



Paint and Polymer Analysis using LabTech CDS Model 6400 Pyroprobe with Sample Splitting

Application Note

Paint Polymer Splitting

Abstract

This application note demonstrates using the splitting function of a Pyroprobe to adjust the sample amount transferred to the gas chromatograph.

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Introduction

The Pyroprobe 6400, a member of the 6000 Series Pyrolyzers, has distinguishing features that set it apart from previous 6000 Series models. To begin with, the pyrolysis chamber has been redesigned to accept larger capacity sample tubes, which can hold a sample volume as high as 50 μ L. This is more than 4x larger than CDS's DISC tubes for the 6150 and 6200. Larger sampling tubes are helpful for applications in which a high volume is needed to quantify the polymeric portions in an inorganic matrix, such as micro/nanoplastics on a glass fiber filter. Also, the larger tube size makes it easier for the analyst to load samples into the tube.

Secondly, as a complimentary feature to the larger capacity tubes, the 6400 has a unique splitting capability up to an 8:1 split. Therefore, 9 times the amount of polymer can be loaded without overloading the capacity of the GC, which generally handles under 0.1 mg polymer size best with a high GC split ratio. Additionally, preparation of small sample sizes, such as viscous samples, can sometimes be tricky. Adding a larger portion to a large sample tube, and using the splitting function, can allow for effortless sample preparation. Working with larger sample sizes also has the advantage of obtaining a sample more representative of the whole, for enhanced data reproducibility.

In this application note, paints from two different paint pens were studied using Evolved Gas Analysis (EGA) + multi-step pyrolysis (MSP) to understand each of their formulations. The unique splitting feature to optimize the signal in relation to the amount of sample loaded.



Experiment Setup

Paint from 2 different paint pens were each applied to microscope slides and allowed to dry overnight at room temperature. Next, paint flakes were removed from the microscope slide using a craft knife and loaded into 6400 DISC tubes. For EGA + MSP. Sample mass for each was recorded so that the Pyroprobe split ratio could be adjusted according to the sample mass.

EGA

Pyroprobe 6400

Split: As Indicated
Initial: 50°C
Final: 1000°C
Ramp Rate: 100°C per min
Interface: 300°C
Transfer Line: 325°C

GC-MS

Column: Fused silica (1m x 0.10mm)
Carrier: He 1.25mL/min spl- as indicated
Injector: 360°C
Oven: 300°C
Ion Source: 230°C
Mass Range: 35-600amu

Multi-Step Pyrolysis Pyroprobe 6400

Split: As Indicated
Pyrolysis: 300°C 60 sec
350°C 60 sec
400°C 60 sec
650°C 60 sec

Interface: 300°C
Transfer Line: 325°C
Valve Oven: 300°C

GC-MS

Column: 5% phenyl (30m x 0.25mm x 0.25µm)
Carrier: He 1.25mL/min, spl- as indicated
Injector: 360°C
Oven: 40°C for 2 minutes
12°C/min to 320°C (20min)
Ion Source: 230°C
Mass Range: 35-600amu

Results & Discussion

For many applications, a sample size of 100µg with a GC split of at least 50:1 is recommended to not exceed the capacity of the GC column. The splitting capability of the Pyroprobe 6400 means that larger samples may be loaded without introducing too much sample and overloading the GC. Here, paint from 2 different paint pens were examined using the split function to reduce sample load to the GC based on the sample mass.

Paint A (black) released from the microscope slide in very small shards, so only small sample sizes were easily loaded. The flakes of the paint (0.1mg) were added a sample tube using tweezers, and the tube was placed in the DISC chamber for Evolved Gas Analysis (EGA). Evolved Gas Analysis is a 10-minute screening technique used to understand the nature of the gases that evolve from the material with respect to the amount of applied heat. The mass of 0.1 mg is an ideal amount to introduce to the GC without introducing a split with the Pyroprobe 6400, so the split was set to 0, meaning 100% of the sample was introduced to the GC inlet. A 50:1 split was used on the GC injection port.

This quick screening shows two large areas of outgassing (Figure 1), the first region occurring between 200 and 400°C, which represents the vaporization of semi-volatile ingredients such as additives (Figure 1). The second region, between 400 and 600°C, represents decomposition of the paint binder.

