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# Suppression of the effect of metal impurities in alkylsilylated silica packing materials

## Kazuhiro Kimata, Nobuo Tanaka* and Takeo Araki

*Kyoto Institute of Technology, Department of Polymer Science and Engineering, Matsugasaki, Sakyo-ku, Kyoto 606 (Japan)*

## ABSTRACT

Octadecylsilylated silica packing materials prepared from octadecyltrichlorosilane showed much better performance than those prepared from octadecyldimethylchlorosilane for chelating compounds that can interact with metal impurities in the silica support. Stationary phases containing an ether linkage in the alkyl group also showed improved performance. The presence of polar groups and the increased hydrophilicity of such stationary phases can account for the results based on the better accessibility of metal sites in a hydrophobic stationary phase. Similar results were obtained with carboxylic acids and phenols. Packing materials prepared from high-purity silica gel showed good performance for all the solutes studied, regardless of the functionality of the silylating reagents.

## INTRODUCTION

The retention of a solute in reversed-phase liquid chromatography (RPLC) is primarily determined by the interactions between the solute and aqueous–organic solvents in the mobile phase and between the solute and the alkylsilyl groups on silica surfaces containing solvent molecules extracted from the mobile phase [1–4]. In addition to these essential constituents of RPLC systems, surface silanols and metal impurities are known to participate in the retention of solutes.

The sources of undesirable secondary retention processes which cause peak tailing in RPLC were accessible silanols, surface acidity and metal impurities [5–14]. The binary metal oxide structures provided by the presence of metals other than silicon in the silica skeleton seem to provide surface acidity as in silica–alumina acidic catalysts [14–16]. The metal impurities also participate in the interaction with chelating reagents [14,17].

Much effort has been made to eliminate these secondary retention processes from silica-based packing materials. Trimethylsilylation (end-capping of silanols) proved to be effective for reducing the effect of hydrogen bonding between silanols and proton acceptors. Extensive alkylsilylation, however, was not totally successful in eliminating tailing associated with amines and chelates, and sometimes showed adverse effects for carboxylic acids and phenols [18].

The effects of isolated silanols can be minimized by hydrating the silica surface by using hydrofluoric acid and other bases [5]. The effects of surface acidity caused by metal impurities on the elution of amines can be suppressed by the use of mobile phase additives or by treating silica gel with hydrochloric acid or nitric acid prior to alkylsilylation [11,13]. The acid treatment reduces the metal content of the silica gel. This treatment, however, was insufficiently complete to eliminate the effect of metal impurities on the elution of chelating reagents.

The use of high-purity silica gel as a support, particularly in combination with polymer coating, has been shown to be very effective in eliminating all the secondary retention processes related to metal impurities in silica [13,14,19,20]. However, the availability of high-purity silica gel is relatively limited at present. The polymer coating cannot be readily carried out in common laboratories. More practical

ways to eliminate the secondary retention processes related to metals would be valuable in this respect.

We report here that the extent of the undesirable secondary retention process related to metal impurities is strongly dependent on the hydrophobic property of the stationary phase, and that RPLC packing materials containing some hydrophilic groups can perform much better with metal-interacting solutes even in the presence of metal impurities. Such hydrophilic groups can be easily introduced into the stationary phase by using octadecyltrichlorosilane or an alkylsilane containing an ether linkage in the alkyl group. These stationary phases are easy to prepare, not requiring high-purity silica gel, and can provide a practical solution for reducing the secondary retention process for chelating compounds, carboxylic acids and phenol derivatives.

EXPERIMENTAL

*Materials*

Two types of silica gel particles [Develosil, 5 $\mu$m, 330 m$^2$/g (Nomura Chemicals, Seto, Japan) and Kromasil, 5 $\mu$m, 340 m$^2$/g (Eka Nobel, Surte, Sweden)] were used to prepare $C_{18}$ packing materials with octadecyldimethylchlorosilane (I), octadecylmethyldichlorosilane (II) and octadecyltrichlorosilane (III), with end-capping (designated as T) or without. The silica gels were treated with 6 $M$ hydrochloric acid (10 ml/g silica) under reflux for 2 h. This process was repeated three times. The alkylsilylation was carried out in dry toluene and dry pyridine as described previously [21]. Octadecylsilyl-

ation was repeated twice to ensure maximum surface coverage with octadecyl groups.

Octadecylsilylating and trimethylsilylating reagents were purchased from Petrarch Systems (Bristol, PA, USA). Tetradecyloxypropyldimethylchlorosilane [E: $C_{14}H_{29}O(CH_2)_3Si(CH_3)_2Cl$] was prepared by the reaction of allyl tetradecyl ether with dimethylchlorosilane in the presence of platinum catalyst. Other chemicals were of analytical-reagent grade obtained from Nacalai Tesque (Kyoto, Japan).

