CDS solutions

APPLICATIONS INFORMATION USING ADVANCED SAMPLE HANDLING TECHNOLOGY

The Pyrolytic Injection Inlet Autosampling System for the Analysis of Polymer Samples

The **CDS Analytical Pyrolytic Injection Inlet (PII)** combines the benefits of split, splitless, and on-column inlets with analytical pyrolysis of soluble materials. Pyrolysis is the breaking apart of large, complex molecules by heat, which creates smaller, volatile compounds which can be analyzed by gas chromatography, and by other techniques. Now, pyrolysis can be combined with autosampling to improve reproducibility and save analysis time.

The PII is based on the CDS Pyroprobe 2000. The coil of the Pyroprobe, containing a quartz pyrolysis tube, is inserted into the GC injection port in place of the usual injection port liner. Manual or autosampler injections place the sample directly into the quartz tube. The solvent can be allowed to vent, if desired, before the sample is pyrolyzed. Since sample size, pyrolysis temperature, and the placement of the sample within the Pyroprobe coil affect the pyrolysis behavior of materials, the use of an autosampler improves reproducibility by standardizing these parameters.

For these experiments, soluble polymers were pyrolyzed using a GC autosampler to demonstrate the reproducibility of the pyrolysis conditions using the PII. The ratio of the peak areas of the pyrolysis products was used as an indication of reproducibility.

In the first group of experiments, a mixture of polymethylmethacrylate (PMMA) and poly-

Figure 1

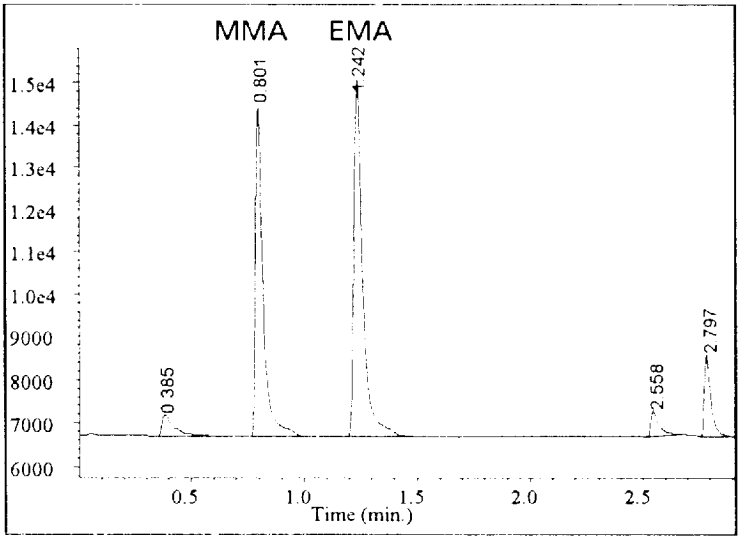
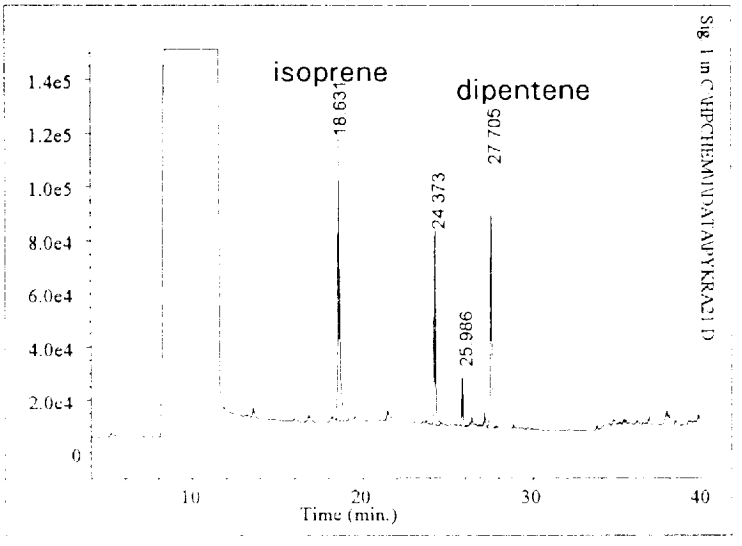


