Polymer Analysis using the Pyroprobe 6000 Series coupled with GC-MS

Application Note
General Interest

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Abstract

This application note demonstrates the capabilities of the CDS 6000 Series Pyroprobe.

Introduction

The latest version of the Pyroprobe from CDS Analytical includes easier sample preparation and introduction with the new DISC (Drop In Sample Chamber) coupled with DISC sample tubes, and an add-on conveyor fed autosampler module.

Pyrolysis-GC-MS

A CDS 6000 Series Pyroprobe Autosampler was interfaced to a GC-MS for these analyses. Samples were prepped in DISC tubes, which easily handle both liquid and solid samples without the need for quartz wool. They were then heated inside a DISC using the platinum coil of the Pyroprobe. The resulting volatiles were transferred via a transfer line to the gas chromatograph for analysis. The gas chromatograph was equipped with a 30M 5% phenyl column, which was held at an initial temperature of 40°C for 2 minutes, then ramped at 10°C per minute to a final temperature of 300°C, which was held for 10 minutes. The detector was set to scan from 25 to 600 amu. Figure 1 shows an example of the resolution achieved in the analysis of a sample of Poly t-butyl styrene.

CDS 6000 DISC and sample tubes

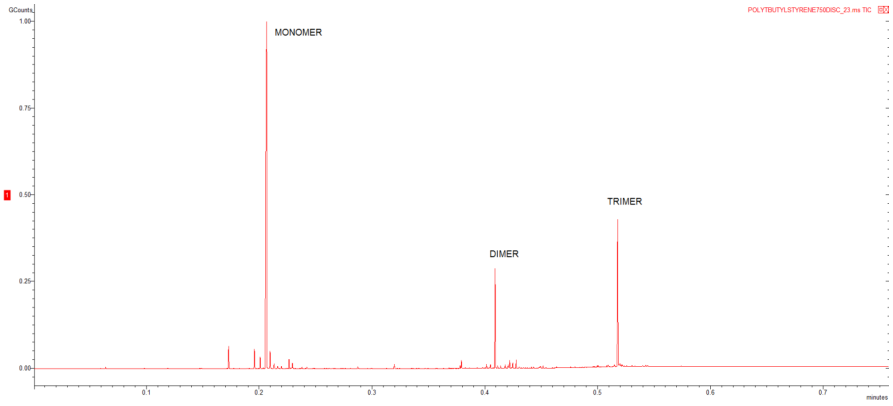


Figure 1. Poly Butyl Styrene at 700°C.

Reproducibility

Analytical value depends on the reproducibility of the technique. Reproducibility in pyrolysis depends greatly on temperature accuracy, as well as sample related issues like homogeneity. Pyroprobe filaments are calibrated using optical pyrometry. Using this technique, a series of 20 firings at 1100°C produced an average measured temperature of 1100.15°C with a relative standard deviation of only 0.04%. This ensures that Pyroprobe instruments perform with the highest precision. Figure 2 shows five runs of rubber cement diluted in hexane, at 600°C using a Pyroprobe Series Autosampler. For each run, 0.5µl of the solution was added to a quartz DISC tube, for a sample weight of 5 µg. This produced an RSD for the monomer to dimer ratio of 1.5%

Experimental Parameters
The samples were pyrolyzed in a quartz DISC tube, using a CDS Pyroprobe 6000 Series Autosampler interfaced to a GC-MS.

Pyroprobe :
Setpoint as indicated

Iso Zones:

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

GC/MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium, 50:1 split
Injector:	320°C
Oven:	40°C for 2 minutes
	10°C/min to 300°C
	hold 10 minutes
Ion Source:	230°C
Mass Range:	25-600

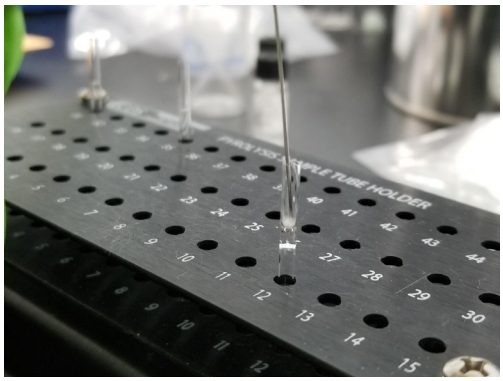


Figure 5: Prepping liquid sample into a DISC sample tube with a microliter syringe.

