

# GC-MS Analysis of Heart-Cut Fractions During Evolved Gas Analysis of Polymeric Materials



The combination of evolved gas analysis, trap-and-purge sampling of desired portions of the evolved fraction (heartcutting), and gas chromatography-mass spectrometry characterization (GC-MS) can be a very powerful method to investigate complex polymeric materials. The authors conducted a preliminary survey by conventional evolved gas analysis and MS total ion detection to select evolution temperature ranges for heart-cut fractions in subsequent GC-MS analyses. In the heart-cut evolved gas analysis with GC-MS analysis, each heart-cut fraction was cryotrapped and analyzed by high-resolution capillary GC-MS. They used MS library searching to identify the components in each fraction and to comprehensively characterize the polymeric materials with regard to substrate polymers and additives such as plasticizers and stabilizers.

**P**yrolysis gas chromatography (GC), in which a nonvolatile sample is decomposed thermally before GC analysis, is a simple, rapid, and extremely sensitive technique for investigating nonvolatile materials such as polymers. It often provides unique structural information for polymeric materials soluble in ordinary solvents and for intractably cured polymeric compounds. Pyrolysis GC in its early development, however, had some limitations associated with the many factors involved, including difficulty in attaining specific pyrolysis of the sample, complex chemical reactions in pyrolysis, insufficient separation of the resulting degradation products, and poor peak identification and interpretation of the pyrograms. Therefore, this method for a long time has been regarded as a relatively crude polymer-characterization technique that provided less-reproducible results.

Pyrolysis GC has become a more powerful tool for polymer identification, compositional determination of copolymers, and microstructural characterization of polymers due to recent developments such as highly specific pyrolysis devices (1-5), highly efficient capillary columns (6), and specific identifications of the peaks in the pyrograms and polymers (7,8) by capillary GC-mass

spectrometry (MS) systems. The structural information obtained by high-resolution pyrolysis GC sometimes is unique and complementary to that obtained by conventional spectroscopic methods such as infrared and nuclear magnetic resonance spectroscopy (9). Even using the advanced pyrolysis GC technique, however, analysts often find it difficult to thoroughly characterize complicated polymer formulations encountered in practical uses.

Evolved gas analysis using MS, in which the evolved gases are analyzed during the programmed heating of the sample, often is effective in characterizing complex polymeric materials. Of the various evolved gas analysis techniques, the use of a thermogravimeter and a GC-MS system has been noted as a powerful combination for individual analysis of volatile compounds and polymeric substrate in a given formulated sample (10).

In this method, evolved gases usually are analyzed by GC and transferred through a heated rotary switching valve. However, its application is limited primarily to measuring highly volatile and chemically inert compounds such as hydrocarbons and esters with carbon numbers less than approximately 20. The larger compounds and polar components such as amines and free fatty

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acids could be susceptible to cold trapping, adsorption, or decomposition, either in the switching valve or in the transfer lines. Moreover, investigating the desired fractions in the evolved components selectively by the conventional evolved gas analysis system is no easy task.

To overcome these limitations, we developed a novel heart-cut evolved gas analysis–GC–MS method, which we applied to a ceramic composite sample, as described in this article.

## Experimental

**Apparatus:** Figure 1 shows a schematic diagram of a model 2020 thermal analysis system, which includes a 2020iD Double-Shot microfurnace pyrolyzer (1), an SS-1030E Selective Sampler heartcutting device (5), an MJT-1030E MicroJet cryotrap (11), and a built-in evolved gas analysis–MS polymer library (all from Frontier Laboratories, Ltd., Fukushima, Japan). The system also includes an Agilent 6890 gas chromatograph equipped with an Agilent 5973 MSD mass spectrometer (both from Agilent Technologies Inc., Wilmington, Delaware).

The heartcutting device to switch evolved gas analysis flows between the cryotrap and the vent was constructed based upon the Dean switching method (11,12). This device, mainly comprising deactivated stain-

less steel tubes (6) without using any rotary switching valves, was attached to the bottom of the heated GC injection port. The built-in MS library of polymers was operated with the Agilent ChemStation software (7).

