Volatile Mixture Analysis by Repetitive Injection
Fast Gas Chromatography/Mass Spectrometry

Robert L. White*

Department of Chemistry & Biochemistry, University of Oklahoma, Norman, Oklahoma 73019

An apparatus designed for repetitive sampling and characterization of evolved gas mixtures generated during thermal analysis is described. The apparatus combines fast temperature ramp gas chromatography separations with mass spectrometric detection to selectively monitor volatile mixture component concentration changes as a function of sample temperature. The apparatus was tested by using it to repetitively sample and analyze the volatile products generated when poly(styrene) was catalytically cracked by an HY zeolite solid acid catalyst by heating the polymer/catalyst mixture in an inert helium atmosphere. Eleven mixture components contained in the gas stream were separated and detected at 90-s intervals when the polymer/catalyst sample was heated from 200 to 400 °C. Mass spectral extracted ion chromatograms were employed to generate species-specific evolution temperature profiles, which provided insight into thermal reaction mechanisms.

Characterization of volatiles generated during thermal analyses may provide information that can be helpful for elucidating temperature-dependent reaction mechanisms. The type of analysis needed for evolved gas monitoring depends on the characteristics of the species to be monitored and the rate at which concentrations are expected to change. Detection methods that produce a unique, selective response for a specific substance can be employed for monitoring without interference from other species that may also be present in the gas stream. For those instances when it is desirable to monitor multiple substances, methods that can simultaneously detect and quantify volatile mixture components are needed. Gas chromatography is a method that is commonly employed to separate and quantify multiple gas phase mixture components.3–2 The advantages of using gas chromatography for separation of the volatile mixtures generated during thermal analyses have been known for at least forty years.3–3 Additional information regarding evolved gas mixture components can be obtained by combining gas chromatography with mass spectrometry detection (GC/MS).6–18 By using isothermal gas chromatography separations, GC/MS evolved gas sampling intervals of 1–2 min have been reported.11,13–15 Somewhat longer sampling intervals (3–5 min) have been reported when temperature-programmed GC separations are required.12,17,18 The assay cycle time required for repetitive GC/MS analyses depends on the length of time required for chromatographic separation and, when temperature programmed separations are employed, the time required to cool the chromatographic column back to the ramp starting temperature.

The tradeoffs between gas chromatographic analysis time and separation resolution are well-known.19–22 Faster gas chromatographic separations are possible when a separation method provides more resolution than is needed to isolate mixture components. For these instances, the separation method can be modified to permit a faster analysis by sacrificing some of the excess chromatographic resolution.22 For mixtures containing species with widely varying retention characteristics, separations often involve heating the column with a fast temperature ramp. One of the most effective methods for achieving fast column heating rates involves using resistive heating to localize heat transfer at the column. This can be done by placing a heating element next to a fused-silica column,20 by coating a fused-silica

* E-mail: rlwhite@ou.edu. Fax: (405)325-6111.
column with a metal that is then heated electrically, or by using a metal capillary column and resistively heating the column. These methods are reportedly capable of providing column heating rates of \(30 \degree C/s\). In addition to providing high heating rates, resistively heated columns can be rapidly cooled when they are placed inside commercial instruments by making use of the instrument’s highly efficient fan and baffle cooling system.

An alternative approach for achieving fast column heating rates involves minimizing the heated volume by reducing the size of a gas chromatograph oven. By drastically reducing the amount of space required for a capillary gas chromatography column, it is possible to achieve heating rates approaching those reported for resistively heated columns. Because the oven is typically the largest component in a gas chromatography instrument, the use of a small oven that has been optimized to contain a separation column with minimal empty space makes it possible to incorporate fast gas chromatography into an analysis system that occupies significantly less space than a typical commercial instrument. The apparatus described here, which incorporates a small volume gas chromatography oven, is capable of automated gas stream sampling, can be used for fast gas chromatographic separations, and includes a heated column effluent splitter interface to facilitate GC/MS analyses.

