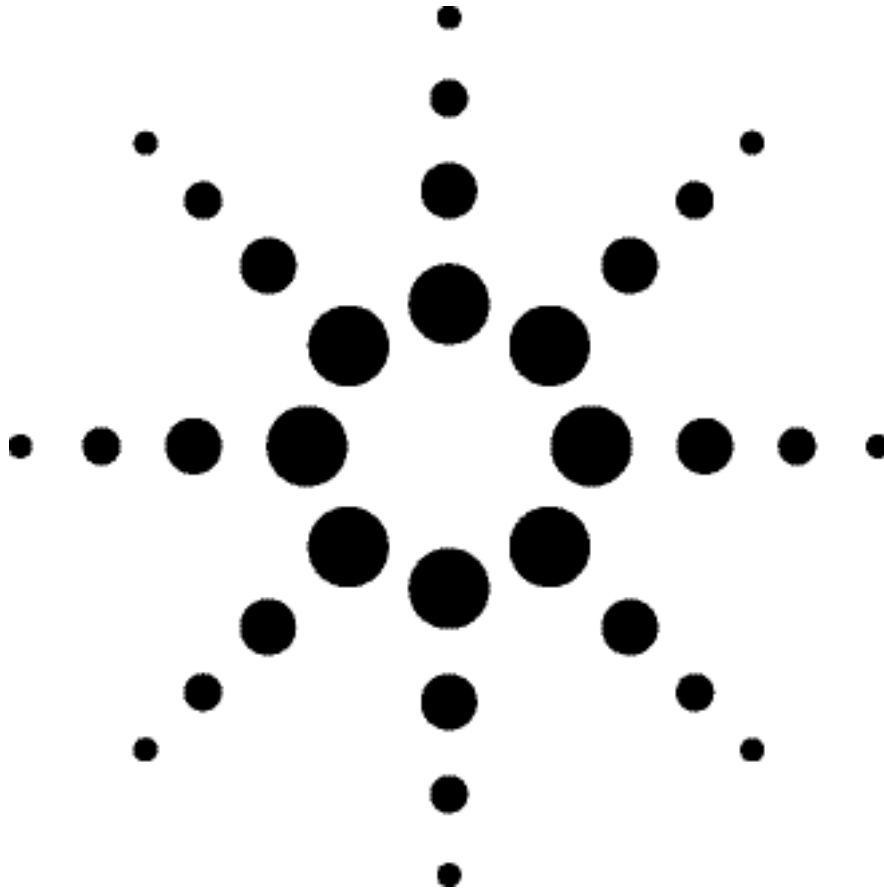


Inertness Comparison of a Sample of 5% Phenyl dimethyl polysiloxane columns

Pittcon 2003 Poster



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Introduction

A few nascent manufacturers of capillary columns have taken the provocative position in the marketing of their capillary columns by stating that "The only difference is the price." It has previously been shown that this is not the case in terms of 5% phenyldimethylpolysiloxane columns and carbowax columns in the performance categories of column bleed, selectivity (the ability of one of these new columns to mimic the elution order of an industry standard column) and general column inertness, (the ability to chromatograph even modestly active compounds such as phenols, amines, and multifunctional group compounds).¹

Three questions arise, just how different are these columns, for which analyses do the differences matter, and how can you tell? To the latter, the types of analyses that typically demand the most inertness from a GC system (inlet, column and detector) are those interested in trace amounts of active analytes. Trace analysis is generally defined as less than 10 nanogram of analyte on-column. These analyses uncover weaknesses inherent in a column's design and/or manufacture because there is so little analyte present on column. Thus, a greater percentage of analyte molecules are affected by the fixed number of column (and inlet and detector) active sites, resulting in more readily detectable tailing and loss of response. Real world examples include analytical methods for drugs of abuse (methamphetamine and others which are basic, barbiturates which are generally mild acids), many pesticides analyses (which have acidic, basic, nitro, phosphorous and sulfur moieties), and environmental analyses for semivolatile industrial contaminants including USEPA method 8270 which has some of the more notoriously difficult compounds to chromatograph without loss to column activity.

It is impractical to test all chromatographically problematic compounds on all columns. However, it is reasonable to assign as proxy probes, known active analytes with functional groups that are the same as many of the chromatographically active compounds in the previously mentioned analyses. Further, if the test conditions are truly demanding, one can get a more accurate evaluation of how different manufacturers' columns compare. The work that follows takes this approach.

The Test

There are three things a column manufacturer can do with their column test to make the column look better than it really is: 1) select chromatographically undemanding probes, 2) run the test on a temperature program, and 3) run the test at higher temperatures.