In the evolved gas analysis–MS operation, we used a 2.5 m × 0.15 mm deactivated stainless steel capillary tube (evolved gas analysis capillary tube, Frontier Laboratories) to couple the pyrolyzer and mass spectrometer directly. The tube was positioned in an isothermally heated GC oven, and the temperature was controlled to be greater than 250 °C to avoid any condensation of less-volatile evolved gases. In the heart-cut evolved gas analysis–GC–MS operation, the evolved gas analysis capillary tube was replaced with a GC separation column made of a 30 m × 0.25 mm deactivated stainless steel capillary tube.

**Analytical procedure:** To analyze a complicated polymeric material systematically, we first used the evolved gas analysis–MS system to survey the whole evolved gas analysis thermogram and determine the appropriate subsequent heart-cut temperature ranges. Next, we performed the heart-cut evolved gas analysis–GC–MS analysis to determine detailed composition.

In the heart-cut evolved gas analysis–GC–MS procedure, the sample mounted in the pyrolyzer was heated in the evolved gas

analysis temperature-programming mode from near-ambient temperature to pyrolysis temperatures as high as 700 °C. We assigned the heart-cut fractions in advance in the evolved gas analysis profile and cryotrapped them during their corresponding heating ranges. Each of the trapped fractions was subjected to GC separation followed by MS analysis. Finally, we identified the components — residual solvents and plasticizers — in the volatile fractions by conventional MS searching. We identified the polymeric substrates from their pyrolysis products observed in the pyrogram for the heart-cut fractions at higher temperatures by using a built-in library search algorithm of the evolved gas analysis–MS library of polymers (7).