**EXPERIMENTAL SECTION**

A detailed description of the small-volume gas chromatography oven employed for the studies described here is provided elsewhere. Previous tests have shown that it is possible to heat this oven at a rate of \(10 \degree C/s\) when 150 W of power is supplied to the heating element. A diagram of the automated repetitive injection gas chromatography apparatus is shown in Figure 1. The gas chromatograph oven was placed inside an 8 in. \(\times\) 6 in. \(\times\) 3 in. aluminum enclosure along with an automated gas sampling valve (model 6C6UWT, VICI Valco Instruments) and a variable flow splitter valve (model MCVT-1, SGE Analytical Science). By using pieces of \(\frac{1}{4}\) in.-thick fiberglass insulation, the aluminum enclosure was divided into three thermally isolated sections. The center section contained the gas chromatograph oven. As shown in Figure 1, the injection compartment containing the 6-port sampling valve was located on one side of the oven and the effluent splitter valve that was used to vary the amount of gas exiting the column that was diverted to the mass spectrometer was located on the other side of the GC oven. Separate heaters and temperature controllers (model CN76000, Omega Engineering, Inc.) allowed the injection and splitter valve sections to be maintained at constant high temperatures (>200 \degree C) while the gas chromatograph oven temperature was varied during temperature-programmed gas chromatographic separations. The aluminum enclosure, which contained the injection valve, GC oven, and splitter valve, was mounted on the ion source side of a Hewlett-Packard 5973 quadrupole mass spectrometer vacuum system to facilitate GC/MS measurements. GC oven temperatures were measured and adjusted by using a model CN3251 (Omega Engineering Inc.) temperature controller when the oven was heated and a model CN3202 temperature controller (Omega Engineering Inc.) when the oven was cooled. A computer was used to record oven temperatures and to select which temperature controller was active. A flow of liquid nitrogen coolant to the GC oven was turned on and off based on signals from the CN3202 temperature controller by using an ASCO model 8263G205LT (Teragon Research) solenoid valve. Repetitive injections were made by using a DVSP-2 digital valve sequence programmer (VICI Valco Instruments) attached to an ETMA microelectric actuator (VICI Valco Instruments). Injections were made as a result of a signal sent from the CN3251 temperature controller to the digital valve sequence programmer.

Fast gas chromatography separations were made by using a 1-m-long, 100-\(\mu\)m-i.d. fused-silica capillary column with a 0.5-\(\mu\)m methyl silicone stationary-phase film thickness (Quadrex Corp.). Reproducible injection volumes were obtained by using a 50-\(\mu\)L stainless steel sample loop with the 6-port injection valve. The column flow rate was maintained at 3 mL/min for separations by using a mass flow controller. Thermal analyses were carried out using a mass flow controller by using an ASCO model 8263G205LT (Teragon Research) solenoid valve. Repetitive injections were made by using a DVSP-2 digital valve sequence programmer (VICI Valco Instruments) attached to an ETMA microelectric actuator (VICI Valco Instruments). Injections were made as a result of a signal sent from the CN3251 temperature controller to the digital valve sequence programmer.

![Figure 1](image_url) **Figure 1.** Diagram of the repetitive injection analysis system.

![Figure 2](image_url) **Figure 2.** Repetitive injection GC/MS chromatograms.
inside a heated stainless steel chamber, which is described in detail elsewhere. This apparatus accommodated ~10-mg sample sizes and was connected to the repetitive injection GC/MS apparatus via a heated \( \frac{1}{16} \)-in.-o.d. stainless steel transfer line. The HP 5973 quadrupole mass spectrometer was operated with a 5 \( \times \) \( 10^{-6} \) Torr ion source pressure by scanning from \( m/z \) 50 to 150 at a rate of 12 scans/s.

Zeolite Y was obtained from Universal Oil Products in the sodium form. It was refluxed with ammonium nitrate overnight and calcined at 550 °C for 3 h to convert it to the HY form. Poly(styrene) with a molecular weight of 850 000 was obtained from Aldrich Chemical (Milwaukee, WI). The sample, which was a mixture of HY zeolite and poly(styrene) containing 5% by weight polymer, was heated in 25 mL/min helium from 200 to 400 °C at a rate of 2 °C/min.

**RESULTS AND DISCUSSION**

The repetitive gas stream sampling and analysis capabilities of the apparatus shown in Figure 1 were evaluated by using it to characterize the volatiles produced when a sample consisting of a mixture of poly(styrene) and a solid acid catalyst was heated in helium. Acid sites on the HY zeolite surface catalyzed thermal degradation reactions that yielded several volatile products when the mixture was heated at 2 °C/min. The resulting gas stream mixture was analyzed by using fast gas chromatography separations repeated at 90-s intervals. A column temperature program starting with a 4.0 °C/s ramp from 75 to 155 °C, followed by a ramp to 255 at 2.5 °C/s was employed for repetitive separations. On average, 40 mL of liquid nitrogen was required to cool the column after each heating ramp. Liquid nitrogen lowered the column temperature from 255 to ~50 °C within 10 s, which corresponded to a 20 °C/s cooling rate.