Following EGA analysis, the analytical column was re-installed for a thorough multi-step pyrolysis GC-MS analysis. This time, just 0.05 mg was loaded into the tube, and run with no split on the 6400, and a 30:1 split on the GC. Decreasing the GC split from 50:1 to 30:1 helps to increase sensitivity when lower amounts of sample are used. The Pyroprobe can perform up to 10 methods on

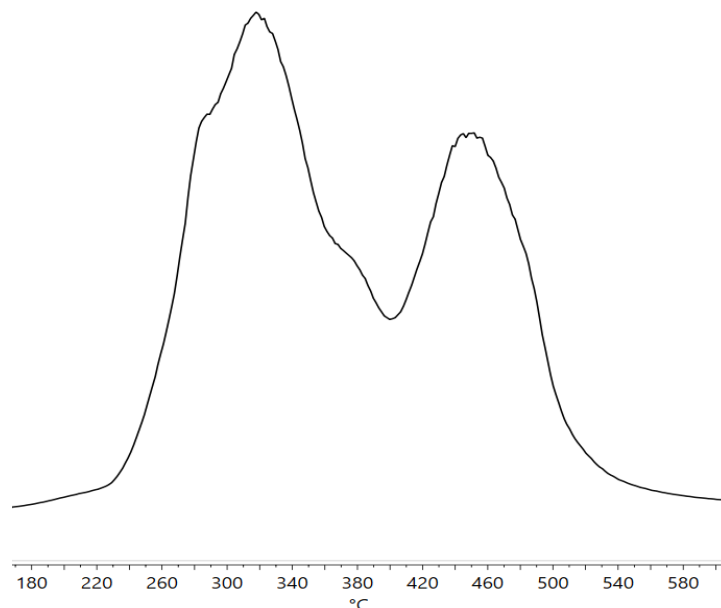


Figure 1. EGA of Paint A.

one sample and unlimited methods when an autosampler is added. So, while the EGA results produced two peaks, indicating that a two-temperature analysis would be sufficient, using 3 or more steps can still be easily used to provide a more complete characterization of the paint binder. Multi-step pyrolysis of paint was performed at 300°C, 350°C, 400°C and 650°C to provide more detail.

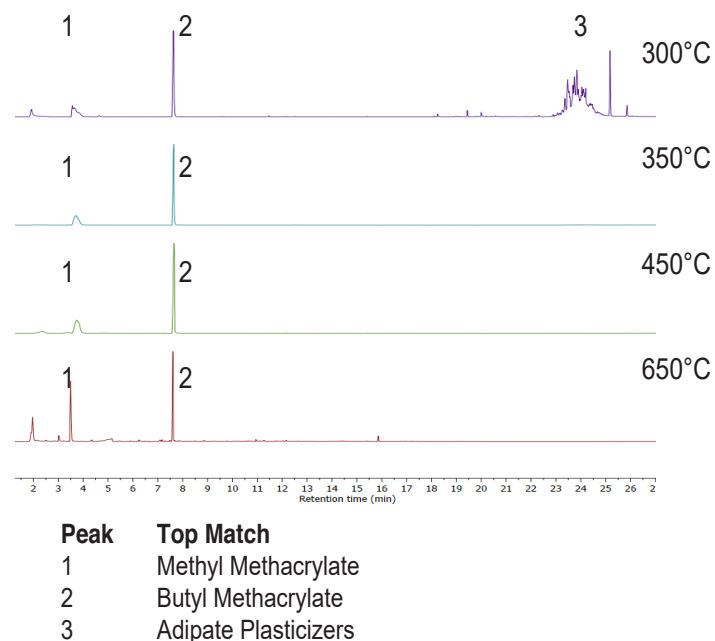


Figure 2. Multi-step Pyrolysis of Paint A.

Figure 1 shows all 4 pyrograms resulting from multi-step pyrolysis. At 300°C (top), an unresolved cluster of peaks between 23 and 25 minutes are adipate plasticizers, used to increase plasticity and fluidity. These physically interact with the polymer binder molecule, without a chemical reaction and form a homogeneous system.

Among all these temperature steps, butyl methacrylate and methyl methacrylate are also seen, with butyl methacrylate strongly released at 450 and 650°C, and methyl methacrylate strongly released at 650°C. Therefore, the paint binder is concluded to be a methyl methacrylate butyl methacrylate acrylic containing adipate plasticizers.

Approximately 0.1mg of Paint B (white) could be easily loaded into a tube and run using 0 split on the Pyroprobe 6400, and a 50:1 split on the GC. This brand had an EGA with one major peak occurring between 300°C and 650°C (Figure 3).