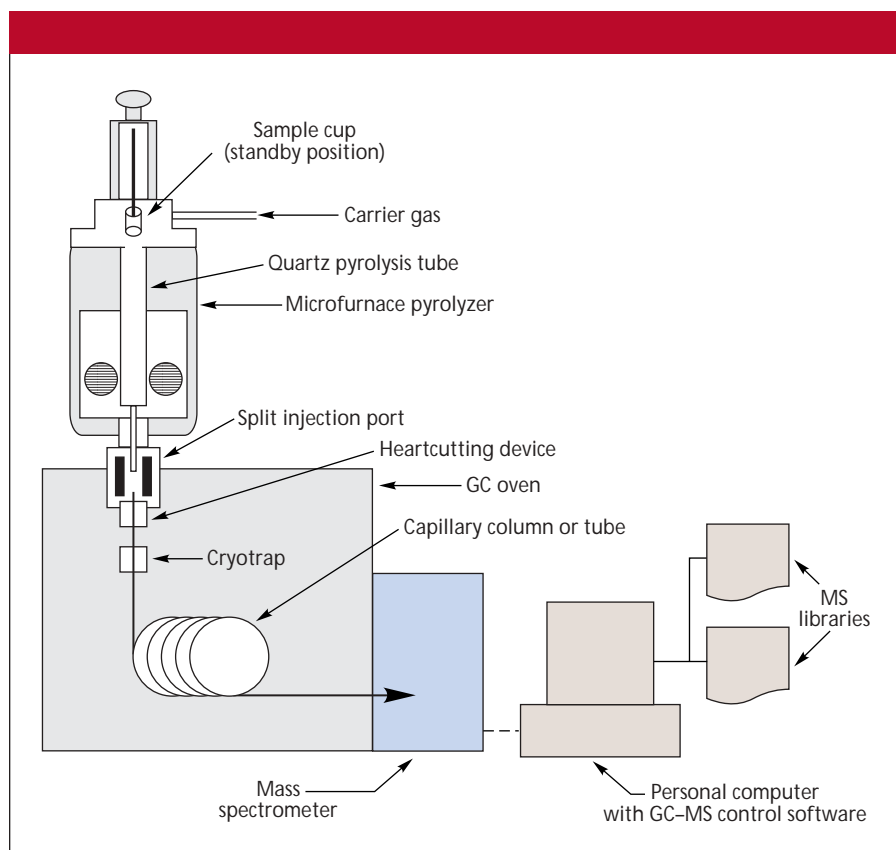
## Analysis of Ceramic Composite Sample

We used a formulated ceramic composite as a test sample for the heart-cut evolved gas analysis analyses. This sample contained polymeric components and additives such as stabilizers, although its main component (more than 90%) was thermally inactive alumina.

**Analytical condition of evolved gas analysis–MS:** We heated a 0.5-mg formulated sample from 40 to 600 °C at 20 °C/min and transferred the resulting evolved gases through the evolved gas analysis capillary tube to the mass spectrometer. To obtain an evolved gas analysis thermogram, we set the MS scan range at  $m/z$  29–400 with a relatively slow scan speed of 0.1 scans/s to provide thermograms with good signal-to-noise ratios.

Figure 2 shows the observed evolved gas analysis thermograms for the ceramic composite sample obtained by total ion monitoring together with five mass thermograms by specific ion monitoring at  $m/z$  41, 57, 69, 104, and 149, which exhibited relatively strong ion intensities on the observed averaged mass spectrum for the entire range of the thermogram. Thus, we divided the observed evolved gas analysis thermograms into four fractions, as shown in Figure 2. The accumulated mass spectra for fractions A and B exhibited relatively intense ions of  $m/z$  149 and a series of ions at  $m/z$  41, 43, 57, and 71 that suggest those fractions contain organic phthalates and saturated hydrocarbons.

Figure 3 shows the accumulated mass spectra of fractions C and D. In this figure, the probable candidates for the polymeric materials suggested by the built-in evolved gas analysis–MS library search are listed together with matching quality data. From



**Figure 1:** Diagram of the thermal analysis system.

the data for fraction D, we estimated the associated polymeric material to be a styrene-related polymer with higher proba-

bility. From the data for fraction C, however, it was difficult to make unequivocal estimation based upon the lower matching

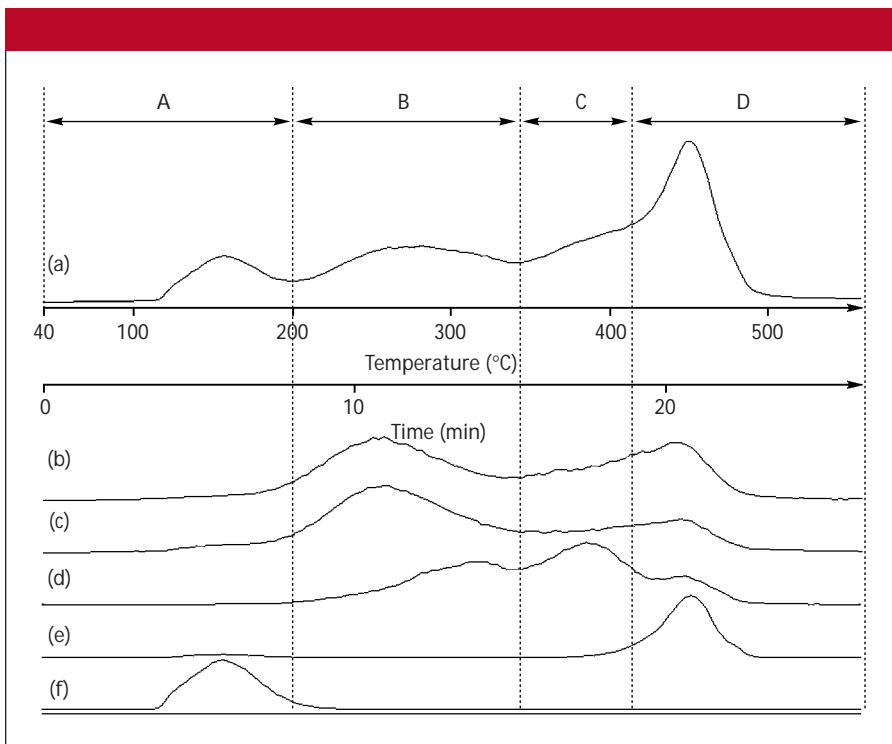
values, which most likely can be attributed to the severe overlapping of the fraction between B and D. Therefore, we performed subsequent heart-cut evolved gas analysis–GC–MS analyses for the ceramic composite for the four fractions defined in Figure 2.

