

Minimizing decomposition of components during GC analysis

Sometimes we see in our chromatogram a peak shape that we know is not 'normal.' Last month we discussed the overloading phenomena, which directly impacts peak shape. In this instalment we will again look at peak shape, but from a different perspective. If a component is not thermally stable, the peak shape and size may be a good indicator. There are several actions we can take if we observe the phenomena, but we need to recognize it first.

Gas chromatography is performed under conditions where the components to be separated are in the gas phase. We use a temperature-controlled oven to heat the column to evaporate components with higher boiling points. These ovens are typically used up to 450 °C, which allows analysis of components with boiling points of up to 700 °C.

However, not all components are stable when heated and decomposition can occur. This can happen when the component is evaporated during the injection step, or it can happen when the component is 'traveling' through the capillary column.

Decomposition and peak shape

If a component is thermally labile, or reactive, we can expect a non-reproducible and lower response for that component.

In most cases the component decomposes into a 'smaller' product. If the decomposition happens inside the injector, the response of the component will be lower, and we will see sharp decomposition peaks. We can change injection conditions to minimize this effect.

If the decomposition happens while the component is traveling through the column we see a strong 'leading' peak (Figure 1).

The 'lead' of the peak is formed by the decomposition products, as they elute faster. As these products are formed during the time the component is inside the column, these products will not elute as a peak, but as an elevated baseline.

Components that are known for thermolability are pesticides (e.g., DDT, carbamates etc.), and brominated diphenyl ethers (e.g., flame retardants). Sometimes unsaturated compounds, such as propadiene and pentadienes decompose on activated alumina surfaces.

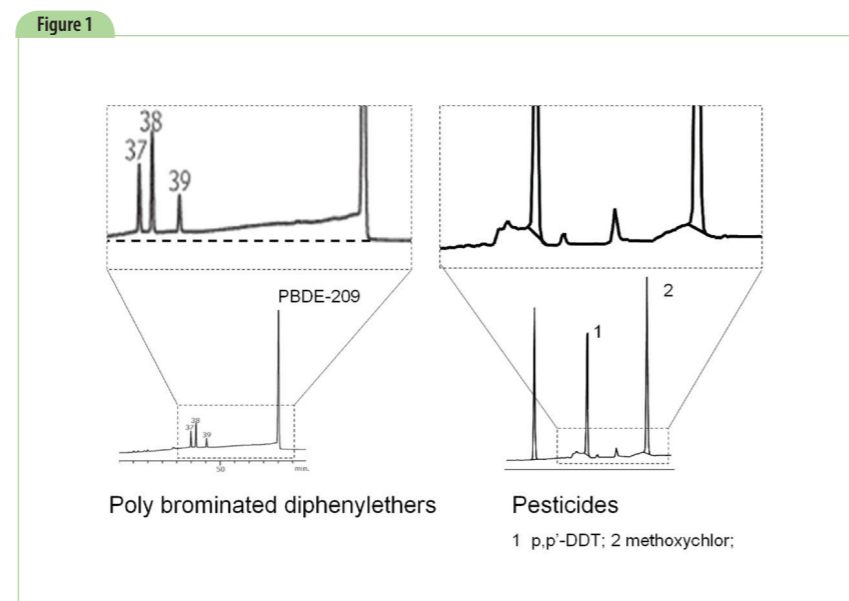


Figure 1: Example of decomposition during chromatographic separation.

Reduction of component breakdown

The decomposition reaction is strongly temperature-dependent. Practically, we need to do the analysis at the lowest possible thermal stress, meaning creating optimal conditions for injection port temperature and elution temperatures while performing the GC separation.

Injection: Using evaporating injection systems is always very challenging as the component is exposed to high temperature and will decompose. In splitted injection, the injection takes a fraction of a second, which usually is not a problem. With splitless injection, the sample is initially exposed to high injection port temperature. During this time, interactions can take place and components will decompose. Figure 2(a) shows an example of what can happen with carbamates when they are introduced via splitless injection. The carbamates are broken down into their phenolic esters. These compounds will elute as sharp peaks as they are focused on the column.

Figure 2(b) shows the same analysis using on-column injection. Because of the absence of thermal stress during injection, the carbamates are injected onto the column without decomposition.

If on-column is not an option and splitless injection is to be used make sure that:

- the lowest possible injection port temperature is used
- the highest possible flow rate (use 0.32 mm columns) is used
- a pressure pulse is used
- inert liners (siltek or siloxane-deactivated) are used
- care is taken with glass wool packings as these may initiate decomposition

This way we can minimize thermal stress. An alternative injection technique to consider is 'programmed temperature injection' or PTV. Here the sample is introduced into a cold liner, and flash separation science — volume 1 issue 5

evaporated when the injector is heated. PTV is not as good as the cold-on-column method, but better than the splitless technique.