Figure 2 shows the gas chromatograms obtained during the thermal analysis. Sixty-six repetitive injection chromatograms were obtained during the 100-min analysis. During this time, the sample temperature increased linearly from 200 to 400 °C. Because chromatograms were measured at 90-s intervals, gas stream injections occurred at 3 °C sample temperature increments. Figure 3 shows that the largest peak in repetitive injection GC/MS chromatograms gradually increased in intensity until the injection at 43.5 min (287 °C sample temperature), after which the peak intensity gradually decreased. The largest chromatographic peak was identified as benzene by its characteristic mass spectrum. This finding is consistent with previous reports of acid-catalyzed poly(styrene) cracking studies, in which benzene was identified as the main volatile product.

Inspection of Figure 3 reveals the presence of a second chromatographic peak, which is much smaller than the benzene peak and appears in chromatograms obtained between 42 and 64.5 min. The profile for the second peak, which was identified as ethylbenzene, is shifted to higher temperatures relative to the benzene peak, and its intensity maximized with the injection at 52.5 min (305 °C sample temperature). Mass spectral data indicated that the gas stream contained more than just these two substances. In fact, chromatograms obtained between 31.5 and 69 min contained 11 distinct chromatographic elutions that overlapped to varying degrees. Figure 3 shows the GC/MS chromatogram obtained by sampling the evolved gas stream at 46.5 min. The ordinate axis in the Figure 4 plot was expanded in order to reveal peaks corresponding to minor mixture components and the abscissa time axis was adjusted so that zero represented the time at which the sampled gas stream was injected into the column. The small peak labeled \( \text{CH}_2\text{Cl}_2 \) was not associated with the thermal analysis, and consequently, its intensity remained relatively constant throughout the repetitive injection measurements. This peak resulted from volatilization of residual solvent remaining after cleaning the injection valve and heated transfer line with methylene chloride. The other 10 peaks labeled in Figure 4 are consistent with known volatile products produced when poly(styrene) is cracked by a solid acid catalyst. These volatile products were identified based on their characteristic mass spectra. Unfortunately, Figure 3 shows that the chromatographic resolution provided by the column conditions and fast temperature ramp employed in this study was insufficient to fully separate all

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Table 1. Mixture Component Retention Times and Characteristic Ions

<table>
<thead>
<tr>
<th>Substance</th>
<th>Retention Time (s)</th>
<th>RSD (%)</th>
<th>Characteristic Ion (m/z)</th>
<th>bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylenec chloride</td>
<td>44.2</td>
<td>1.5</td>
<td>84</td>
<td>39</td>
</tr>
<tr>
<td>Benzene</td>
<td>46.4</td>
<td>1.5</td>
<td>78</td>
<td>80</td>
</tr>
<tr>
<td>Toluene</td>
<td>48.1</td>
<td>1.0</td>
<td>92</td>
<td>111</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>49.7</td>
<td>0.5</td>
<td>91</td>
<td>136</td>
</tr>
<tr>
<td>Styrene</td>
<td>51.2</td>
<td>1.0</td>
<td>104</td>
<td>145</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>52.4</td>
<td>1.3</td>
<td>105</td>
<td>152</td>
</tr>
<tr>
<td>Propyl benzene</td>
<td>53.5</td>
<td>0.8</td>
<td>91</td>
<td>159</td>
</tr>
<tr>
<td>Indane</td>
<td>54.6</td>
<td>0.7</td>
<td>117</td>
<td>170</td>
</tr>
<tr>
<td>Sec-butyl benzene</td>
<td>56.1</td>
<td>0.9</td>
<td>134</td>
<td>173</td>
</tr>
<tr>
<td>Methylindane</td>
<td>56.8</td>
<td>0.8</td>
<td>117</td>
<td>189−205</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>65.0</td>
<td>0.8</td>
<td>128</td>
<td>218</td>
</tr>
</tbody>
</table>

a Derived from retention times for the five largest characteristic ion chromatographic peaks. b Boiling point depends on isomer.

10 mixture components. However, it was still possible to distinguish these substances by making use of the structure selectivity provided by mass spectrometric detection.