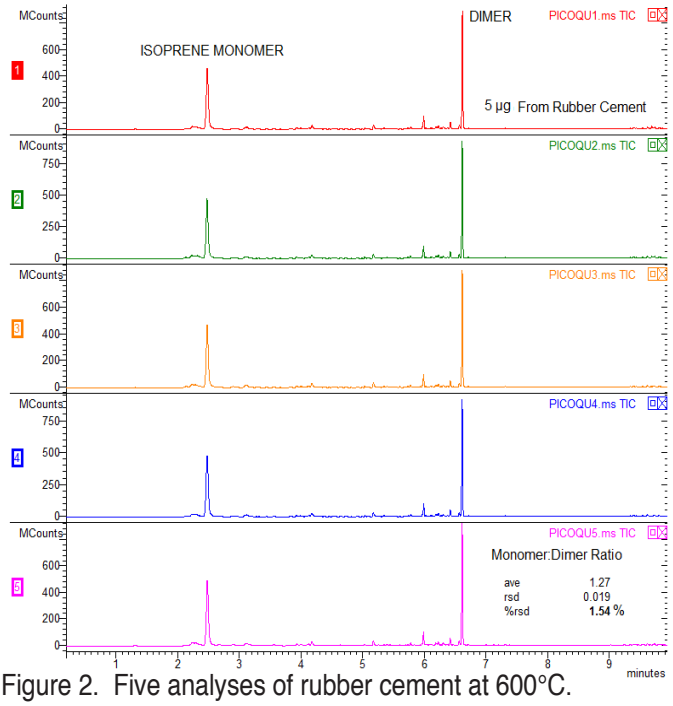


Figure 2. Five analyses of rubber cement at 600°C.

This reproducibility carries over into other temperature labile techniques with complex sample matrices, like thermally assisted hydrolysis. In the next example, thermally assisted hydrolysis was performed with tetramethyl ammonium hydroxide and polyester resins. Approximately 10mg of polyester was dissolved directly into 0.25mL of TMAH (25% wt/wt in methanol). Two microliters of solution was added to a DISC sample tube containing a small pad of quartz wool, and run at 540°C. The resulting chromatogram is shown in Figure 3. Low peak area ratio RSDs were computed for 4 identified compounds. Replicates are shown in Figure 4.

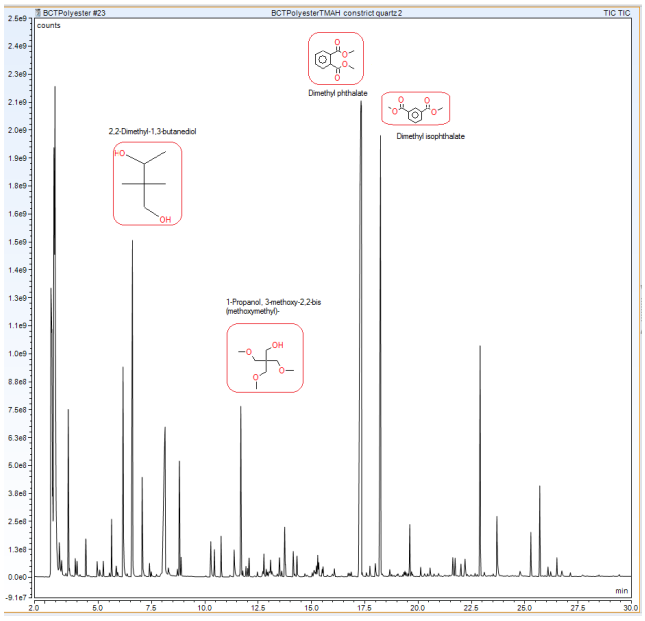
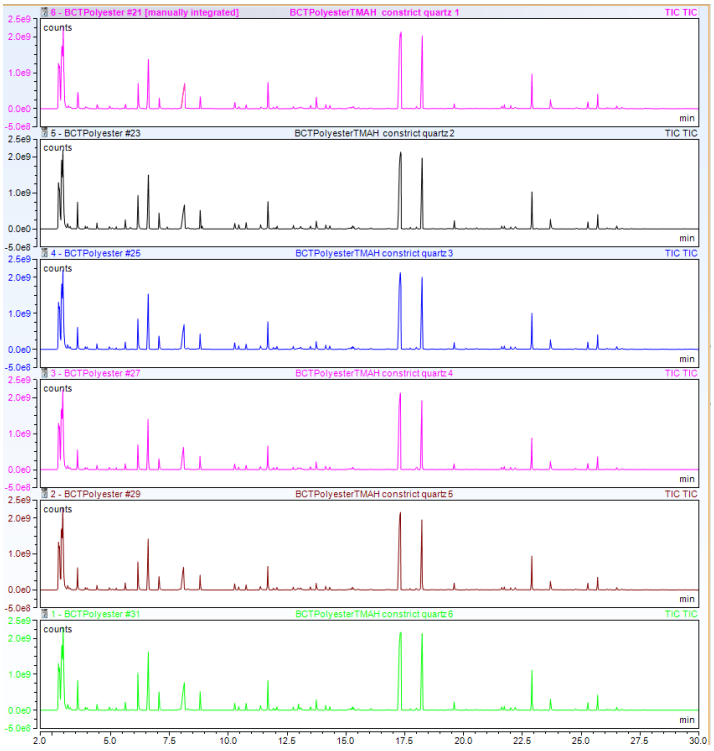


