Journal of Chromatography, 189 (1980) 255–258

CHROM. 12,464

Note

Binary liquid phase system for gas–liquid chromatography with *in situ* variable polarity

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(Received October 16th, 1979)

The idea of combining two liquid phases in a single gas–liquid chromatographic (GLC) column is certainly not new. It is most often used to achieve intermediate polarities and may take the form of mixed liquid phases, mixed packings, or sequential packings.

In order to produce a number of phases with different polarities —as may be used in scouting for a particular optimized separation— an equal number of columns has to be prepared. This is laborious and, furthermore, provides only stepwise change in polarity. One may therefore prefer to have available a single column whose polarity can be continuously varied.

Now, changes in apparent polarity can be brought about by changes in the nature or the pressure of the carrier gas. However, these are relatively small and therefore of importance only in capillary gas chromatography.

In contrast, we were interested in using a binary liquid phase system that could be used with low-resolution, packed columns and whose polarity could be changed over a wide range. This communication demonstrates that such a system is possible.

Contrary to most binary systems, however, only one liquid phase in our system is truly stationary. The other "liquid phase", a highly retained alkane dopant introduced continuously into the injection port by a syringe pump, is quasi-stationary. The amount of alkane retained can be controlled by feed-rate and temperature and, when it becomes appreciable, will influence solute retention. The alkane thus acts as if it were a stationary phase (hence the term "quasi-stationary").

Consequently, by using a polar liquid phase and doping with a controlled but variable amount of alkane, one essentially produces a binary liquid phase system whose polarity can be adjusted in the range given by the stationary and quasi-stationary liquids. It is, of course, also possible to use a non-polar stationary phase and a polar dopant. The obvious criterion for the dopant is that it should be highly retained, *i.e.* enter the detector only in very small amounts, and that its response in the detector should be negligible or minimal.

Since we wanted to use alkanes as dopants in our attempt to demonstrate the principle of the method, the electron capture detector (ECD) was a natural choice. Alkanes exhibit little response in the ECD, they can improve its linear range[1] and

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response to other compounds[2], and they provide a practically unlimited temperature range.

EXPERIMENTAL

The carrier gas, high-purity grade nitrogen doped with approximately 1 ppm hydrogen, was further cleaned by passage through cartridges containing absorbents for moisture, oxygen, and hydrocarbons. Two column packings of different type were used: a thin-layer, bonded phase and a thicker layer, regular GLC phase. In both cases the support was silica gel Davison grade 62, 60–80 mesh. It carried a bonded layer based on Surfynol 485 (ref. 3), or a 15% OV-275 load, respectively.

A $^1/_{16}$ in. hole was drilled through the sidewall of the injection port and a piece of $^1/_{16}$ in. O.D. stainless-steel tubing inserted and silver-soldered to it. The other end of the tubing ended in a Swagelok union with a silicone septum at the opposite end.

This septum served as the inlet for the alkane dopants. It was penetrated permanently by the needle of a gas-tight syringe (Hamilton No. 1001, capacity 1 ml), driven by a Sage Instruments Model 355 syringe pump.

RESULTS AND DISCUSSION

The dopant has to comply with certain criteria. First, it should not contain electron-capturing contaminants. Second, its partial pressure in the gas chromatograph may never exceed its vapour pressure, *i.e.* it must be capable of remaining in the vapour phase. Third, the dopant must be retained strong enough to produce a significant change in polarity. Fourth, equilibrium (a constant composition of the binary phase throughout the column) should be established fast after initial introduction of the dopant.

Obviously, the two last criteria oppose each other and a compromise has to be struck. How one chooses to compromise depends largely on the chromatographic requirements and the time available.

Given our columns and solutes of interest, dodecane was found to be the most satisfactory of all alkanes tested. It should perhaps be stressed that under the high-load conditions required by this study the amount of dodecane present as quasi-stationary phase may not necessarily be a linear function of the amount introduced. Dodecane load, if desired, could be calculated from the sorption isotherm.

A plot of adjusted retention times for several analytes against dodecane flow-rates is shown in Fig. 1. Retention increases according to the increased load of dodecane. Still it is obvious that the retention pattern changes: note, for instance, the crossover of compounds 4 (chloroform) and 5 (carbon tetrachloride).

This situation is somewhat clearer portrayed in Fig. 2. Here are plotted the relative retentions of particular analytes; relative with respect to the "non-polar" standard hexane (which was injected in larger amounts to obtain a signal from the ECD).

Evidently the slopes of the curves correlate with the polarity of the solute. The relative retention of polar compounds like nitroethane decreases strongly with increasing dodecane flow (*i.e.* decreasing polarity). Non-polar compounds, like carbon tetrachloride, show little change (*i.e.* they behave similar to the standard hexane).

