Complete Polymer Analysis using the Pyroprobe 6000 Series coupled with MS and 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.

System Setup
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

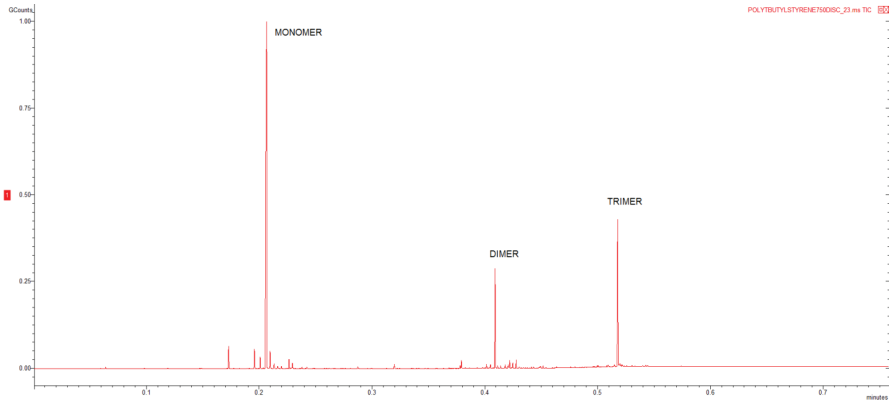


Figure 1. Poly Butyl Styrene at 700°C.

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. When tested with optical pyrometry, a series of 20 firings at 1100°C of a Pyroprobe filament 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 6000 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%.

Pyrolysis 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

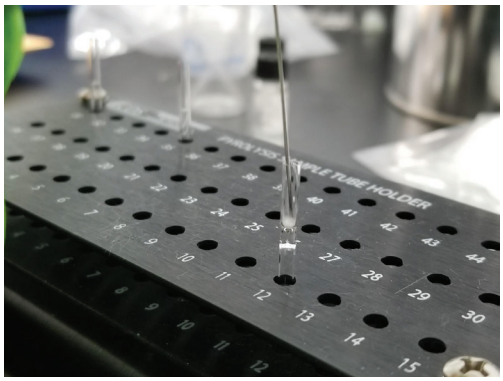


Figure 5. Prepping liquid sample into a DISC sample tube with a microliter syringe.

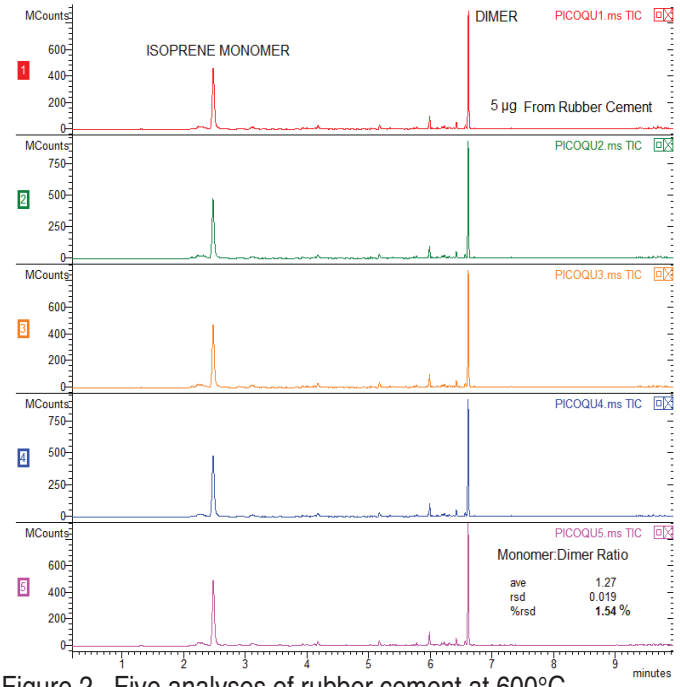


Figure 2. Five analyses of rubber cement at 600°C.

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.

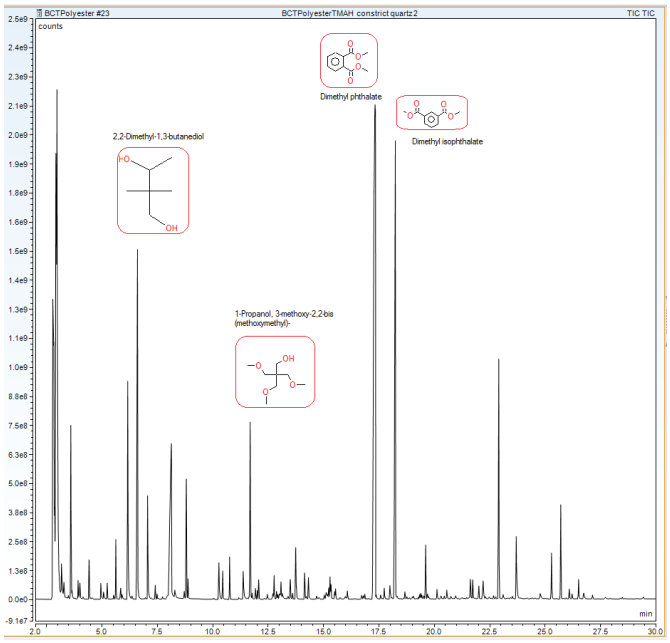
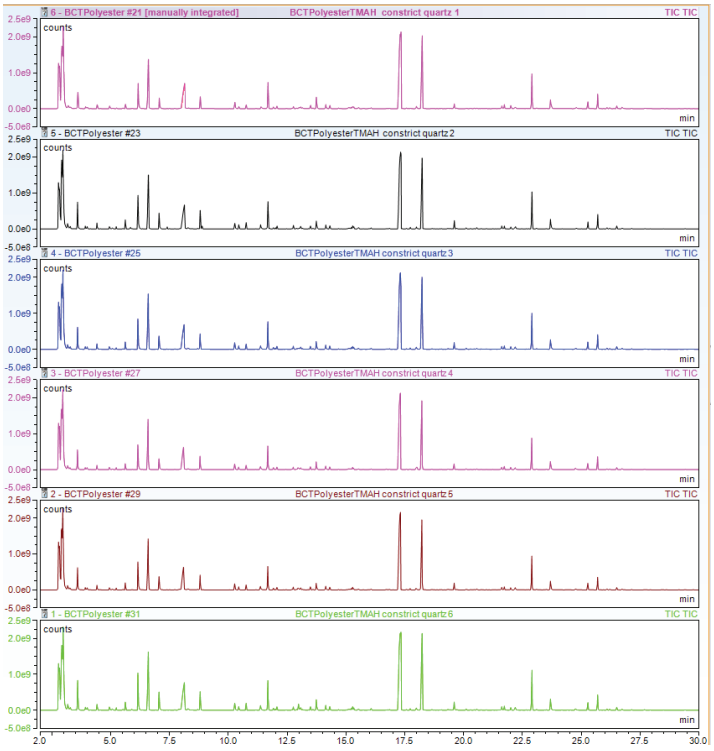