For the study of the effect of highly acidic silanols, heat treatment of silica particles was carried out at 700°C for 7 h in a ceramic pot. Thermally treated silica was cooled, then refluxed in 6 $M$ HCl for 2 h to rehydrate the surface. Thermal treatment is designated as H and the subsequent acid treatment as A in the designation of the stationary phases. The silica gels were subjected to Fourier transform IR analysis (FIRIS 100; Fuji Electric, Tokyo, Japan) for the surface hydroxyl groups. Metal analysis of silica particles was carried out by inductively coupled plasma atomic emission spectrometry (ICPS-1000 plasma spectrometer; Shimadzu, Kyoto, Japan), following dissolution of silica gel in 50% aqueous hydrofluoric acid.

*Equipment*

The high-performance liquid chromatographic (HPLC) system consisted of an LC-6A pump, SPD-6A variable-wavelength UV detector and C-R5A data processor (all from Shimadzu). Chromatographic measurements were carried out at 30°C by immersing the column in a thermostated water-bath.
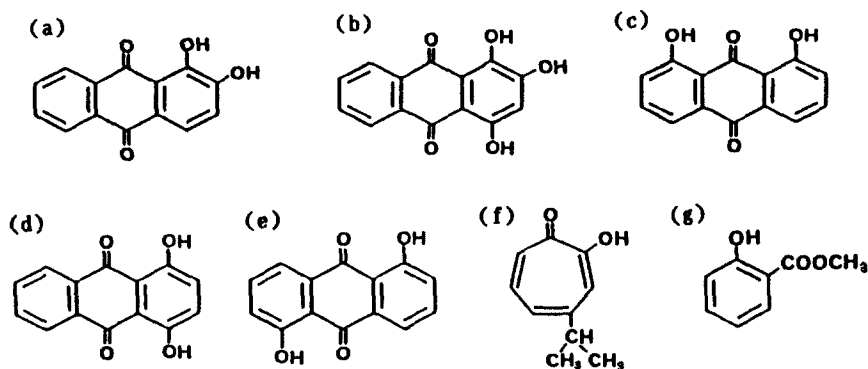


Fig. 1. Structures of chelating reagents. (a) Alizarin; (b) purpurin; (c) chrysazin; (d) quinizarin; (e) anthrarufin; (f) hinokitiol; (g) methyl salicylate.

TABLE I

METAL ANALYSIS OF SILICA GEL PARTICLES

| Silica | Metal content (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Al | Ca | Fe | K | Mg | Na | Ti | Zr |
| Develosil | 54 | 215 | <0.2[a] | <0.5[a] | 51 | 25 | 38 | 5 |
| Kromasil | <1[a] | <1[a] | <0.2[a] | <0.5[a] | <0.1[a] | 25 | 2 | <0.2[a] |

[a] Lower than the detection limit indicated.

## RESULTS AND DISCUSSION

$C_{18}$ phases with and without end-capping were prepared from the two types of silica gels with different metal contents. The silica gel particles were treated with acid prior to octadecylsilylation to remove as much metal impurities as possible. Table I lists the metal contents of the two silica gels after acid treatment. Kromasil is one of the few high-purity silica gels available at present (high-purity silica gels can also be obtained from other manufacturers, including Rockland Technologies and Separations Group, and from others as chemically bonded phases).

The alkylsilylation was carried out under conditions that would allow maximum surface coverage. Table II shows that the $C_{18}$ packing materials prepared from the trifunctional silane, D-$C_{18}$(III)

TABLE II

SURFACE COVERAGE AND HYDROPHOBIC PROPERTIES OF $C_{18}$ PACKING MATERIALS

D = Develosil; K = Kromasil; $C_{18}$(I) = prepared with octadecyldimethylchlorosilane; $C_{18}$(II) = from dichlorosilane; $C_{18}$(III) = from trichlorosilane; $C_{18}$(E) = from tetradecyloxypropylsilane; T = trimethylsilylation; H = heat treatment; A = acid treatment.