**Conditions for the heart-cut evolved gas analysis–GC–MS analysis:** We used the following parameters for the heart-cut evolved gas analysis–GC–MS analysis of the ceramic composite sample. The furnace temperature program was 40–600 °C at 20 °C/min. The heart cuts were at 40–200 °C, 200–340 °C, 340–410 °C, and 410–560 °C, respectively, for fractions A, B, C, and D. The cryotrapping temperature was –196 °C.

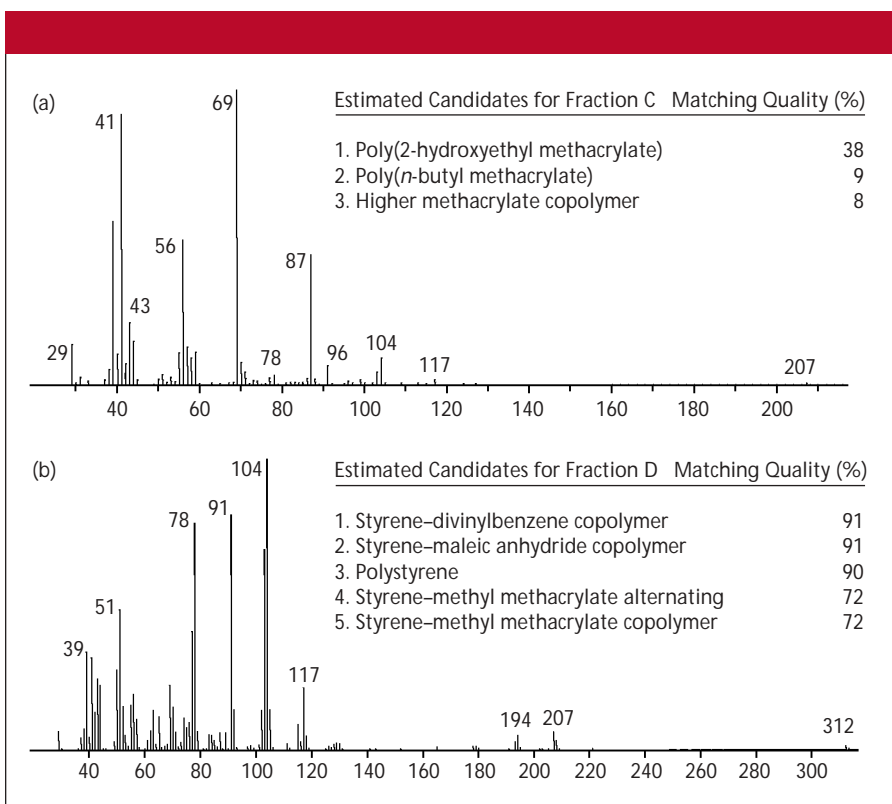
We used a 30 m × 0.25 mm, 0.25- $\mu$ m *d*<sub>f</sub> deactivated stainless steel GC column (Ultra Alloy capillary column, Frontier Laboratories) with a 5% phenylpolydimethylsiloxane stationary phase. The GC oven program was 40–320 °C at 20 °C/min. The MS scan range was *m/z* 29–400 with a scan speed of 2 scans/s.

