On-Column Cryofocusing for Improved Resolution in Pyrograms

Application Note

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Pyrolysis has been used for years as a means to permit the analysis of natural and synthetic polymers by gas chromatography. Inherent in the system is a chamber in the GC carrier gas stream where the pyrolysis is to take place. Unfortunately, this adds dead volume to the GC system upstream from the column, and may produce broad or poorly resolved peaks in the pyrogram. One solution to this problem is the use of a split capillary injection system with a high enough split ratio to permit rapid sweeping of the pyrolysis chamber. This solution, however, necessitates the use of larger samples, since most of the pyrolysates are consequently swept out the splitter vent, and large samples are not generally the best for reproducible pyrolysis results.

Another solution is to refocus the pyrolysates directly onto the capillary column using a cryogenic trap. The example shown here used a Cryogenic Focuser, which mounts onto the gas chromatograph at the injection port, and uses liquid nitrogen to focus the organic volatiles onto the GC column.

For the pyrolysis of polypropylene shown in Figure 1, the fused silca capillary column was brought up through the injection port of the GC and passed through the cryofocuser. It was then inserted into the interface of the Pyroprobe and sealed with a graphite ferrule. Now all of the flow through the interface went directly into the column, with no splitting. Prior to pyrolysis, the cryofocuser was cooled to -100°C, so that the pyrolysates would be collected as they left the interface. Once the pyrolysates were collected, the cryofocuser was heated to 280°C and the GC program was started.

For comparison, Figure 2 shows a pyrogram of polypropylene using a split capillary system, with a 60:1 split ratio. Not only could a much smaller sample be used with the cryofocusing system, but a comparson of the first 10 minutes of the two chromatograms shows how much more information is revealed by the improved resolution gained with the cryofocuser. Now many well resolved peaks may be seen which were formerly hidden in the broad, unresolved peaks seen in the split capillary chromatogram.

Equipment:
PYROLYSIS

Pyrolysis temperature: 750°C for 10 seconds
Interface temperature: 280°C

CRYOFOCUSER
Collection Temperature: -100°C for 10 minutes
Desorption temperature: 280°C

GC Conditions:
Varian 3700 equipped with FID
Column: 50m x 0.25mm SE-54
Program: 50°C for 2 minutes, then 7 C/min to 290° C

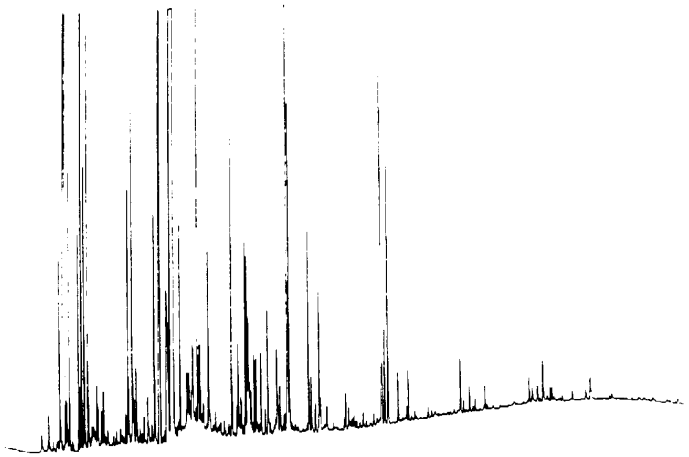

Figure 1: Pyrolysis of Isotactic Poly(propylene) With On-Column Cryofocusing

For more information on this and related applications, we recommend the following readings:

E. Levy, and T. Wampler, "Identification and Differentiation of Synthetic Polymers by Pyrolysis Gas Chromatography," J. Chem. Ed., 63, (1986), 64-68.

T. Wampler, and E. Levy, "Cryogenic Focusing of Pyrolysis Products for Direct (Splitless) Capillary Gas Chromatography," J.A.A.P., 8, (1985), 65-72.

T. Wampler, W. Bowe, J. Higgins, and E. Levy, "Systems Approach to Automatic Cryofocusing in Purge and Trap, Headspace, and Pyro lytic Analysis," American Lab., 1986, (August).

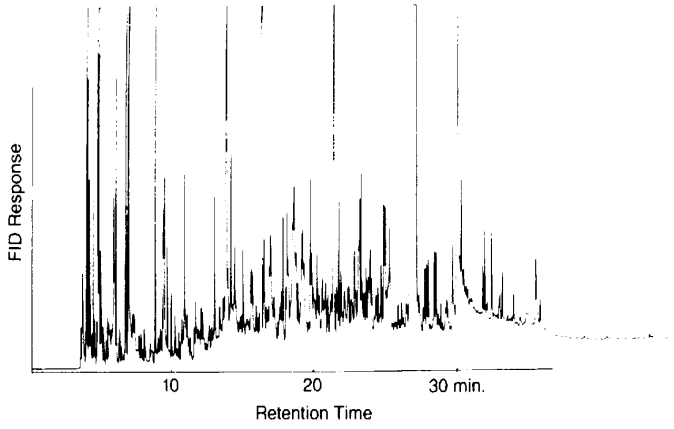

Figure 2: Pyrolysis of Isotactic Poly(propylene) Split Capillary GC