

## Gas Chromatography Problem Solving and Troubleshooting

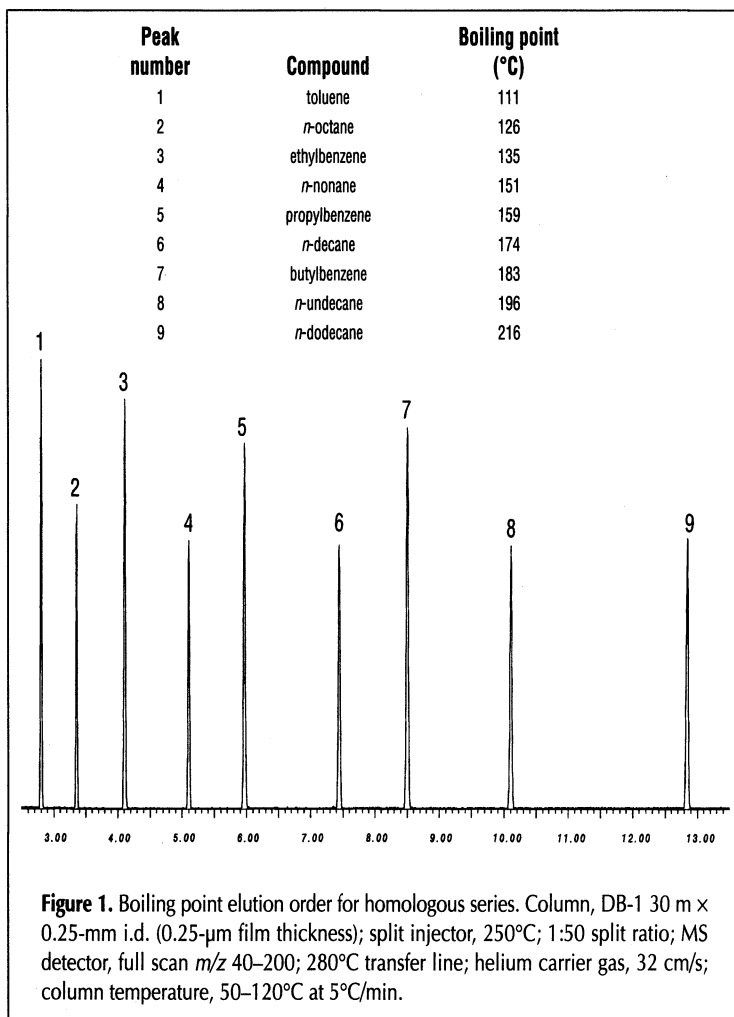
### Question:

I was using a methyl silicone stationary phase, and some of the compounds in one of my new samples did not elute in boiling point order. Is there something wrong with my capillary column or GC?