Figure 4 shows the schematic time sequence for the automated heart-cut evolved gas analysis–GC–MS operations. During the first heating span, the sample mounted in the furnace was subjected to a temperature program from 40 to 200 °C at a rate of 20 °C/min, and the total effluent was trapped at the head of the capillary column in the cryotrap maintained at –196 °C. At the end of this heating process, we cooled the furnace to the initial temperature (40 °C) to stop further thermal desorption. Next, the cryotrapped components were subjected to GC separation, when the GC column oven temperature is programmed from 40 to 320 °C at a rate of 20 °C/min, followed by MS detection. After the first GC run finished, we cooled the GC oven temperature to its starting temperature (40 °C) and started the second evolved gas analysis temperature program of 200 to 340 °C at the same rate of 20 °C/min after boosting the furnace temperature up to 200 °C. The second heart cut for fraction B was collected at the head of the capillary column in the cryotrap for the next GC–MS run. Similarly, the third and fourth heart-cut evolved gas analysis–GC–MS runs were performed for fractions C and D evolved from 340 to 410 °C and 410 to 560 °C, respectively. At the end of the temperature program, the furnace was cooled to the initial temperature for the next sample analysis.

Figure 5 shows total ion chromatograms of the four heart-cut fractions obtained for



**Figure 2:** Observed mass thermograms (evolved gas analysis curves) monitored by total and specific ions. Shown are (a) the total ion mass thermogram for *m/z* 29–400 and specific-ion thermograms at (b) *m/z* 41, (c) *m/z* 57, (d) *m/z* 69, (e) *m/z* 104, and (f) *m/z* 149.



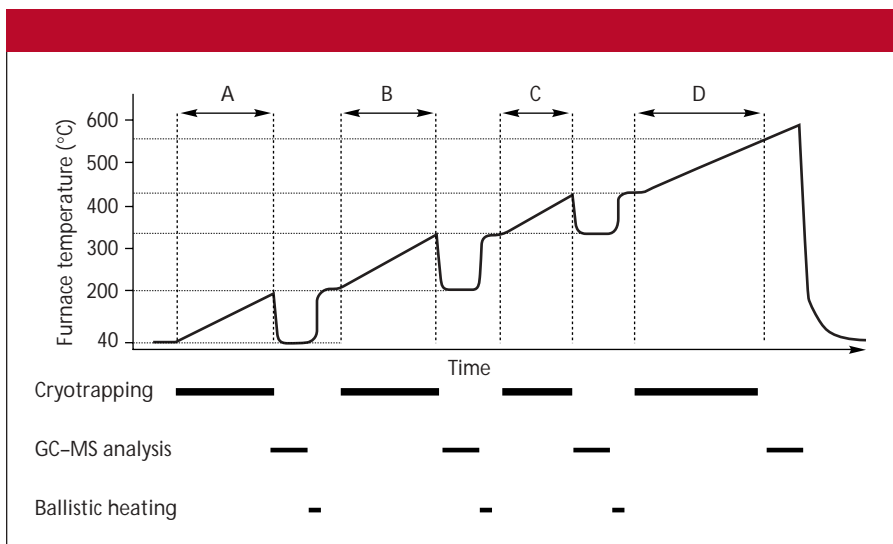
**Figure 3:** Averaged mass spectra of the evolved gas analysis for (a) fraction C and (b) fraction D from the ceramic composite sample. Fractions C and D correspond to those shown in Figure 2.

the ceramic composite sample. It is apparent that discriminative heart-cut evolved gas analysis–GC–MS analyses were attained for the additive (dibutyl phthalate) in Figure 5a and a small amount of fatty acids and a series of waxes in Figure 5b. All of these compounds were identified using the MS library search. Although the prominent, common peaks can be attributed to the

