

CHROM. 13,304

## GROUP SEPARATION BY REVERSED-PHASE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

### RAPID DETERMINATION OF REMAINING ALKANES IN ALKANOLS

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#### SUMMARY

The dependence of the group separation of *n*-alkanol–*n*-alkane mixtures using reversed-phase systems on both the water content of the methanol used and the chain length of the alkyl groups chemically bonded on the silica surface has been investigated. Considering the experimental results in terms of the ratio  $\log a_{21}/\Delta \log k'_{\text{CH}_2}$ , it seems to be possible to choose group separation conditions systematically. Low contents of water together with highly inert silica substituted by short carbon chains seem to favour group separation. The conditions elaborated permit the determination of the sum of remaining alkanes using a refractive index detector.

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#### INTRODUCTION

As a result of increasing efforts to achieve the more intensive utilization of the high-boiling hydrocarbons contained in petroleum or coal products there is increasing interest in group separations by modern chromatographic methods<sup>1–5</sup>. In order to solve such separation problems, in addition to size-exclusion chromatography<sup>6</sup> adsorption liquid chromatography<sup>7</sup> has mainly been applied. However, reversed-phase (RP) systems have been less investigated for the separation of groups of homologous substances from complex mixtures. Nevertheless, the application of reversed-phase systems can be interesting in view of the sensitive refractive index detection of pure and substituted alkanes, using highly polar mobile phases, e.g., methanol–water mixtures.

The investigations described here were carried out in order to obtain a more systematic choice of the reversed-phase chromatographic conditions suitable for group separation.

## THEORETICAL

In order to achieve an efficient separation of two groups of homologous substances a chromatographic system should be characterized by a high alkane-alkanol selectivity,  $\alpha_{21}$ , but low methylene group increments,  $\Delta k'_{\text{CH}_2}$ , in order to separate the groups as effectively as possible but to elute each series of homologue within a small retention interval;  $\alpha_{21}$  is the separation factor of the two species, alkanol (1) and alkane (2), with equal chain lengths,  $n$ , but different functional groups X1 (C-OH) and X2 (C-H), respectively. Therefore, a high value of the ratio

$$\frac{\log \alpha_{21}}{\Delta \log k'_{\text{CH}_2}} = \sigma_G \quad (1)$$

is required for a chromatographic system to yield an effective group separation.

Additivity of group contributions to the retention can also be assumed in reversed-phase chromatography<sup>9</sup>. Therefore, the  $\sigma_G$  relationship can be written in terms of group contributions of the free energy:

$$\frac{\Delta G_{\text{X}_2}^0 - \Delta G_{\text{X}_1}^0}{\Delta G_{\text{CH}_2}^0} = \sigma_G \quad (2)$$

According to eqn. 2, both low hydrophobic interactions and small interactions of the  $\text{CH}_2$  groups should be favoured group separations of an alkane-alkanol mixture.

## EXPERIMENTAL

The measurements were carried out by means of the Hewlett-Packard 1010 A high-pressure liquid chromatograph, fitted with an LDC 1107 differential refractometer detector, at ambient temperature. SGE high-pressure syringes were used for sampling.

Each alcohol was injected pure or mixed with the alkane of the same chain length. The injection of pure alkanes yielded asymmetric peaks, whereas symmetric peaks were obtained if the alkane-alkanol mixtures were injected. The columns (stainless steel,  $250 \times 4$  mm I.D.) were packed using the fast filtration technique.

The polymeric reversed phases RP-1 and RP-4 were prepared according to Hastings *et al.*<sup>10</sup>. RP-6 and RP-16 were synthesized by Dr. Tänzer (Merseburg) and Dr. Eppert (Leuna), respectively. The chemical modification was monitored by IR spectroscopy and elemental analysis. The other products were brush-type reversed phases. RP-2, RP-8 and RP-18 were commercial materials (Merck, Darmstadt, G.F.R.).

The sum of remaining alkanes was determined quantitatively in groups of  $n$ -alkanols with similar chain length ( $n \pm 2$ ). Calibration was carried out by constructing a calibration graph for a representative alkane of medium chain length in the sample. On determining the peak area by planimetry, the relative standard deviation of the results was about 5%. Better results should be obtained if electronic integration is used.

