Pyrolysis Autosampling Reproducibility

Application Note

Author:

T. Wampler

To be analytically useful any technique must be shown to be reproducible. In the analysis of polymers by pyrolysis-gas chromatography, analysts are interested in reproducible retention times and peak areas for the pyrolysis products, and how they may be affected by the pyrolysis instrumentation used.

Automating sample introduction eliminates many of the operator associated variables which can adversely impact reproducibility. To demonstrate pyrolysis-GC reproducibility in the analysis of polyethylene, seven samples were loaded into a Pyroprobe Autosampler and pyrolyzed at 850°C to a capillary GC equipped with an FID. Figure 1 shows four consecutive runs, with the distribution of hydrocarbons - straight chain alkanes, alkenes and dienes - characteristic of polyethylene.

Retention times were averaged for decene (9.4 min) and undecene (12.5 min), and then the peak area ratio for these peaks was calculated for each run. The retention times averaged 9.424 ± 0.008 and 12.514 ± 0.008 respectively, and the peak area ratio averaged 1.284 ± 0.04, for a relative standard deviation of 3.08%.

In a separate evaluation, ten samples of a styrene/butadiene copolymer were pyrolyzed at 750°, again using the Pyroprobe 2500 autosampler. The average peak area ratio for the butadiene dimer peak to the styrene monomer in this case showed an RSD of 2.6%.

Instrument Conditions

Pyroprobe

Valve Oven:	300°C
Interface:	300°C
Pyrolysis:	850°C
Time:	20 seconds

GC/MS

Column:	5% phenyl (30m x 0.25mm x .25μm)
Carrier:	Helium, 75:1 split
Injector:	300°C
Oven:	40°C for 1 minutes
	5°C/min to 300°C hold 12 minutes

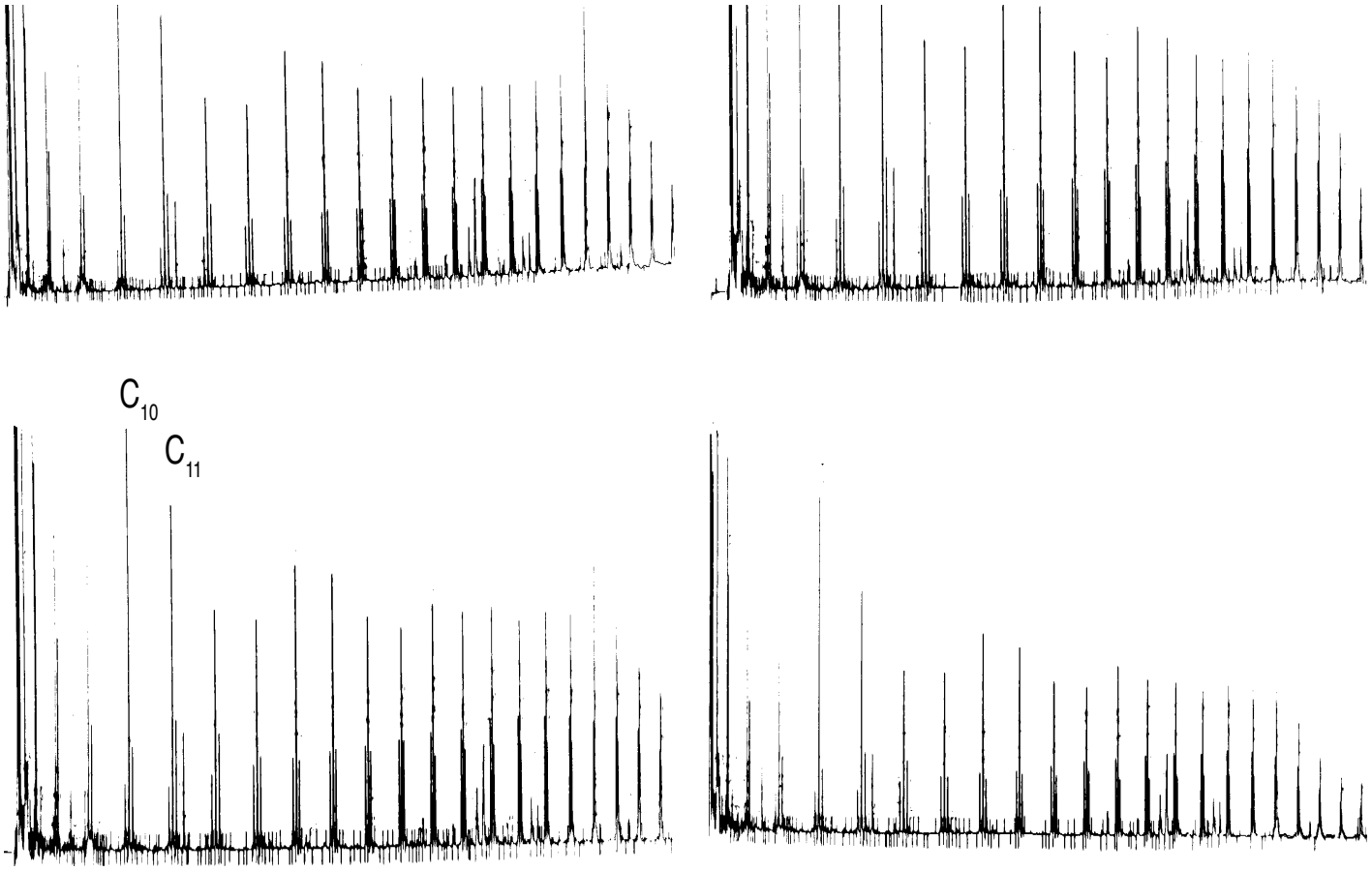

Figure 1. Polyethylene in Pyrolysis.

REPRODUCIBILITY DATA

Item	Average	± SD	RSD
C10 Retention time	9.424 min	0.008	0.08%
C11Retention time	12.514 min	0.008	0.06%
C10/C11 Area ratio	1.284	0.04	3.08%
Butadiene dimer/ Styrene area ratio	0.114	0.003	2.63%

FOR MORE INFORMATION CONCERNING THIS APPLICATION,
WE RECOMMEND THE FOLLOWING READING:

Reproducibility in Pyrolysis, Recent Developments, T. Wampler and E. Levy, J.A.A.P., 12 (1987) 75-82.

Thermometric Behavior of Polyolefins, T. Wampler, J.A.A.P, 15 (1989) 187-195.