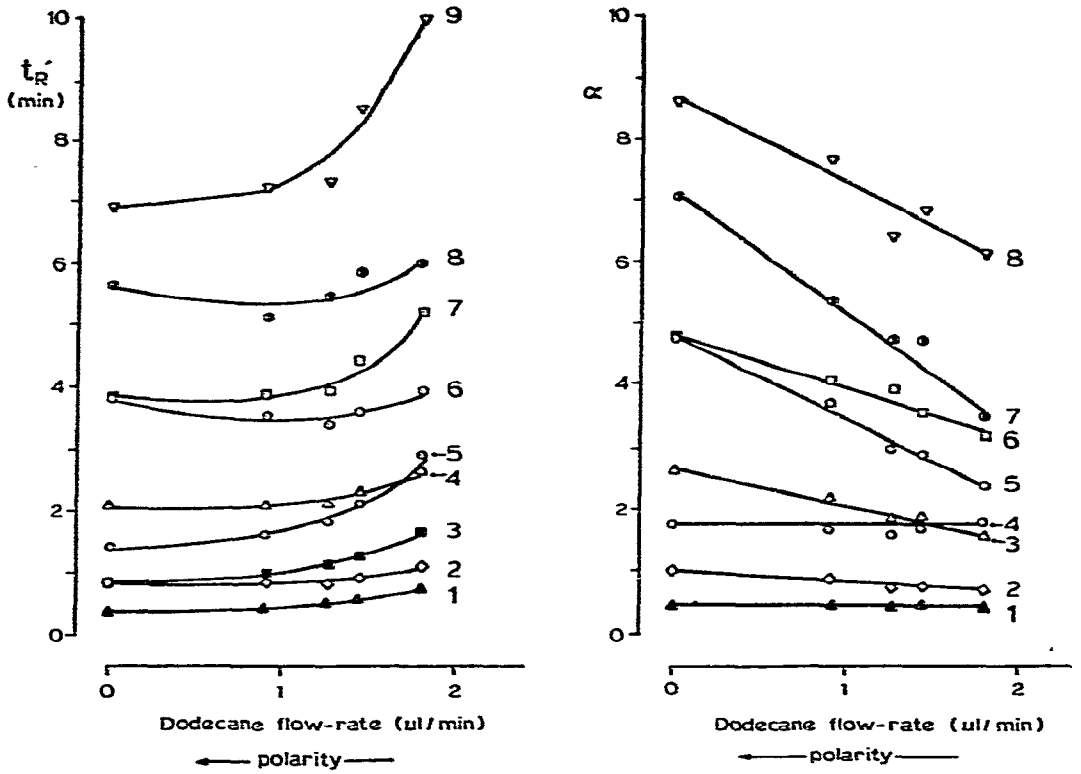

Fig. 1. Adjusted retention time *versus* dodecane flow-rate. Detector temperature 290°, column temperature 100°, injection port temperature 245°. Compounds: 1 = pentane; 2 = freon 113; 3 = hexane; 4 = $CHCl_3$; 5 = CCl_4; 6 = $CH_3CH_2NO_2$; 7 = $CHBrCl_2$; 8 = $CH_3CH_2CH_2NO_2$; 9 = $CHClBr_2$.

Fig. 2. Relative retention time α (t_R' analyte/t_R' hexane) *versus* dodecane flow-rate. Compounds: 1 = pentane; 2 = freon 113; 3 = $CHCl_3$; 4 = CCl_4; 5 = $CH_3CH_2NO_2$; 6 = $CHBrCl_2$; 7 = $CH_3CH_2CH_2NO_2$; 8 = $CHClBr_2$. Conditions as in Fig. 1.

Figs. 1 and 2 show results obtained with the Surfynol column; those obtained with the OV-275 column were very similar.

The main purpose of these experiments was to demonstrate the feasibility of performing *in situ* polarity modification or regulation. While this purpose was achieved, it is obvious that "polarity" is just one of several dimensions that can be used to influence retention patterns. Either component of the binary liquid phase system could provide selective interactions in terms of, say, complexing ability, optical activity, hydrogen bonding, or acid-base behaviour.

A further possibility to influence retention patterns could be the use of gradients. Gradients could be produced by the dopant; for instance, in the simplest case, the dopant supply would be turned off and the analyte injected. Or a gradient could be obtained by changing chromatographic conditions; for instance by imposing a mild temperature program.

We would also consider it interesting to reproduce a similar system on capillary columns. All things considered, the effects of continuous changes in selectivity could

probably be easier observed and better exploited with capillaries. Such studies, however, are beyond our present means and intentions.

ACKNOWLEDGEMENTS

This research was supported by NSERC Grant A-9604 and a Killam Scholarship for one of us (K.W.M.S.). We express our appreciation to Palitha Wickramanayake for donating the Surfynol-deactivated silica gel 62 and to Noshir F. Chinoy of Air Products, Allentown, Pa., U.S.A., for donating a sample of Surfynol 485.

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