| Stationary phase | Carbon content (%) | Surface coverage ($\mu$mol/m$^2$) | Selectivity | | $N^c$ |
|---|---|---|---|---|---|
| | | | $\alpha(CH_2)^a$ | $\alpha(CO)^b$ | |
| D-$C_{18}$(I) | 15.92 | 2.53 | 1.500 | 0.332 | 9930 |
| D-$C_{18}$(I)-T | 15.99 | − | 1.511 | 0.321 | 10900 |
| D-$C_{18}$(II) | 17.57 | 3.08 | 1.495 | 0.324 | 11790 |
| D-$C_{18}$(II)-T | 17.81 | − | 1.500 | 0.315 | 11140 |
| D-$C_{18}$(III) | 17.31 | 3.25 | 1.469 | 0.368 | 10420 |
| D-$C_{18}$(III)-T | 17.69 | − | 1.488 | 0.327 | 10440 |
| K-$C_{18}$(I) | 14.42 | 2.46 | 1.510 | 0.316 | 9670 |
| K-$C_{18}$(I)-T | 14.64 | − | 1.523 | 0.300 | 8830 |
| K-$C_{18}$(II) | 15.12 | 2.79 | 1.497 | 0.325 | 8780 |
| K-$C_{18}$(II)-T | 15.63 | − | 1.507 | 0.308 | 7270 |
| K-$C_{18}$(III) | 15.01 | 2.97 | 1.474 | 0.380 | 6570 |
| K-$C_{18}$(III)-T | 15.85 | − | 1.496 | 0.315 | 7610 |
| D-$C_{18}$(E) | 11.77 | 1.86 | 1.428 | 0.379 | 9210 |
| D-$C_{18}$(E)-T | 12.14 | − | 1.434 | 0.373 | 8850 |
| D-H-$C_{18}$(I) | 11.87 | 1.77 | 1.425 | 0.464 | 10930 |
| D-H-A-$C_{18}$(I) | 15.01 | 2.35 | 1.485 | 0.370 | 7290 |
| D-H-A-$C_{18}$(III) | 13.56 | 2.37 | 1.468 | 0.357 | 6740 |
| D-H-A-$C_{18}$(E) | 11.96 | 1.90 | 1.378 | 0.429 | 8810 |

[a] $k'$(amylbenzene)/$k'$(butylbenzene), 80% methanol.
[b] $k'$(butyl phenyl ketone)/$k'$(butylbenzene), 80% methanol.
[c] Number of theoretical plates for amylbenzene, 80% methanol. 15 cm × 4.6 mm I.D. column.

and K-$C_{18}$(III) with or without end-capping, are less hydrophobic that those prepared from the mono-chlorosilane, D-$C_{18}$(I) and K-$C_{18}$(I), respectively, as determined by comparison of the retention increase with the addition of one methylene group to the solute structure, $\alpha(CH_2)$ [13]. The $\alpha(CH_2)$ values (1.51–1.52) found with D-$C_{18}$(I) and K-$C_{18}$(I) are the maximum obtainable with $C_{18}$ packing materials, as shown previously [13]. (The retention increase due to one methylene group is a convenient measure of the hydrophobicity of stationary phase, because it can be related to the free energy change associated with the transfer of a methylene group from the mobile phase to the stationary phase.) Stationary phases prepared from trichlorosilane and also that containing an ether linkage showed a greater $\alpha(C = O)$ together with a smaller $\alpha(CH_2)$, indicating

either reduced hydrophobicity or the contribution of silanols.

Among the secondary retention processes in RP–LC, the effect of neutral silanols on hydrogen bonding can be reduced by trimethylsilylation of a $C_{18}$ phase. The effect of surface acidity on peak tailing of amines at acidic pH caused by metal impurities was reduced by acid treatment of silica particles prior to the bonding process that removed the extraneous metals from silica surface [11,13,22]. These methods have been utilized in the preparation of many currently available packing materials. However, it was not possible to obtain good peak shapes for chelating compounds if these preparation methods were used with silicas containing substantial metal impurities. The use of high-purity silica gel in combination with polymer coating was shown to
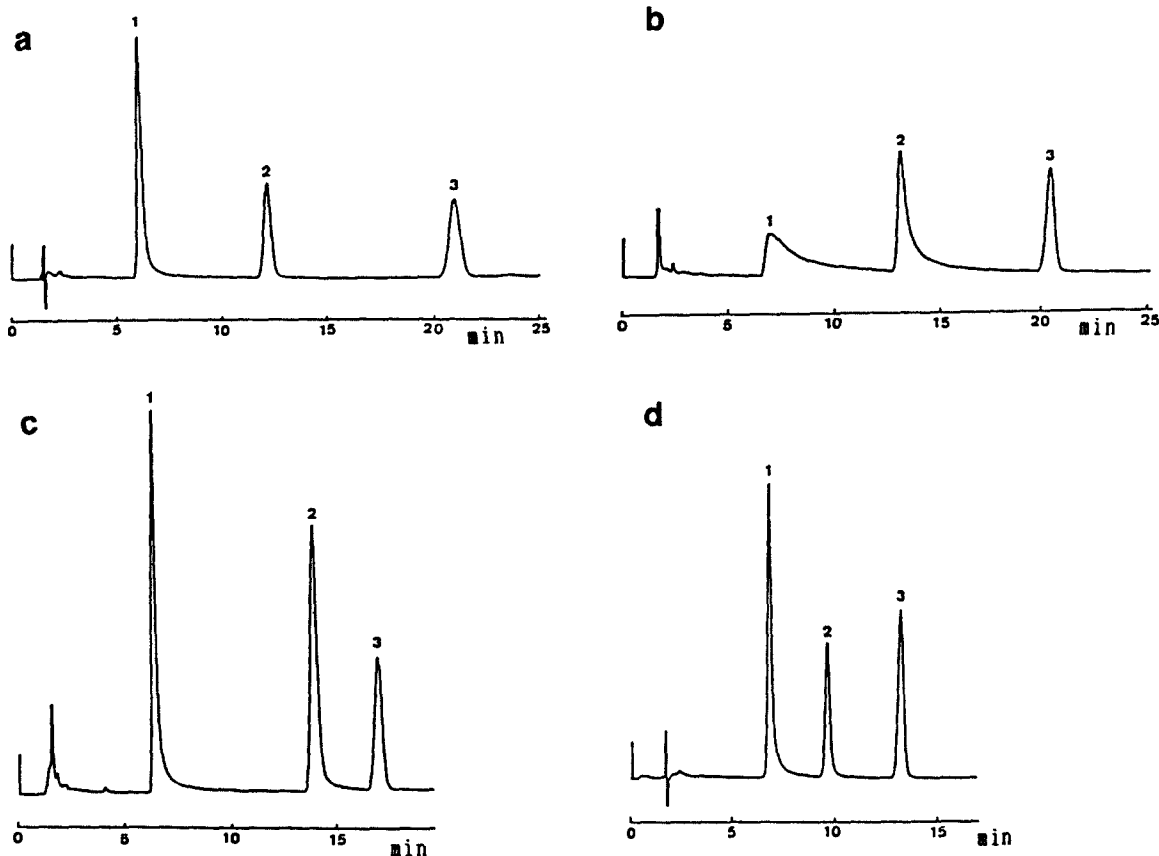