Undemanding Probes

Almost all column manufactures include in their test mixes an organic acid (a substituted phenol), base (an amine), and an alcohol, along with non-active probes. Assuming inert compound (hydrocarbons) chromatography is good, the acid, if it tails or loses response, indicates that the column is "basic." The base, likewise, will indicate if the column is acidic. The alcohol will give an indication if there has been oxygen damage, or if there are any surface silanols exposed as it will not lose response except in severe damage situations, but will tail. If peak shapes for all these compounds are symmetrical, then the column is considered "inert" toward them.

By selecting undemanding probes, column activity can go undetected. This is the equivalent of using a magnifying glass instead of a microscope when you need to look for bacteria-you won't see anything wrong because you don't have a powerful enough tool to see. A surprising number of column manufacturers use undemanding probes to check the quality of their columns to "improve" their manufacturing yield and then sell at a lower price. Additionally, the ratio of the active functional group relative to the overall size of the molecule, and the less sterically hindered this active moiety, the more potential there is for the moiety to interact with an active site in the column. Here are a couple examples of undemanding probes based on these assumptions:

2,6-Dimethylphenol-Sterically shielded -OH function, very, very weak acid

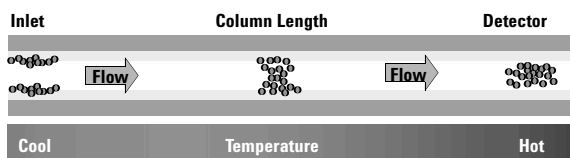
Dicyclohexylamine-Sterically shielded, secondary amine function, weaker base

Temperature Programming

As depicted in figure 8, when a probe chromatographs under temperature programmed conditions, the percentage of molecules of the probe in the mobile phase is increasing as the probe passes from the inlet to the detector end of the column. As such, it is spending more time interacting with the column stationary phase toward

the inlet end of the column, so the probes are not testing the entire column equally, a problem with traditional test mixes like the Grob mix. Oven programming also can hide the appearance of tailing (i.e., activity). In short, a column's inertness should be tested isothermally.

Figure 8.



Test Temperature

Generally, the longer a test probe is in the column, the more it interacts with active sites in the column. Additionally, the lower the column temperature, the greater the strength of these adverse interactions. A demanding test will be one that is run at lower temperatures thus, increasing k and enhancing the interaction opportunity for all the test probes. In practice, we have observed significantly more revealing results at test temperatures below with all probes². At lower temperatures even a moderately retained probe is just as revealing as a homologue probe that is retained longer. (For example, n-heptanol reveals just as much about column activity as n-decanol, once they achieve a k of 3 or more).

"Demanding" Test Criteria-Separating Wheat from Chaff

Taking all the above under consideration, and working through roughly 50 test probe candidates, the following test conditions were selected to compare a variety of 5% phenyldimethylpolysiloxane columns:

Injection: ALS (with nanoliter adapter)
 0.1 μ l, Split, 250°C

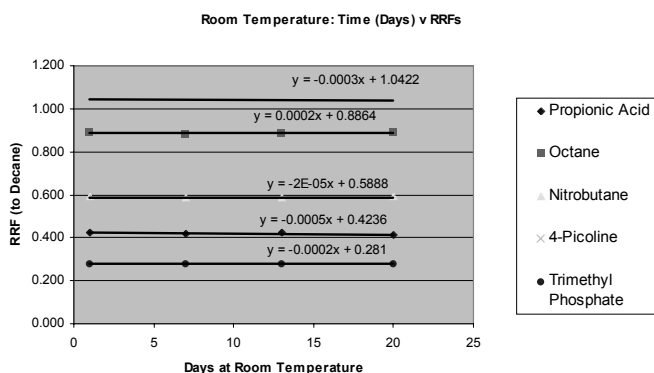
All Columns tested: 30m x 0.25 mm I.D., 0.25 μ m
 5% phenyldimethylpolysiloxane

Carrier: 34 cm/sec or 1.0 mL/min flow, H₂

Oven: 65°C for 14 min
 (until last probe elutes)
 65-300°C, 25°/min
 300°C until solvent elutes

This test mix is somewhat unconventional as it uses a solvent which elutes after the probes. Many solvents used in test mixes are polar solvents. It can be reasonably argued that such polar solvents and their low level impurities might actually temporarily "mask" active sites on the column, interfering with the interaction between the test probes and the column, again making the column look better than it is. For this reason, a solvent eluting after the probes was used. Also, methane could be introduced and retained into the standard for determining linear velocity. Test probes and their estimated on-column amounts (in nanograms) are shown below. Amounts cannot be determined exactly because the injection mode is split.