Figure 4 shows a stacked plot of extracted ion chromatograms derived from the mass spectra obtained during the chromatographic separation represented in Figure 3. All extracted ion chromatogram peak intensities were normalized and the abscissa in Figure 4 was expanded to better show peak shapes. The vertical dashed lines in Figure 4 denote retention times for specific species. Table 1 lists the mixture components along with the mass spectral ion (characteristic ion) that was employed for selectively monitoring each eluting substance. The ions chosen for generation of the substance-characteristic ion chromatograms were selected to provide discrimination between adjacent, overlapping elutions. Characteristic ions were often the base peaks in mass spectra for the corresponding substance. When the base peak for a particular substance was also present with a substantial intensity in the mass spectra for adjacent eluting substances, a different characteristic ion was chosen. As shown in Figure 4, appropriate selection of the mass spectral ions used to generate chromatograms permitted baseline separation of all 11 volatile products even though they were not resolved chromatographically.

For each separated substance, an average retention time was calculated from the five repetitive injection chromatograms that contained the highest characteristic ion intensities. These retention times and their corresponding relative standard deviations are listed in Table 1. Naphthalene began to elute just after the column reached 255 °C and finished eluting during column cooling. The symmetrical naphthalene peak shape (Figures 3 and 4) suggests that the eluting peak was already in the heated mass spectrometer interface by the time that the column oven was cooled. Methylindane and sec-butylbenzene were the closest overlapping elutions with retention times that differed by only 700 ms. Several other adjacent peaks had retention time differences of slightly more than 1 s. Retention time reproducibility, represented by the relative standard deviation of the five measured retention times, varied from 0.5% for ethylbenzene to 1.5% for methylenec chloride and benzene.

By taking advantage of the substance differentiation capabilities provided by the combination of chromatographic separation and mass spectrometric detection, species-specific evolution temperature profiles (plots of volatile product concentration versus sample temperature) were generated for each eluting substance. The methylene chloride evolution temperature profile was a horizontal line, which confirmed that it originated from the background. Evolution temperature profiles for four of the volatile poly(styrene) cracking products are shown in Figure 5. Each dot in the Figure 5 plots represents a characteristic ion peak area for the specified substance derived from a single chromatogram. The profile shapes indicate that benzene evolution maximized at the lowest temperature followed by isopropylbenzene, toluene, and naphthalene. Profiles for the other six poly(styrene) cracking products listed in Table 1 were similar to the isopropylbenzene profile. The fact that there were four different volatile product evolution profiles suggests that the thermal decomposition of the poly(styrene)/solid acid mixture occurred in stages. This is consistent with proposed reaction mechanisms in which benzene is initially formed by proton attacks on aromatic rings. The initial loss of benzene yields a polymer consisting of aromatic rings attached to a backbone containing significant unsaturation. Acid-catalyzed decomposition of this polymer structure resulted in the formation of substituted aromatics. When the polymer backbone contained sufficient conjugated unsaturation, indanes and naphthalene could be formed via a cyclization mechanism. Because aromatic rings in the initial poly(styrene) structure must be lost in order for backbone unsaturation to form, detection of indanes and naphthalene was delayed relative to benzene. Compared to indanes, naphthalene formation required more backbone unsaturation. Therefore, the naphthalene evolution temperature profile was shifted to higher temperature compared to the indane and methylindane profiles.

CONCLUSIONS

As shown by Table 1, all of the volatile products generated by heating the poly(styrene)/HY zeolite sample were aromatics. By using a column with a nonpolar methylsilicone stationary phase, the elution order for separated mixture components was mainly determined by boiling point (see Table 1). The 138 °C difference between benzene and naphthalene boiling points necessitated the 180 °C column temperature ramp for fast gas chromatographic separations. Mixture component differentiation and a 90-s assay cycle time were achieved by using a fast column temperature.
ramp, a 20 °C/s column cooling rate, and mass spectrometric
detection of eluting components. However, as the poly(styrene)
acid-catalyzed cracking thermal analysis example described here
illustrates, baseline chromatographic resolution is not required
for selective mixture component monitoring. The minimum gas
stream sampling interval for repetitive injection GC/MS analysis
with the apparatus described here depends primarily on the
chromatographic separation time needed to achieve adequate
mixture component resolution. Therefore, gas streams containing
volatile mixtures that can be separated in a shorter time can be
sampled faster than the 90 s employed for the poly(styrene)
cracking study described here.

Received for review August 21, 2008. Accepted October
26, 2008.

AC801757W