The capillary separation column: Once the sample is injected into the column, the component must pass the whole column and during this process decomposition can occur. This decomposition is directly dependent on temperature, but also on column activity. If the column is not properly deactivated, component breakdown will be much higher.

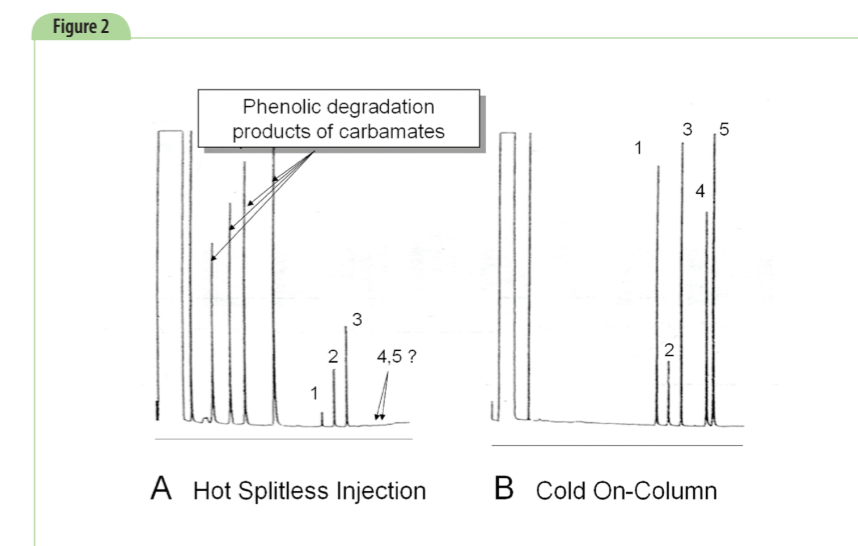


Figure 2: Impact of injection technique on decomposition of carbamates: (a) = hot splitless, (b) = cold on-column; Peaks: 1 = bendiocarb, 2 = dimethoate, 3 = aminocarb, 4 = dioxacarb, 5 = carbaryl. (Ref: J. of HRC., Vol 13, nov.1990, p. 759.)

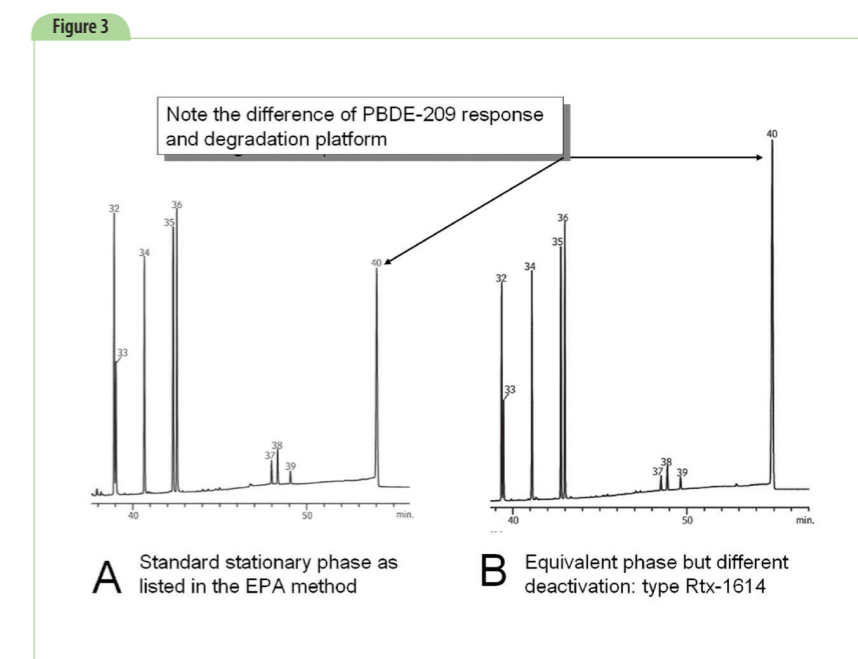


Figure 3: Analysis of BDE according to EPA 1614 using the following EPA protocol: (a) using column as listed in method; (b) equivalent column, but with different deactivation. Both columns under exact similar conditions.