Fig. 2. Chromatograms of chelating reagents on (a) K-$C_{18}$(I)-T, (b) D-$C_{18}$(I)-T, (c) D-$C_{18}$(III)-T and (d) D-$C_{18}$(E)-T. Mobile phase: 75% methanol–0.02 $M$ phosphate (pH 3). Solutes: (1) purpurin, (2) quinizarin and (3) amylbenzene.

be one way to prepare a stationary phase free from the secondary retention process related to metals [14]. Hence the most rigorous test for silica $C_{18}$ packing materials with respect to the contribution of the secondary retention mechanism is the elution of chelating compounds, such as those in Fig. 1.

Fig. 2a and b show the chromatograms obtained for 1,2,4-trihydroxy-9,10-anthracenedione (purpurin) and 1,4-dihydroxy-9,10-anthracenedione (alizarin) on stationary phases prepared from the two silicas, Kromasil and Develosil, by using octadecyldimethylchlorosilane followed by trimethylsilylation, K-$C_{18}$(I)-T and D-$C_{18}$(I)-T. In each instance, the peak shape should be compared with that of amylbenzene. The stationary phase prepared from the high-purity silica gel with any silylating reagent showed little effect of the metal on the elution of hydroxyanthraquinones. The peaks of these chelating compounds, however, were severely distorted on the stationary phase prepared from the silica gel containing some metal impurities, D-$C_{18}$(I)-T.

Table III shows the performances of various stationary phases prepared from Develosil. The data

indicate that D-$C_{18}$(I) and D-$C_{18}$(II) showed a poor performance for all the chelating reagents. Trimethylsilylation of the $C_{18}$ bonded phase was not effective, and sometimes worked adversely. Table III also indicates that the effect of metal chelate formation is reduced by the addition of phosphoric acid or acetylacetone to the mobile phase. Some very effective chelating reagents, such as hinokitiol and 8-quinolinol, cannot be eluted from stationary phases prepared from metal-containing silicas with octadecyldimethylchlorosilane.

Fig. 2c and 2d show how to overcome the effect of metals. The stationary phases bonded with a trifunctional silane, D-$C_{18}$(III)-T, gave comparable results to K-$C_{18}$(I)-T for the hydroxyanthraquinones. The stationary phases prepared from tetradecyloxypropyldimethylchlorosilane containing an ether linkage, D-$C_{18}$(E)-T, also showed much better results than D-$C_{18}$(I)-T. As shown in Table III, better performance of a stationary phase prepared from trichlorosilane than that from monochlorosilane was also noted when the silica gel was used without acid treatment.

TABLE III

PERFORMANCE FOR CHELATING COMPOUNDS

Mobile phase: 75% methanol–0.02 $M$ phosphate buffer (pH 3).