## RESULTS AND DISCUSSION

In order to examine the dependence of the group separation on the chromatographic conditions, experiments were carried out by changing both the eluent composition and the type of chemically modified silica. The results in Fig. 1 and Table I are given in terms of the  $\sigma_G$  ratio corresponding to eqn. 1.

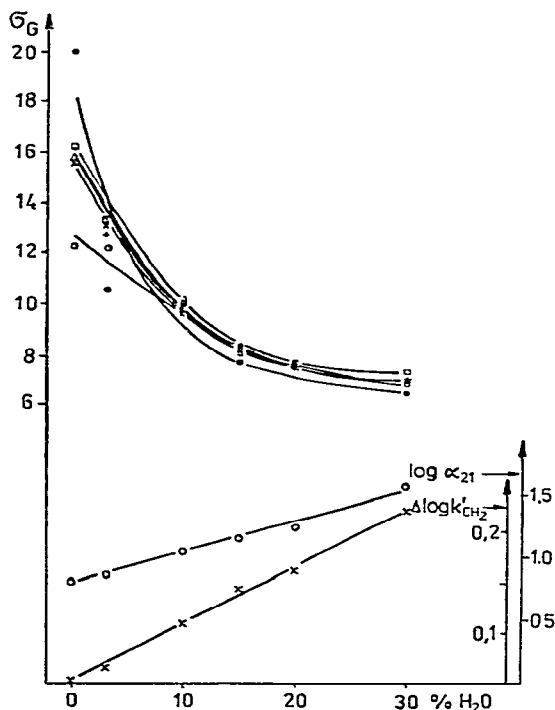


Fig. 1. Influence of the water content in methanol on  $\sigma_G$  ratio. Length of the carbon chain: upper curves: ●, C<sub>6</sub>; ○, C<sub>9</sub>; ×, C<sub>11</sub>; +, C<sub>13</sub>; △, C<sub>15</sub>; □, C<sub>17</sub>; lower curves: ○, C<sub>11</sub>; ×, average C<sub>6</sub> to C<sub>17</sub>.

Fig. 1 demonstrates the strong influence of the hydrophobic nature of the eluent on the  $\sigma_G$  ratio. The stationary phase used was RP-4. As expected, an increase in the content of water in the methanol gives an increase in both the selectivity ( $\log \alpha_{21}$ ) and the contributions of the alkyl groups ( $\Delta \log k'_{\text{CH}_2}$ ) to the retention of the aliphatic species. However, because the  $\Delta \log k'_{\text{CH}_2}$  values increase twice as fast as  $\log \alpha_{21}$ , the  $\sigma_G$  ratio decrease rapidly up to a content of 15% (v/v) of water. Higher contents of water give only small alterations in  $\sigma_G$ , because the relative change becomes smaller if the absolute values of  $\alpha_{21}$  and  $\Delta k'_{\text{CH}_2}$  increase.

Accordingly, in order to achieve efficient group separations methanol containing only small contents of water should be applied. The dependence of  $\sigma_G$  values on the type of chemically modified silica from RP-1 to RP-18 is shown in Table I. The relative retentions,  $\alpha_{21}$ , increase with increase in both the percentage of carbon bonded to the silica and the carbon chain length, as expected.<sup>11</sup> In comparison, the methylene group increments,  $\Delta k'_{\text{CH}_2}$ , seem to be nearly independent of the carbon content, although dependent on the length of the carbon chains.

TABLE I

SEPARATION OF HOMOLOGOUS *n*-ALKANOLS AND *n*-ALKANES ON CHEMICALLY MODIFIED SILICAEluent: methanol-water (97:3). 1 = *n*-Dodecanol; 2 = *n*-dodecane.

Stationary phase	Carbon content (% w/w)	RP	$\log \alpha_{21}$	$\Delta \log k'_{C_{H_2}}$	$\sigma_G$
Si-methyl*	19.0	1	0.696	0.064	10.9
Si-butyl*	16.3	4	0.863	0.066	13.1
Si-ethyl	6.4	2	0.538	0.055	9.8
Si-butyl**	8.1	4	0.33	0.05	6.6
Si-hexyl	10.2	6	0.63	0.09	7
Si-octyl	13.1	8	0.568	0.086	6.6
Si-decyl**	14.8	10	0.49	0.75	6.5
Si-hexadecyl	16.9	16	0.651	0.149	4.4
Si-octadecyl	22.1	18	0.773	0.252	3.1
Si-octadecyl**	22.3	18	0.75	0.135	5.5

\* Polymer type.