Figure 3. Polyester with TMAH 540°C.



	area ratio RSD
2,2-Dimethyl-1,3-butanediol	4.33 %
1-Propanol, 3-methoxy, 2,2-bis(methoxymethyl)-	3.69 %
Dimethyl phthalate	1.65 %
Dimethyl isophthalate	2.97 %

Figure 4: Replicates of Polyester with TMAH.

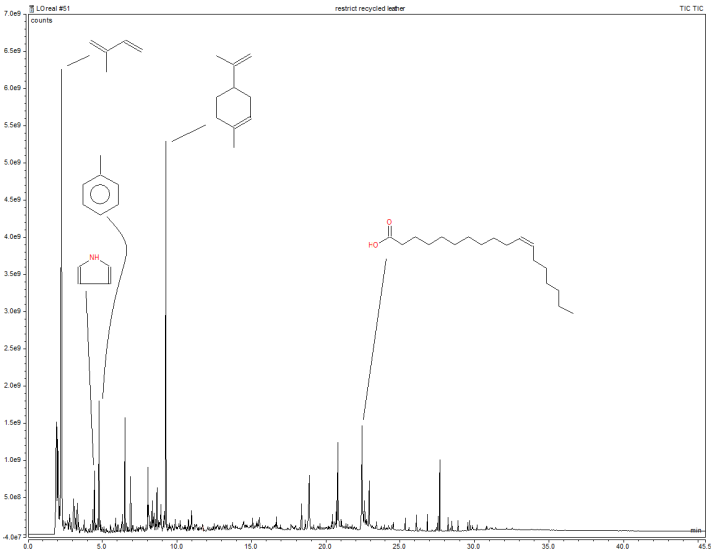


Figure 8. Recycled leather at 600°C.

Carryover

Because of the generation of large, non-volatile fragments, chromatographic carryover is always a concern with Py-GC-MS. Careful heat-tracing and interfacing provide the CDS 6000 Series with a sample path greatly resistant to product condensation. Figure 6 shows an analysis of poly butyl styrene, followed by a blank run on the system.

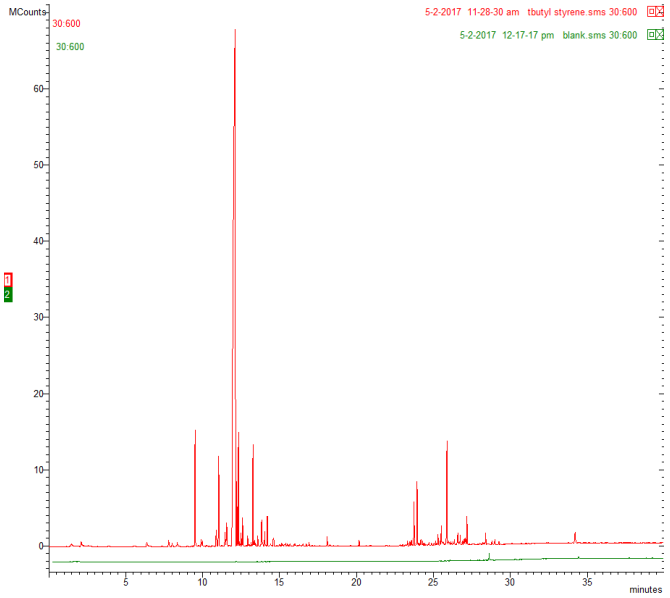


Figure 6. Poly butyl styrene at 700°C in red, with a blank run immediately after, in green.