| Stationary phase[a] | Column efficiency[b] | | | | | |
|---|---|---|---|---|---|---|
| | Alizarin | Purpurin | Chrysazin | Quinizarin | Anthrarufin | Hinokitiol |
| $C_{18}$(I) | 0.32 | 0.01 | 0.81 | 0.22 | 0.48 | NE[c] |
| $C_{18}$(I)-T | 0.32 | 0.02 | 0.75 | 0.23 | 0.40 | NE |
| $C_{18}$(II) | 0.37 | 0.05 | 0.80 | 0.42 | 0.59 | NE |
| $C_{18}$(II)-T | 0.38 | 0.06 | 0.79 | 0.35 | 0.49 | NE |
| $C_{18}$(III) | 0.47 | 0.30 | 0.85 | 0.71 | 0.77 | 0.013 |
| $C_{18}$(III)-T | 0.53 | 0.36 | 0.84 | 0.73 | 0.68 | 0.026 |
| $C_{18}$(E) | 0.77 | 0.49 | 0.86 | 0.91 | 0.78 | 0.002 |
| $C_{18}$(E)-T | 0.75 | 0.49 | 0.92 | 0.88 | 0.73 | NE |
| $C_{18}$(I)[d] | 0.94 | 0.64 | 1.36 | 1.29 | 1.16 | 0.014 |
| $C_{18}$(I)-T[d] | 1.00 | 0.80 | 1.45 | 1.38 | 1.34 | NE |
| $C_{18}$(I)[e] | 0.01 | —[f] | 0.29 | 0.01 | 0.06 | NE |
| $C_{18}$(III)[e] | 0.27 | 0.01 | 0.67 | 0.13 | 0.18 | NE |

[a] All stationary phases were prepared from Develosil. $C_{18}$(I), prepared with octadecyldimethylchlorosilane; $C_{18}$(II), from dichlorosilane; $C_{18}$(III), from trichlorosilane; $C_{18}$(E), from tetradecyloxypropylsilane; T, trimethylsilylation.
[b] Number of theoretical plates for the chelating compound divided by that for propylbenzene.
[c] Not eluted.
[d] Mobile phase containing 1 m$M$ acetylacetone.
[e] Stationary phases were prepared without acid treatment of silica gel prior to bonding.
[f] Peak was barely detectable.

TABLE IV

PERFORMANCE FOR ISOAMYL SALICYLATE

| Stationary phase[a] | Column efficiency[b] | | | |
|---|---|---|---|---|
| | 80% CH3OH | 70% CH3CN | 70% CH3CN–H3PO4[c] | 70% CH3CN–acetylacetone[d] |
| $C_{18}$(I) | 0.549 | 0.381 | 0.860 | 1.108 |
| $C_{18}$(I)-T | 0.624 | 0.416 | 0.907 | 1.177 |
| $C_{18}$(II) | 0.684 | 0.523 | 0.879 | 1.135 |
| $C_{18}$(II)-T | 0.637 | 0.573 | 0.781 | 1.085 |
| $C_{18}$(III) | 0.874 | 0.831 | 0.831 | 1.051 |
| $C_{18}$(III)-T | 0.858 | 0.845 | 0.925 | 1.139 |

[a] All stationary phases were prepared from Develosil.
[b] Number of theoretical plates for isoamyl salicylate divided by that for butylbenzene.
[c] 0.02 $M$ phosphate buffer (pH 3).
[d] 1 m$M$ acetylacetone was added.

The shielding of metal sites on the silica surface by a polymeric structure formed from trichlorosilane [23,24] does not seem to be the major reason for the improvement. D-$C_{18}$(E) phase showed good performance without such a contribution. A higher surface coverage by end-capping had no improving effect, and was actually disadvantageous.

A plausible explanation for the improved performance is the association of metal sites with polar functionalities such as silanols or ether oxygen in bonded alkylsilyl groups, or water or methanol brought into the stationary phase from the mobile phase by the presence of the hydrophilic groups.

Solvents in the mobile phase are known to be extracted into the stationary phase, and considerably alter the environment of the alkyl chains [3,4]. The presence of competing groups for the metal sites in the more hydrophilic stationary phase permits the easier displacement of ligands or faster equilibration, and explains the results, as was proposed for the silanophilic retention of amines [25]. Slower flow-rates improved the results, whereas reduced sample size did not effect any improvement.

The undesirable effects of metal impurities were also observed with isoamyl salicylate (Table IV). The use of acetonitrile in the mobile made the results

TABLE V

PERFORMANCE FOR CARBOXYLIC ACIDS

Mobile phase: 30% acetonitrile–0.02 $M$ phosphate buffer.

| Stationary phase[a] | Column efficiency[b] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | pH 2.28 | | pH 3.19 | | pH 3.84 | | pH 4.26 | |
| | B | T | B | T | B | T | B | T |
| $C_{18}$(I) | 0.90 | 0.95 | 0.65 | 0.78 | 0.62 | 0.61 | 0.54 | 0.53 |
| $C_{18}$(I)-T | 0.54 | 0.61 | 0.40 | 0.31 | 0.27 | 0.20 | 0.19 | 0.06 |
| $C_{18}$(III) | 0.80 | 0.88 | 0.60 | 0.75 | 0.76 | 0.82 | 0.31 | 0.73 |
| $C_{18}$(III)-T | 0.71 | 0.69 | 0.64 | 0.59 | 0.60 | 0.60 | 0.53 | 0.56 |

[a] All stationary phases were prepared from Develosil.
[b] Number of theoretical plates for (B) benzoic acid or (T) p-toluic acid divided by that for 3-phenylpropanol.

worse. The addition of phosphoric acid or acetyl-acetone [17], which are metal complexing agents, improved the results considerably.