Table 1. Test Probes in Performance Mixture.



Probe	(ng)	Column functional test
Methane		NA
Propionic acid	1.4	Basicity
Octane	0.5	HC marker (inert)
Nitrobutane	1.0	Acidity
4-Picoline	0.6	Acidity
Trimethyl phosphate	2.6	Acidity
1,2-Pentanediol	1.1	Silanol
Propylbenzene	0.4	HC marker (inert)
1-Heptanol	0.6	Silanol
3-Octanone	0.6	Polarity
Decane	0.4	HC marker (inert)

As these are very chemically reactive probes compared to traditional test mix probes, test mix stability was determined. Results in Figure 9 showing the mixture stable at a higher concentration over a period of 3 weeks demonstrate mix stability sufficient for the duration of this comparison, which was only 1.5 weeks.

Figure 9. Test Mix Stability

The stock standard (at 5X concentration) was run on the day of preparation, 7, 13, and 21 days after preparation, and was kept at room temperature during the course of testing. Relative Response Factors to Decane for the active probes were calculated, and plotted against time (days). A negative slope indicates probe loss, and propionic acid had the greatest rate of loss. This equates to a loss of 0.5% over the 10 days this study was run-not significant-so the standard was deemed "stable."

Conclusions

A Picture is worth a thousand words. As the Figures above show, a demanding test mix reveals the inertness differences in the performance of capillary columns from one manufacturer to the next. In some cases, even comparably priced competitors do not perform as well as Industry Standard columns like the HP-5ms and DB-5ms.

Footnotes

¹M. Hastings, E. Kuhn, A.K. Vickers, Evaluation of Capillary Columns for General Performance Parameters, Poster, Pittcon 2002.

²Personal communication, C. George, J. Ellis, Agilent Technologies, Inc, M.D'Amico, Michrom Inc.

HP-5ms

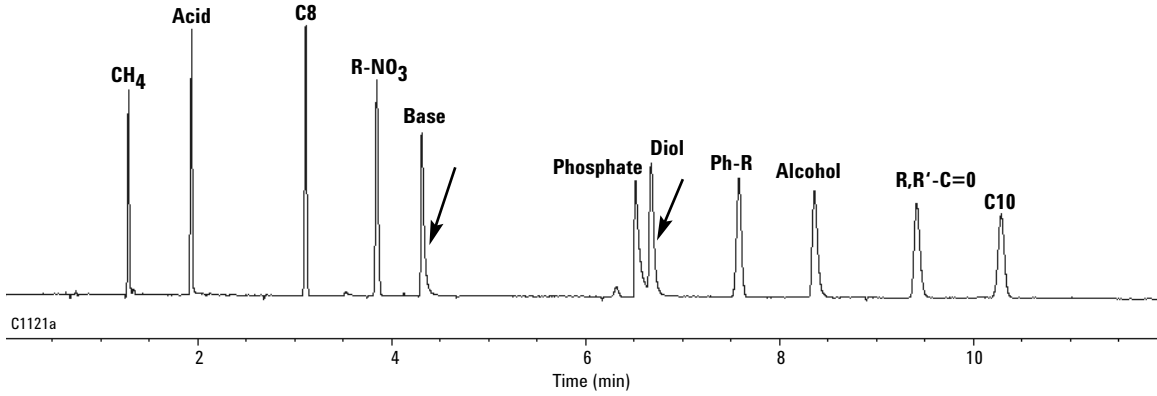


Figure 1. Modest tailing of base and phosphate.