Applications

Using a system with excellent GC resolution and virtually no carryover permits the distinguishing of samples which are extremely similar. For example, the two photocopy toners shown in Figure 7 are both based on polystyrene, but the relative amounts of some of the smaller constituents, and the presence of specific compounds in each formulation not found in the other, makes it possible to distinguish these complex, but still different formulations.

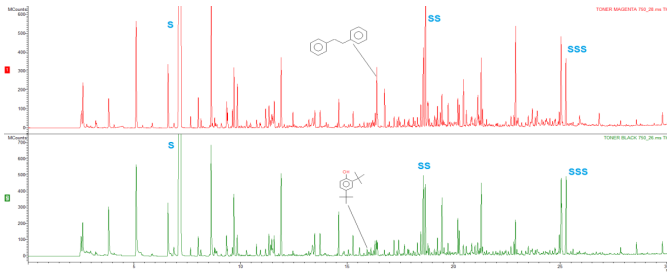


Figure 7. Two styrene based photocopy toners.

The analysis shown in Figure 8 is of a product identified as a recycled leather. Leather is a protein, and produces aromatics and nitrogen containing compounds when pyrolyzed, as seen at about 5 minutes in the pyrogram. The recycling process involves shredding the leather and then gluing it back together as a sheet. The two largest peaks in the pyrogram are isoprene and the dimer of isoprene, indicating that the adhesive used was polyisoprene.

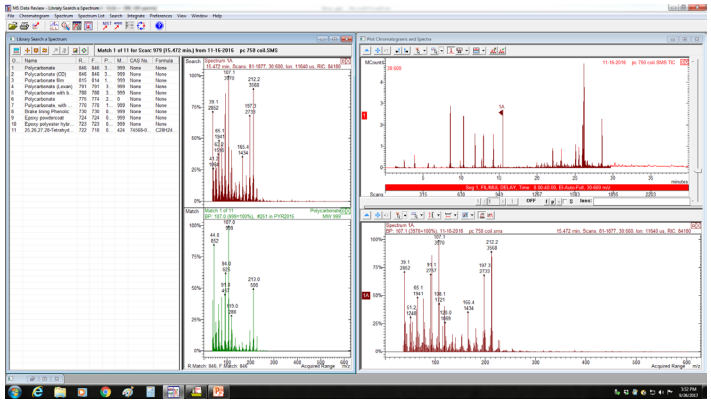


Figure 9. Identification of Polycarbonate using the Polymer Library.

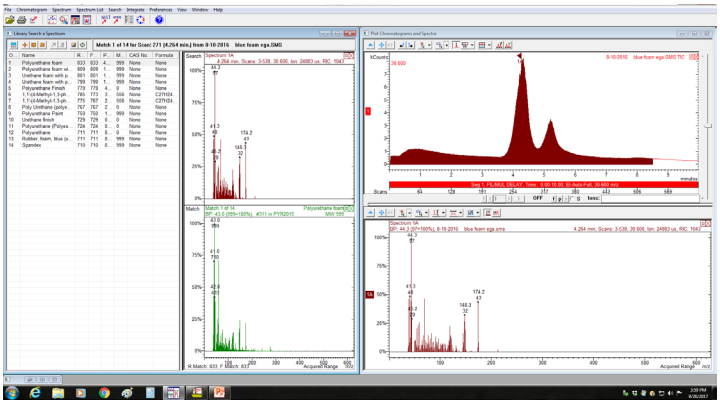


Figure 10. EGA analysis of a polymer with identification from the Polymer Library.

The Pyroprobe 6000 is compatible with the CDS Polymer Library for the identification of unknowns. Figure 9 shows the pyrogram of a polymer searched using the Polymer Library, and properly identified as a polycarbonate. The Pyroprobe 6000 may also be connected to the mass spec detector directly using a 1 m piece of uncoated fused silica. This provides a rapid analysis with identification using the library. Figure 10 shows the EGA analysis of a piece of polymer foam, heated to 250° for 3 minutes, then at 100°C/minute to 800°C. The library search correctly identifies the sample as a polyurethane foam.

Conclusion

The latest version of the Pyroprobe from CDS Analytical including easier sample preparation and introduction with the new DISC and sample tubes; and an add on conveyor-fed autosampler module ensures an improved user experience, as well as repeatable, reliable results, exhibiting low carryover and a polymer matching system to reveal a wealth of information on all your polymer samples.