Table V shows the effect of pH and the method of preparation of the stationary phase on the performance for carboxylic acids with an acetonitrile–phosphate buffer mobile phase. Trimethylsilylated packing materials prepared from monochlorosilane showed tailing for carboxylic acids, especially at pH values near their $pK_a$ values. As shown in Fig. 3, a similar packing material from Kromasil and less hydrophobic D-$C_{18}$(III)-T and D-$C_{18}$(E)-T showed better performances. The improvement with the addition of acetylacetone suggests that the poor performance seen with D-$C_{18}$(I)-T phase is related to metals [26].

The retention of an acid in the ionization control mode is expressed by the equation [27]

$$k' = \frac{k'_{AH}}{1 + K_a/[H_3O^+]} + \frac{k'_{A^-} \cdot K_a/[H_3O^+]}{1 + K_a/[H_3O^+]} \quad (1)$$

where $k'_{AH}$ and $k'_{A^-}$ are the $k'$ values of the neutral and ionized form of the acid, respectively. Hence the retention of a carboxylic acid is the sum of the retention of the neutral form and that of the ionized form at a particular pH. The retention is most sensitive to the variation of elution conditions around the $pK_a$ of the acid, where poor performance was seen with $C_{18}$(I). The source of tailing seems to be the interaction between metals and the ionized form of the acids.

The results indicate that the effect of metal impurities is emphasized with greater hydrophobic properties of the stationary phase, which lead to poor accessibility of competing polar groups to the metal sites, as is the case with chelating reagents. The undesirable effect on D-$C_{18}$(I)-T was reduced by the use of acetate buffer instead of phosphate, by methanol instead of acetonitrile or by the addition of reagents masking the metals. In some instances, however, mobile phase additives such as EDTA, acetylacetone or sodium octanoate [18,28] caused a
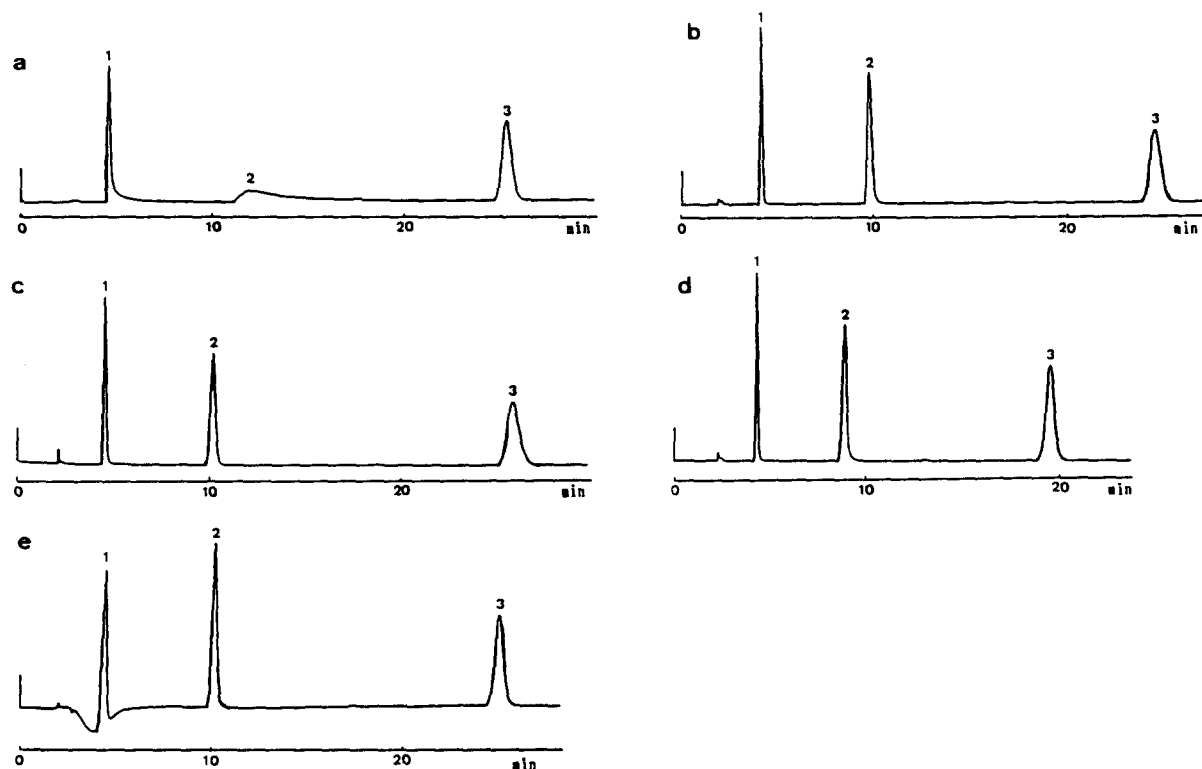