\*\* Eluent: pure methanol (data from ref. 8).

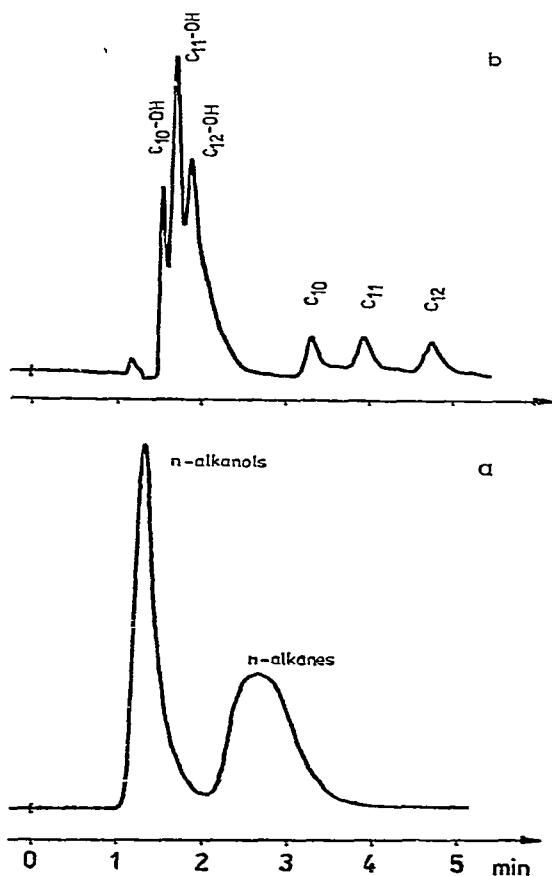


Fig. 2. Influence of the bristle length on the group separation of *n*-alkanols-*n*-alkanes using methanol-water (97:3) as eluent. (a) RP-4 (polymer, flow-rate 0.34 cm/sec, pressure 4.6 MPa; (b) RP-18, flow-rate 0.34 cm/sec, pressure 3.5 MPa.

However the  $\log \alpha_{21}$  values vary only by a factor of 1.33, whereas the contributions of the  $\text{CH}_2$  groups,  $\Delta \log k'_{\text{CH}_2}$ , change systematically by a factor of 5. Therefore, the  $\sigma_G$  ratio decrease significantly from RP-1 to RP-18, owing primarily to this strong increase in the interaction of the alkyl groups. As confirmed by Fig. 2, it can be concluded that reversed phases characterized by short alkyl chains yielding more efficient group separations than those substituted by long carbon chains.

From Fig. 2, in addition to the higher carbon content, the high  $\alpha_{21}$  values may also be caused by a greater inertness of the polymers in comparison with the brushes, yielding lower retentions of the alkanols.

## CONCLUSION

In group separation of *n*-alkanol-*n*-alkane mixtures, the possibility of improving the separation factor,  $\alpha_{21}$ , by changing the chromatographic conditions seems to be limited, because higher values of  $\alpha_{21}$  are connected with higher contributions of the  $\text{CH}_2$  groups, which make the group separation worse by spreading the homologous species. Therefore, the contributions of the  $\text{CH}_2$  groups to the retention must be kept as small as possible by selecting an eluent involving only weak hydrophobic properties. These eluents must be combined with reversed phases, which offer a low surface area for the dispersion interactions between the  $\text{CH}_2$  groups of the sample molecules and the organic layer of the modified silica. In order to separate a group of strongly polar species, for example alkanols, from weakly polar species, polymeric modified silica seems to provide some advantages. Together with further systems investigated in our laboratory, these results offer some general conclusions for the systematic choice of chromatographic systems that yield more efficient group separations of hydrocarbons (for example, by using fluorocarbon-substituted silica). Further basic experimental and theoretical investigations have been carried out.

Using the conditions established here, in analytical practice alkanes can be separated from alkanols in 3–5 min. The reversed-phase system used involves methanol modified by 1–3% of water as eluent, and silica substituted by short alkyl chains. The remaining alkanes can be determined quantitatively in the technically required range down to 0.1% (w/w) using a refractive index detector.

## ACKNOWLEDGEMENTS

We thank Dr. Eppert, Leuna, and Dr. Tänzer, Merseburg, for supplying reversed-phase materials. Dipl. Chem. Bui Trung, Hanoi, is thanked for experimental assistance.

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