Figure 2



ethylmethacrylate (PEMA) was pyrolyzed 58 times. Both PMMA and PEMA revert almost completely to monomer after pyrolysis, as shown in Figure 1. Thus, the ratio of the areas of the resulting methylmethacrylate (MMA) peaks to that of ethylmethacrylate (EMA) was compared. After 58 injections, the RSD of these ratios was 0.52%.

In the second group of experiments, the reproducibility of pyrolysis was studied by pyrolyzing Kraton at 650 C. Figure 2 shows a typical chromatogram obtained from this pyrolysis.

Kraton is a good polymer to use to demonstrate pyrolysis reproducibility because the ratio of isoprene to dipentene peaks is very temperature sensitive. The average ratio at 650 C pyrolysis was 1.398 for 20 injections, and the relative standard deviation was 2.42%. At 625 C, the ratio is 1.28, and at 675 C the ratio is 1.56. Since the mean at 650 C plus s = 1.36 and minus s = 1.43, the ratios at 625 C and 675 C are clearly significantly different. This demonstrates excellent reproducibility of the pyrolysis temperature.

Additional literature on this and related topics may be obtained by contacting your local CDS Analytical representative, or directly from CDS at the address below.

Experimental

For PEMA and PMMA experiments, both polymers were dissolved in dichloromethane at 1 mg/ml. A three step pyrolysis program was used. The sample was injected, then held in the PII while the solvent eluted from the column. The sample was then pyrolyzed at 800 C for 10 seconds, and held at 0 C during the GC run. After the polymer peaks eluted from the column, the PII was cleaned at 1200 C for ten seconds to prepare for the next sample. The complete pyrolysis and GC conditions are given below.

Pyrolysis:

Sample Size: 2 ul
Step 1: Start 0 C; ramp at 20 C/mSec to 800 C; hold 10 seconds.
Step 2: Start 0 C; hold 2 minutes.
Step 3: Start 0 C; ramp at 20 C/mSec to 1200 C; hold 10 seconds.

Gas Chromatography:

GC: Hewlett-Packard 5890 Series II Plus
Autosampler: Hewlett-Packard 7673
Column: 6 meter, DB-1, 0.32 mm ID, 0.25 um
Injection Temperature: 250 C.
Carrier Inlet Pressure: 8 psi
Carrier Gas: Helium.
Oven Program: start 35 C; hold 1.8 minutes; ramp at 25 C/min to 100 C.

A similar program and instrumentation was used for the pyrolysis of Kraton, except that the pyrolysis temperature was 650 C. A 30 meter GC column was used, with the following oven temperature program: start 40 C, hold 17 minutes for the solvent to elute, ramp at 8 C/min to 160 C, and at 25 C/min to 280 C. The Kraton was dissolved in toluene at 1.35 mg/ml, and 1 ul was injected into the PII.

ABOUT CDS

CDS Analytical, Inc. is a leader in the design and manufacture of laboratory instruments for sample preparation and analysis. With 25 years experience in the field, CDS is dedicated to providing the best possible instruments for both research and routine analysis. Well known in the field of analytical pyrolysis, CDS manufactures the Pyroprobe 1000 and 2000 for the introduction and analysis or solid materials by GC, MS and FT-IR. CDS offers a complete line of purge and trap instruments for the analysis of volatile organic compounds in the environmental, food and pharmaceutical areas, as well as custom systems for complex, multicomponent materials investigation. Our customers, their requirements and applications are important to us. To help meet their needs, we offer a wide range of analytical information and the services of our applications laboratory. If you would like additional information, please contact us at the address below, or call us at 1 800 541 6593.

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