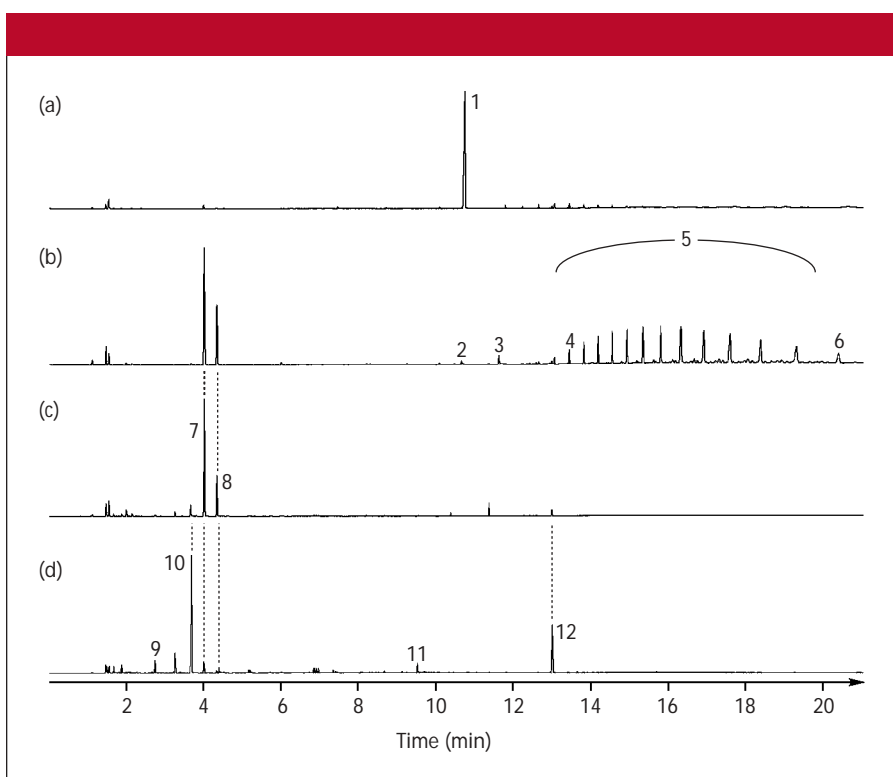
overlapping of the associated fractions shown in Figure 2, the polymer library search (7,8) for fraction C suggests that the associated polymeric material could be poly(butyl methacrylate).

The matching quality to the original evolved gas analysis–MS library for the mass spectrum of the fraction C was remarkably improved from 9% (shown in Figure 3) to

72% by deleting peaks 10 and 12, which are related to the pyrolyzate of fraction D. In Figure 5d, we assigned peaks 9–12 to toluene, styrene monomer, dimer, and trimer, respectively, corresponding to the pyrolyzates of styrene-containing polymers. These candidates in the library search were listed as poly(styrene–divinylbenzene) copolymer (91% matching quality), poly(styrene–maleic anhydride) copolymer (91% matching quality), polystyrene (90% matching quality), and styrene–methyl methacrylate alternating copolymer (72% matching quality). Thus, we finally identified fraction D as polystyrene by comparing each peak on the pyrogram D to the reference pyrolysis data compilation (13).



**Figure 4:** Typical time sequence for the automated heart-cut evolved gas analysis–GC–MS operations. Fractions A–D correspond to those shown in Figure 2.



**Figure 5:** Chromatograms of the heart-cut fractions (a) A, (b) B, (c) C, and (d) D obtained from the sequential GC–MS analyses. Peaks: 1 = dibutyl phthalate, 2 = palmitic acid, 3 = stearic acid, 4 =  $n$ -C<sub>20</sub>H<sub>44</sub>, 5 = a series of wax, 6 =  $n$ -C<sub>32</sub>H<sub>66</sub>, 7 = isobutyl methacrylate, 8 =  $n$ -butyl methacrylate, 9 = toluene, 10 = styrene monomer, 11 = styrene dimer, 12 = styrene trimer.

## Conclusion

To summarize all the comprehensive data mentioned above, we proved that the ceramic composite sample was a complex composite that contained at least two polymeric materials — poly(butyl methacrylate) and polystyrene — and at least three additives — dibutyl phthalate, a series of waxes, and fatty acids.

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