DB-5ms

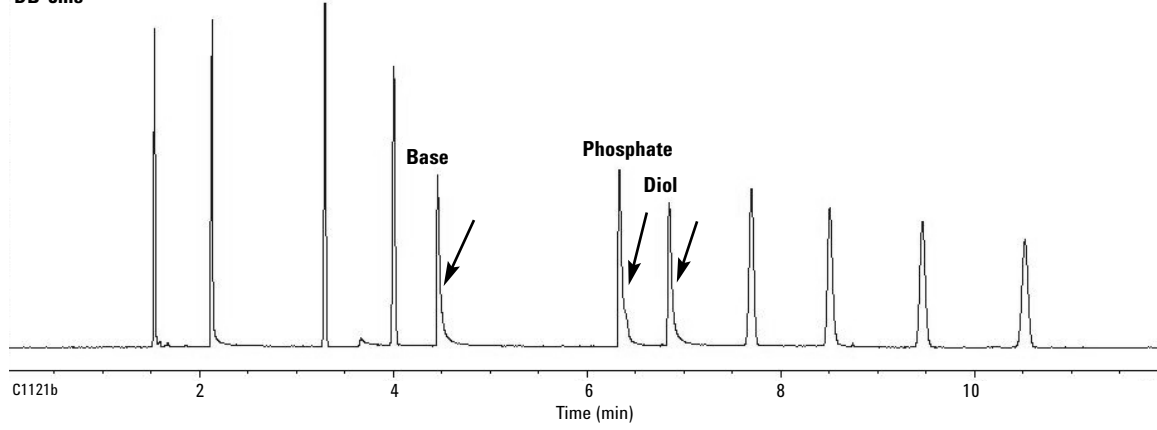


Figure 2. Slight tailing on base, phosphate, and diol, but still good.

Manufacturer A--Comparably Priced

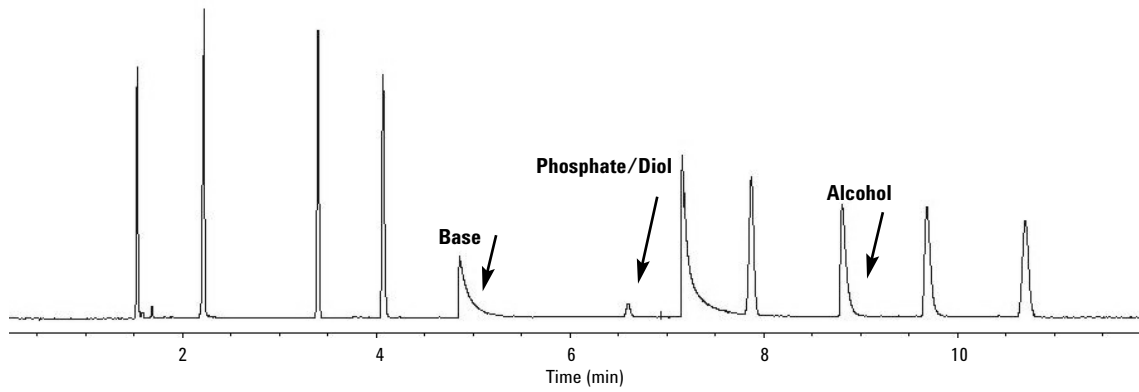


Figure 3. Loss of base and co-elution of phosphate and diol, and tailing alcohol.

Manufacturer B--Low Priced

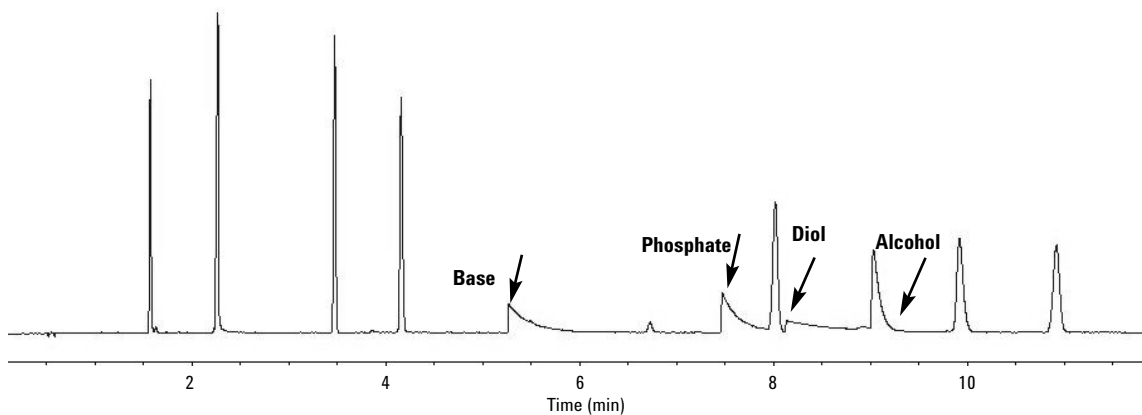


Figure 4. Loss of base and phosphate severe diol response loss, tailing on alcohol.