### Answer:

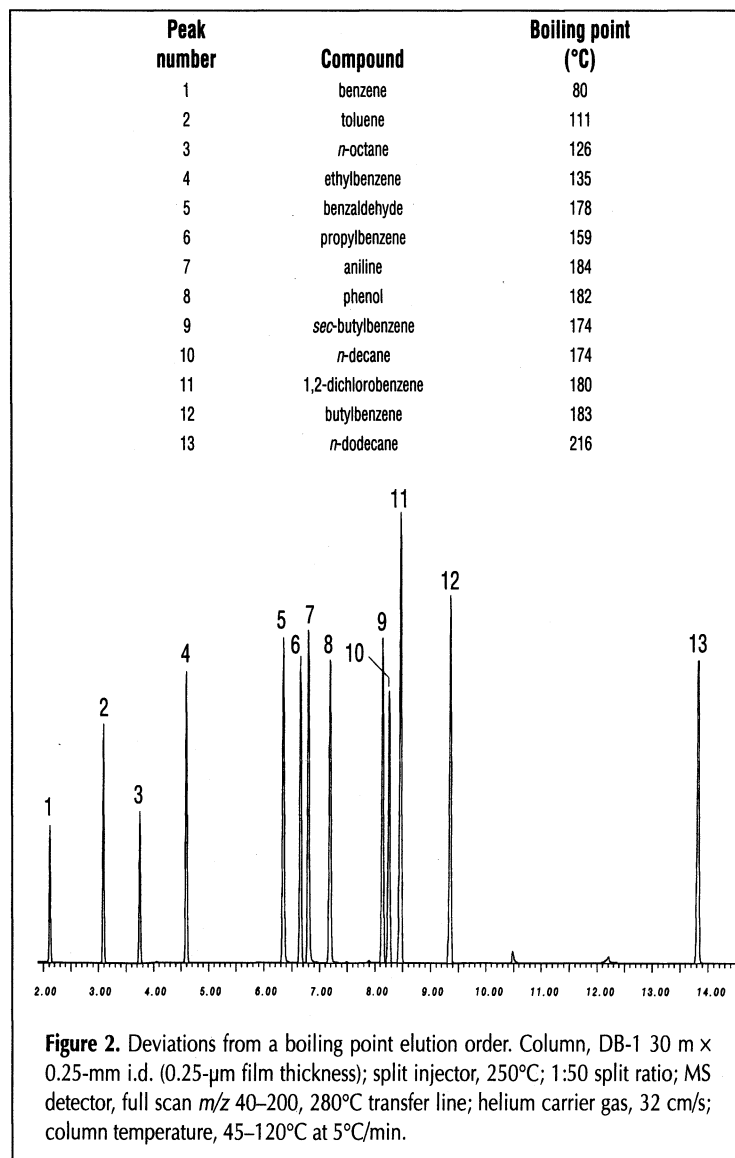
There is nothing wrong or at fault with the column or GC. It is a common misconception that all compounds elute in the order of their increasing boiling points for methyl silicone (or more properly, dimethyl polysiloxane) stationary phases. Depending on the structure of the compounds, there are deviations from the boiling point elution order for dimethyl polysiloxanes. The boiling point elution order is valid only for homologous series. Figure 1 shows an example of this type of behavior. The straight chain hydrocarbons are a homologous series and elute in the order of their increasing boiling points. The *n*-alkyl substituted benzenes show this behavior because they also fall within a homologous series. Because the *n*-alkyl benzenes are structurally related to the hydrocarbons (i.e., containing only carbon and hydrogen without any branching or other substituted groups), these particular compounds as a group do not deviate from the boiling point elution pattern.

If compounds with other types of functional groups are in the sample, exceptions to elution order based on boiling point usually occur. Figure 2 shows an example of this result. Benzaldehyde (peak 5), aniline (peak 7), and phenol (peak 8) are eluting much earlier than their boiling points would indicate if boiling point elution orders were valid. These compounds are more polar than the *n*-alkyl benzenes and hydrocarbons. Because dimethyl



The purpose of *Chromatography Problem Solving and Troubleshooting* is to have selected experts answer chromatographic questions in any of the various separation fields (GC, GC-MS, HPLC, TLC, SFC, HPTLC, open column, etc.). If you have questions or problems that you would like answered, please forward these to the *Journal* editorial office with all pertinent details: instrument operating conditions, temperatures, pressures, columns, support materials, liquid phases, carrier gas, mobile phases, detectors, example chromatograms, etc. In addition, if you would like to share your expertise or experience in the form of a particular question accompanied by the answer, please forward to JCS Associate Editor, *Chromatography Problem Solving and Troubleshooting*, P.O. Box 48312, Niles, IL 60714. All questions/answers are reviewed to ensure completeness. The *Journal* reserves the right not to publish submitted questions/answers.

Dean Rood  
Associate Editor



polysiloxane is a nonpolar stationary phase, reduced retention of these more polar compounds occurs. Outside of a homologous series, even similar compounds with the same boiling point may separate, and dissimilar compounds with very different boiling points may co-elute for dimethyl polysiloxane. *sec*-Butylbenzene and *n*-decane are baseline-resolved, and they have the same boiling point (peaks 9 and 10 in Figure 2). Tetrahydrofuran (THF), iso-butanol, and 2-methoxyethanol co-elute for a dimethyl polysiloxane even though their boiling points are 67, 108, and 124°C, respectively. Except for a homologous series, using compound boiling points is only useful as a rough approximation of elution order for a dimethyl polysiloxane stationary phase.