Fig. 3. Chromatograms obtained for carboxylic acids on (a) D-$C_{18}$(I)-T, (b) K-$C_{18}$(I)-T, (c) D-$C_{18}$(III)-T and (d) D-$C_{18}$(E)-T. Mobile phase: 20% acetonitrile–0.05 $M$ phosphate (pH 4.8). Solutes: (1) benzoic acid, (2) $p$-toluic acid and (3) 3-phenylpropanol. (e) D-$C_{18}$(I)-T, 1 m$M$ acetylacetone added to the mobile phase.
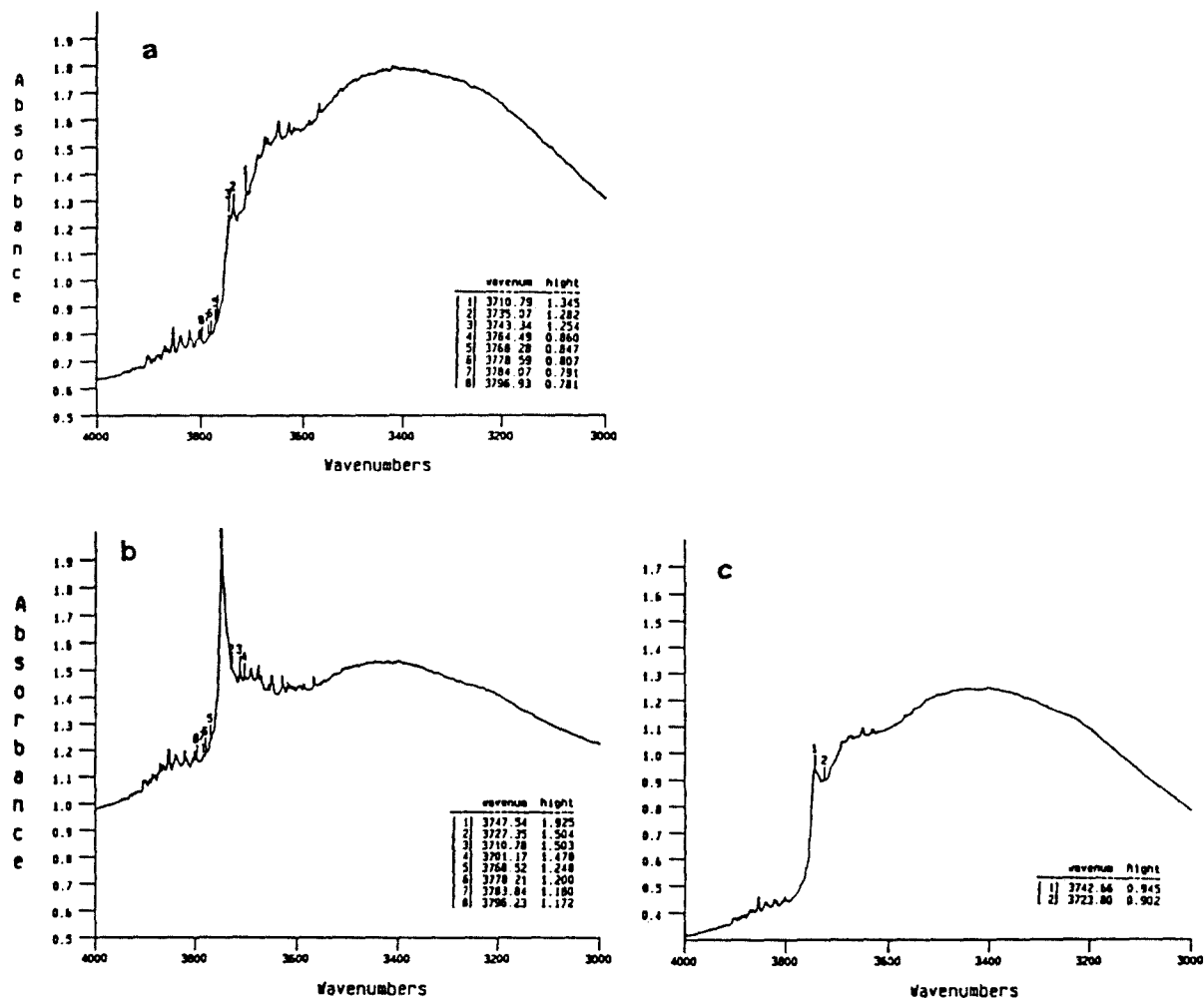
Fig. 4. Fourier transform IR spectra of silica gel. (a) Develosil after the initial acid treatment; (b) Develosil after thermal treatment (D-H); (c) Develosil after acid treatment following the thermal treatment (D-H-A).

noisy baseline or a prolonged equilibration time of the chromatographic system, and hence were unsatisfactory [18].