Figure 4

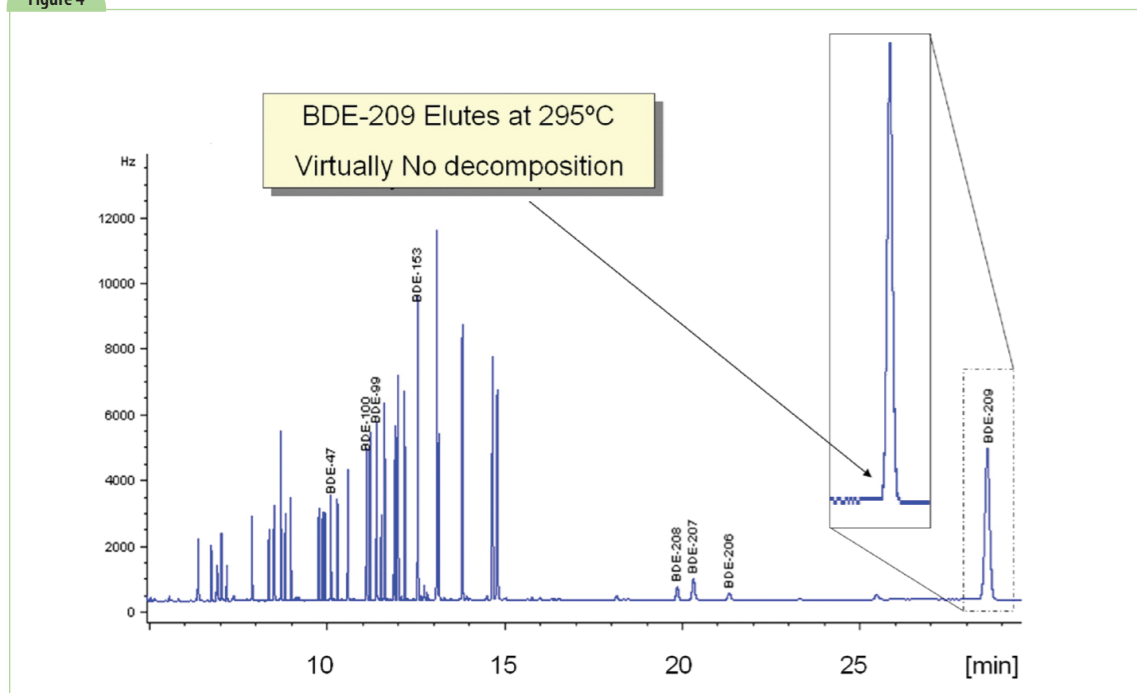


Figure 4: Analysis of BDE using lower elution temperatures. Column: 30 m x 0.25 mm Rtx-1614, $df = 0.1 \mu\text{m}$; Oven: 120 °C (1 min) → 295 °C (15 min) @ 15 °C/min; Injection: splitless; Carrier gas: He @ 2.5 mL/min constant flow

Figure 5

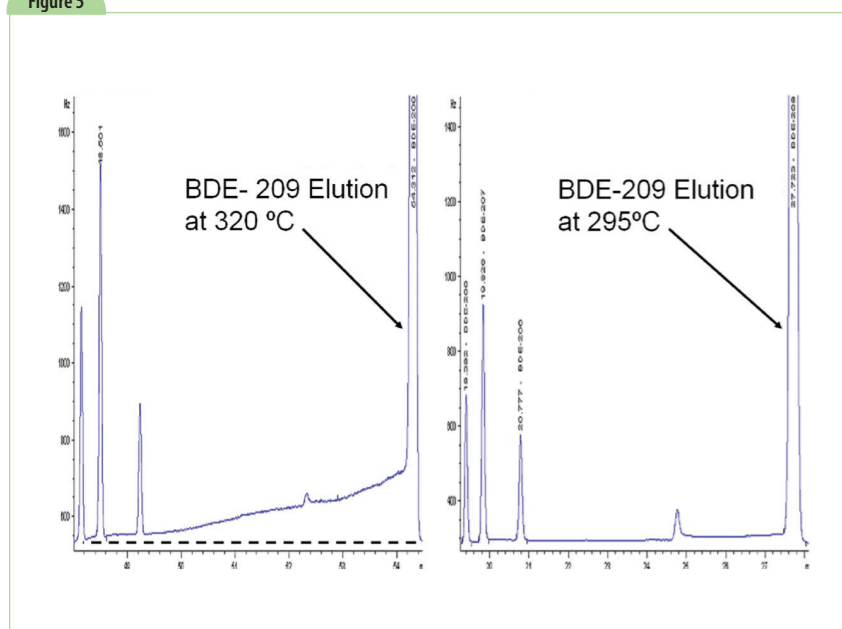


Figure 5 : Expansion of problem area of BDE-209. Elution temperature has big impact on decomposition process.

BDE or 'flame-retardants' are brominated diphenyl ethers designed to be thermally unstable, so they will act better as flame retardants. GC analysis will be a challenge, but it is possible.

