

Thus it is thought probable that this type of phase is of the form described in (1), although the possibility of (2) is not discounted.

Advantages of the combined phase

The active solvent group is chemically bonded to the –Si–O matrix with no apparent diminution of solute–solvent interaction, and thus there is no danger of deterioration of resolving efficiency due to breakdown of uniformity of phase coating on the support particles. Such decrease in column efficiency is commonly observed in the use of Apiezon-type greases and high molecular weight Silicone Oils at column temperatures up to 250°.

The greatly enhanced temperature stability enables the resolution which might be obtained from a $n\text{-}C_{16}H_{34}$ hydrocarbon solvent to be employed up to at least 250°. The preparative methods could perhaps be extended to include other active solvent groups in such combination, giving specific selectivity for various classes of compound.

Resolution is notably superior to that obtained on a silicone oil column operated under similar conditions, both improved peak symmetry and better resolution being noted for a wide range of compounds.

There is an added advantage that it should be possible to clean the phase, should it become contaminated, by the use of suitable solvents, since there is little possibility of Si–O–C bond breakage. Once any low-boiling material is removed, there should be no bleed-off under any normal operating conditions.

The phase could well prove useful for employing with ionisation detectors, where high stability and minimum bleed-off is essential.

SUMMARY

The preparation of a new type of gas–liquid chromatographic phase (where the stationary phase is most probably chemically bonded to the support phase) is described. A brief comparison between this phase and a conventional silicone oil phase for gas chromatography is made.

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