Another interesting observation is the effect of the hydrophilicity of the stationary phase on the appearance of the effect of hydrogen bonding caused by silanol in the stationary phase. When silicas were heated to high temperatures, dehydration caused the silanols to condense to form siloxanes, leaving isolated silanols [29]. The remaining silanols possess higher acidity than the usual silanols hydrogen bonded to each other [5]. The acid treatment with hydrochloric acid rehydrated the surface to some

extent, but not completely [22]. Fig. 4 shows the variation of the type and amounts of silanols on silica gel after each treatment. Some isolated silanols remained after the second acid treatment following the thermal treatment.

$C_{18}$ phase prepared from heat-treated silica [D-H-$C_{18}$(I)] possesses a low surface coverage owing to the scarcity of silanols, and showed a small retention of phenol, in agreement with the low carbon content. However, D-H-$C_{18}$(I) showed a longer retention for caffeine than D-$C_{18}$(I), which possesses a higher carbon content, indicating the effect of hydrogen bonding, as shown in Fig. 5.
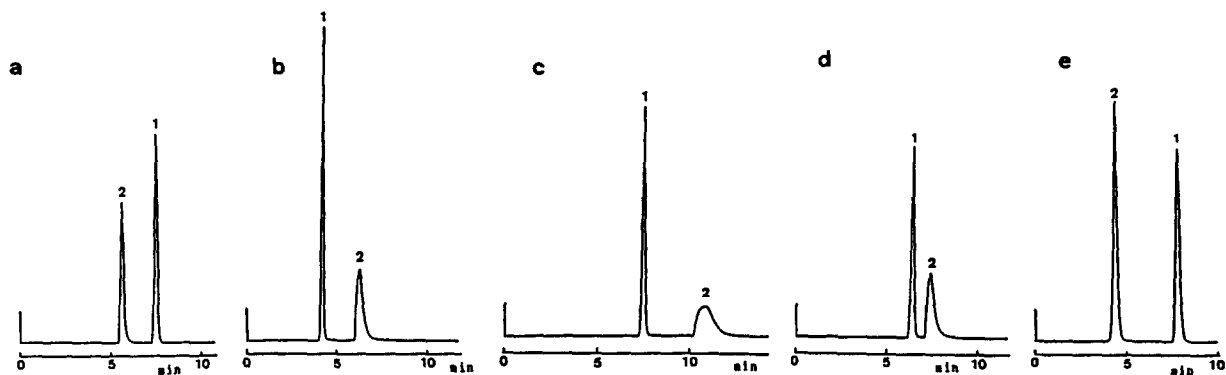
Fig. 5. Chromatograms obtained for caffeine (peak 2) and phenol (peak 1) on (a) D-$C_{18}$(I), (b) D-H-$C_{18}$(I), (c) D-H-A-$C_{18}$(I), (d) D-H-A-$C_{18}$(III) and (e) D-H-A-$C_{18}$(E). Mobile phase: 30% methanol.

Caffeine is known to undergo interaction with silanols [13,30].

$C_{18}$ phase prepared from acid-treated silica following thermal treatment (D-H-A) showed a normal retention for phenol, but a much longer retention for caffeine with a poor peak shape. The incomplete rehydration left some acidic silanols, which participate in more effective hydrogen bonding in the hydrophobic environment provided by the higher surface coverage. Interestingly, D-H-A-$C_{18}$(III) showed a better performance, resulting in a smaller $k'$ value for caffeine in spite of the larger amount of silanols on this stationary phase than D-H-A-$C_{18}$(I). D-H-A-$C_{18}$(E) also showed a much better performance for caffeine with a smaller retention. The results indicate that the acidic, isolated silanols created by thermal treatment become less detrimental when associated with the polar functionality in alkylsilyl groups or polar solvents.

These results may be of little practical importance, because the hydrogen bonding effect can be suppressed by trimethylsilylation. Nonetheless, the present results are interesting in that hydrophilic stationary phases with more silanols showed a better performance for solutes suffering from the hydrogen bonding effect of the silanols. It should be noted that the acidic silanols should be minimized by appropriate treatment of silica gel or by a suitable bonding method to avoid the problems of chemical stability associated with trimethylsilyl-bonded phases.

The results indicate the importance of the presence of competing polar functionalities in stationary phases prepared from metal-containing silica gel for faster equilibration with respect to the silanols and metals which participate in the secondary retention processes.

This study clearly indicates the advantages of the use of high-purity silica gel as a support for RPLC packing materials. It can be stated that stationary phases prepared from metal-containing silica gels with trichlorosilane may not be as good as those prepared from high-purity silica gel, but they are at least much better than comparable stationary phases obtained from monochlorosilane. They are easy to prepare from the usual silica gels and show adequate performance for many chelating compounds, hydroxybenzenes and carboxylic acids. Although most of the newer commercial $C_{18}$ packing materials are prepared from monochlorosilane for better reproducibility and better performance for silanophilic solutes, those prepared with trichlorosilane can provide a solution to one of the most difficult problems in packing materials for RPLC.

ACKNOWLEDGEMENT

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