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LETTER TO THE EDITORS

Response to Letter to the Editor of *Talanta* Re: *Talanta*, 1993, **40,** 1541–1549

Dear Sir,

In his letter, Dr Rohrschneider defines selectivity as differences in the specific retention index of a test probe between two stationary phases. Using this definition, he states that there was a change in selectivity for the phases (*i.e.* index difference of benzene decreasing from 345 for the methyl- to 249 for the pentylsulfonate) contrary to that reported in our paper.[1] Indeed, using Dr Rohrschneider's definition of selectivity, there is an *apparent* change in selectivity for the phases studied. One could say that the phases studied have a change in "selectivity" for hydrocarbons increasing from the methyl- to the pentylsulfonate (resulting in retention index differences), although the only intermolecular interactions being probed are non-specific dispersive interactions.

In fact, selectivity is a measure of the differences in individual intermolecular interactions and the comparison of indexes for individual probes is simply one estimate of selectivity which is inadequate for the phases studied for the reasons detailed in our paper.[1] This example highlights the major limitations of any retention index-based system, namely, that no single test solute can adequately probe a single intermolecular interaction since each exhibit a variety of possible interactions, and that a retention index is a composite indicator of the phases specific interactions with the polar test probes *relative* to the non-specific interactions with n-alkane retention index markers. Dr Rohrschneider states that had 2-octyne and *cis*-hydrindane been reported, their specific retention volumes would have increased in a manner analogous to the n-alkanes, also showing different selectivities of the compared phases. Indeed, the specific retention volumes of 2-octyne and *cis*-hydrindane would have increased similar to the n-alkanes showing different "selectivities" for non-specific dispersive interactions. This information would again only highlight the fact that any *apparent* change in selectivity for the polar test probes on the phases studied is exclusively attributable to changes in retention for the nonpolar index markers.

Finally, Dr Rohrschneider refers to the possible chemical reaction of pyridine with some of the phases and suggests that these results were the basis of the conclusion "These results support previous studies illustrating that McReynolds Constants can be an unreliable measure of selective solute-stationary phase interactions". Actually, that quote came from the final paragraph of the paper which contained the conclusions from the entire work and perhaps should have been labeled "Conclusions" to avoid such confusion. The possible reactivity of pyridine with some of these phases was not the basis for that conclusion, rather the results discussed above formed the basis for this conclusion. Dr Rohrschneider concludes with "Analytical chemists should be warned to these organic salt phases, whose instability was detected with McReynolds test probes" In fact, such reactivity is uncommon with organic salt phases and possible limitations due to chemical interactions has been studied in some detail and interested readers are referred to Ref. 2.

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REFERENCES

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2 S K Poole and C F Poole, *J Chromatogr*, 1988, **435,** 17