Figure 3 shows the analysis of BDE-209 using the EPA 1614 methodology in which the impact of deactivation on peak response is shown. Using exactly similar conditions, the well deactivated column produces less

degradation. Column inertness plays a role.

Even with well deactivated columns, degradation still occurs as confirmed by the 'lead' on DME-209. The key to setting methods for thermolabile components is to reduce the elution temperature.

Figure 4 shows the same column as in Figure 3, but now the final temperature does not exceed 295 °C. Consequently, the decomposition of DBE-209 is greatly reduced. Figure 5 shows an expansion of the problem area.

Ways to reduce the elution temperature

There are several ways to influence the elution temperature. In the example of Figure 5, the program did not exceed 295 °C. Typically, this will increase analysis time as it will take longer to elute heavy components.

Use higher flow rate, a flow program or a pressure program: By doubling the optimal flow rate, the elution temperatures will be reduced by 20-25 °C. This is usually very effective with non-MS detection systems. The higher flow will cause some loss of efficiency,

Figure 6

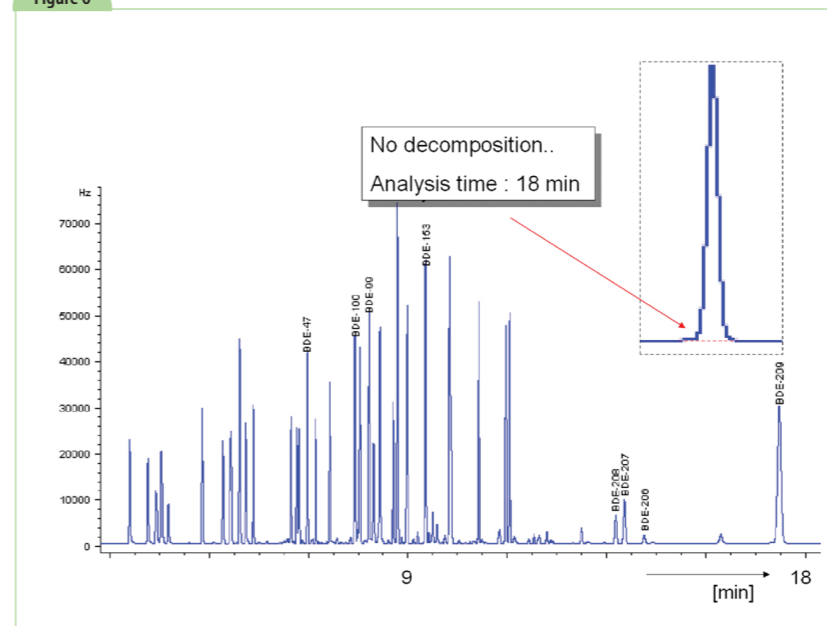


Figure 6: Fast analysis of DBEs using 15 m x 0.25 mm Rtx-1614 column. Shorter time at higher temperature will also result in reduction of decomposition.

so it may be a consideration to initiate the pressure program after the key separations are obtained.

Use a slower temperature program: By using a slower temperature-programming rate, components will elute at a lower temperature. However, the downside of this is longer analysis times and peak broadening (lower response).

Use hydrogen, rather than helium, as the carrier gas: Because of the higher optimal flow rate, we can benefit from lower elution temperatures, while working under optimal conditions. Here, however, you must deal with safety issues, which is another discussion.

Use columns with thinner films: Elution temperature is directly dependent on the amount of stationary phase (film thickness). Use a 0.10 μm film instead of a 0.25 μm one. **Use a 0.32 mm i.d. capillary:** A 0.32 mm capillary with 0.1 μm film will have higher phase ratio, which results again in a lower elution temperature. The 0.32 mm column, however, will be lower in efficiency, so we may lose some separation efficiency. If the target components elute with sufficient resolution from their neighbours, you can

also apply a pressure program. This is very effective with 0.32 mm columns.

Use shorter columns: The absolute time components are in the column should be as short as possible. Shorter columns will, therefore, give higher response, but will have lower efficiency, which will impact on resolution, similar to that discussed using 0.32 mm columns. If we take a 15 m column instead of a 30 m one, resolution is only impacted by a factor 1.4. Figure 6 shows the separation of the BDE. The components elute below 295 °C and the total time in the column is now reduced by a factor of 2. To compensate for efficiency loss, one can choose a smaller diameter column; for example, a 20 m x 0.15 mm column will generate the same efficiency as a 30 m x 0.25 mm one.

Summary

For analysing thermally labile components, the best injection technique is cold-on-column. To minimize exposure to the high temperature environment, we need to use inert columns with a high phase ratio. In addition, short columns are preferably operated with high gas velocity and slow temperature programming.

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