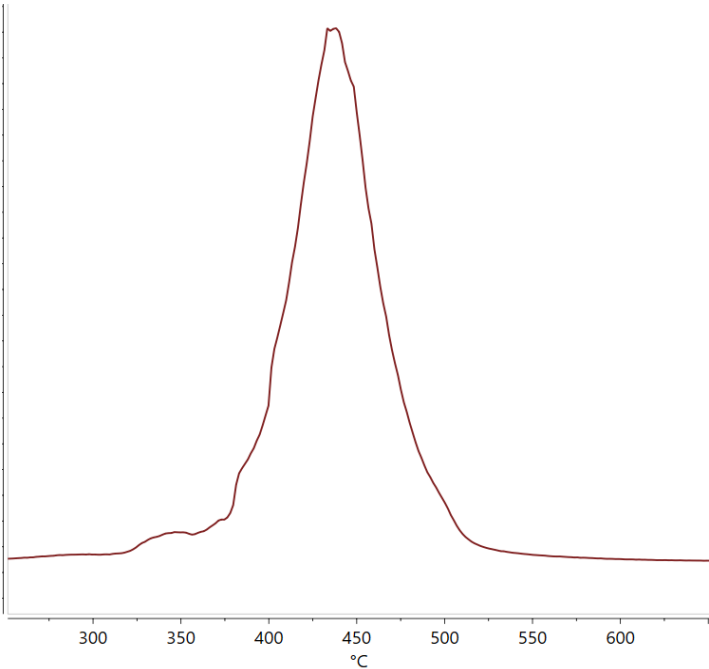


Figure 3. EGA of Paint B.

Double the optimal amount of 0.1 mg, 0.2mg was loaded into a 6400 sample tube for multi-step pyrolysis, using the same temperature setpoints as before. The Pyroprobe 6400 was adjusted to use a 1:1 split, so half the loaded amount, 0.1mg was introduced to the GC inlet with a 50:1 split.

Multi-step Pyrolysis results of the white paint is shown in Figure 4. Like the black paint, white paint also had butyl methacrylate and methyl methacrylate as part of the paint binder. As also indicated in the EGA, by the lack of a peak between 200°C and 400°C, the semi-volatile content was low, and no additives were seen.

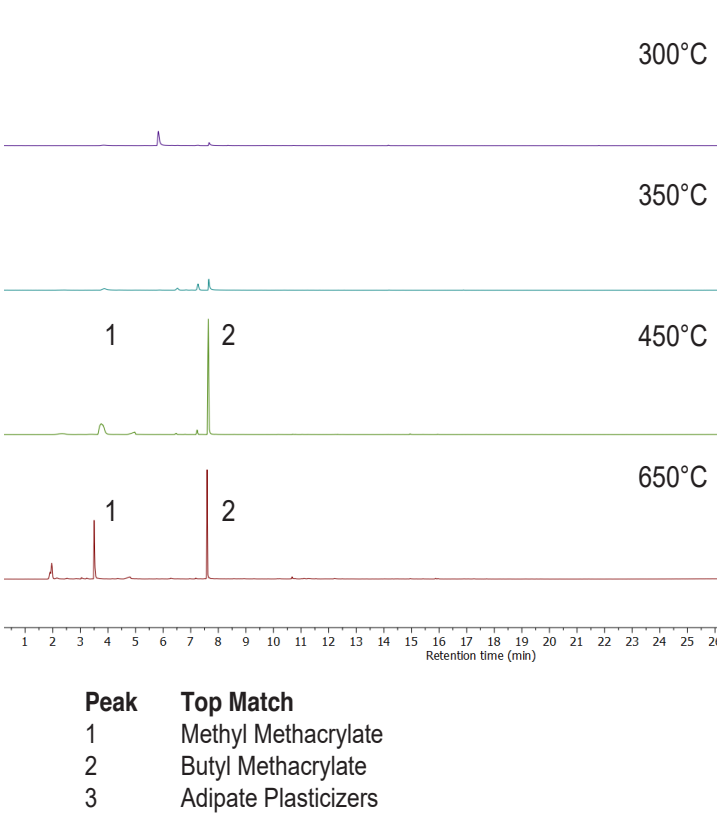


Figure 4. Multi-step Pyrolysis of Paint B.

Conclusion

In this application, paint from 2 different paint pens were analyzed using EGA plus MSP and a unique splitting function on a Pyroprobe 6400. The Pyroprobe 6400 can employ a split as high as 8:1, 9 times the amount of polymer sample can be loaded without overloading the GC column. Here, the splitting function in conjunction with the GC split was used to optimize the sample size despite the amount of sample loaded into the tube. The quick EGA screenings provided by fast and flexible temperature ramping and revealed that the black paint had two large regions of outgassing, while the white paint only had one, and most of the outgassing occurred after 400°C.

When combined with multi-step pyrolysis to provide full characterization of each paint, revealing fundamental differences between each of them, the splitting function provided a versatility in the amount of sample that could be loaded without adverse effects on the GC-MS analyses.