Manufacturer C--Comparably Priced "5ms" Competitor

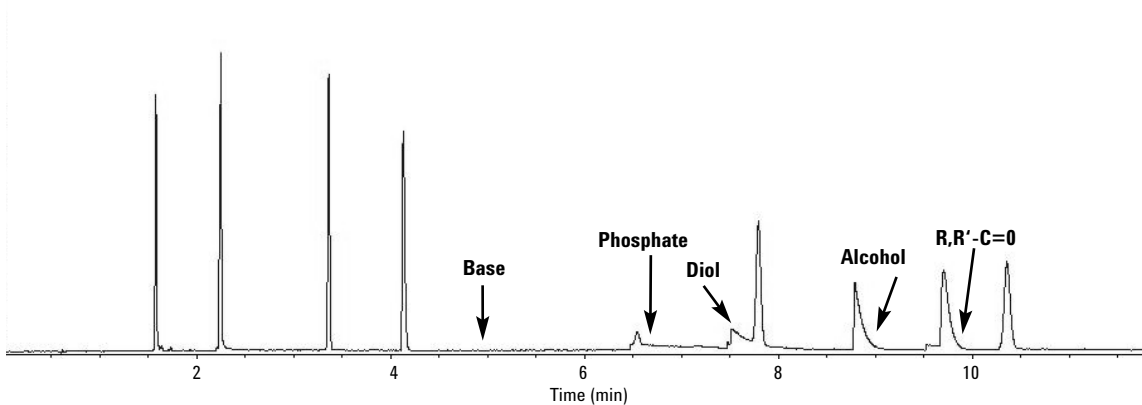


Figure 5. Complete loss of base and phosphate, severe diol response loss, tailing on alcohol and even the ketone, an extreme form of activity.

Manufacturer C--Premium Priced Extra Inertness Column

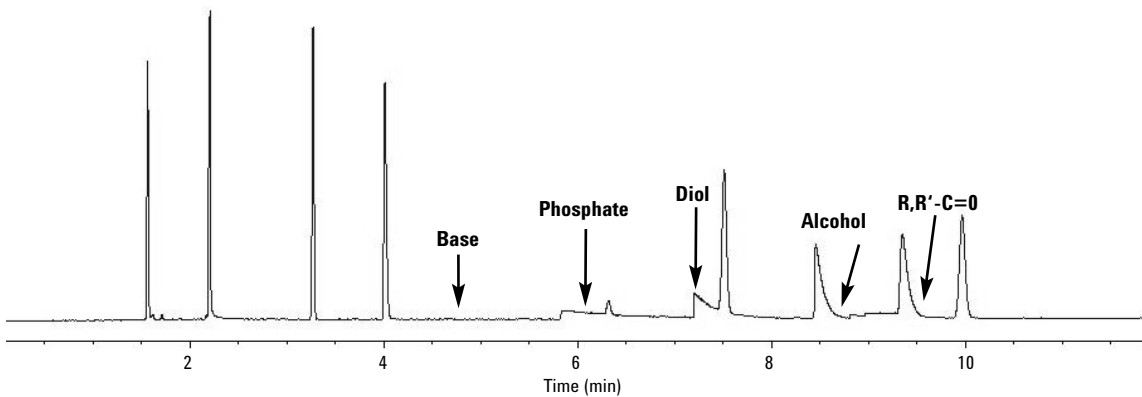


Figure 6. Good response for the acid, but complete loss of base and near complete loss of phosphate, severe diol response loss, tailing on alcohol and even ketone, an extreme form of activity.

Manufacturer D--Low Priced Manufacturer's "MS Grade" Column

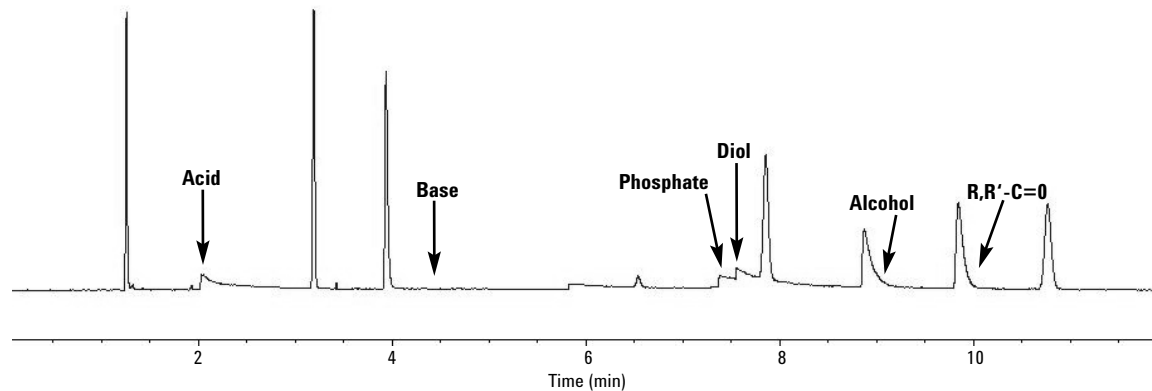


Figure 7. Near complete loss of acid, complete loss of base and near complete loss of phosphate and diol, tailing on alcohol and even the ketone, an extreme form of activity.

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