Figure 3. Polyester with TMAH 540°C.



	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.

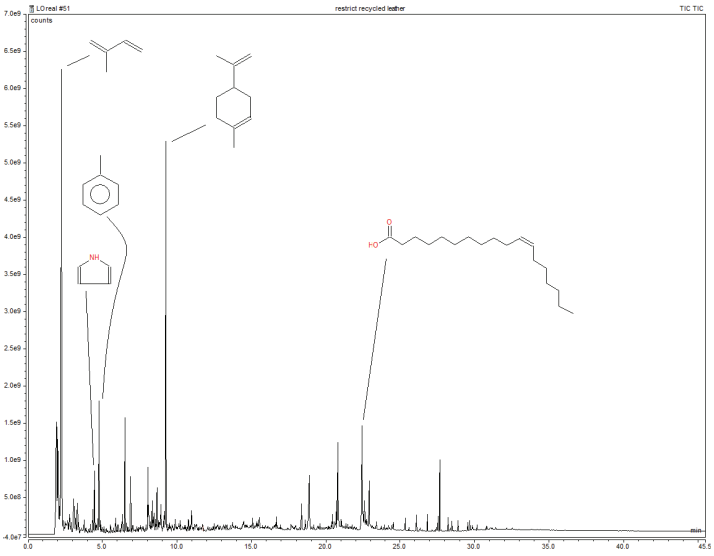


Figure 8. Recycled leather at 600°C.

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.

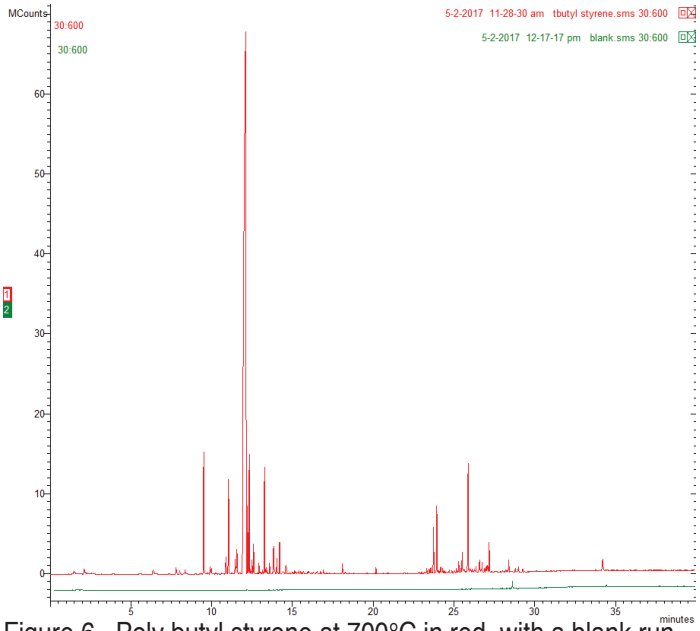


Figure 6. Poly butyl styrene at 700°C in red, with a blank run immediately after, in green.

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.

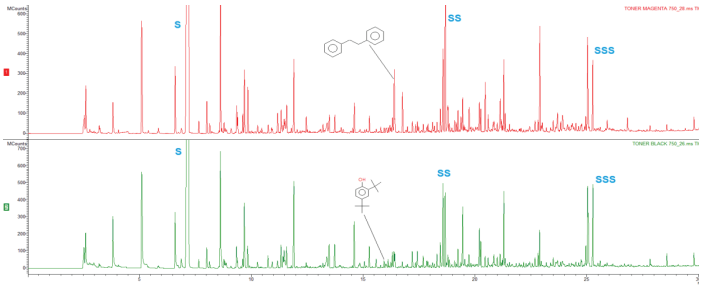


Figure 7. Two styrene based photocopy toners.

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.

EGA-MS

By replacing the analytical column of the GC/MS with a short piece of deactivated fused silica, it is possible to process a sample with nearly immediate transfer of the resulting compounds to the MS. The split inlet function can be used to limit the amount of sample entering the MS, and approximately one meter of 0.10mm fused silica provides enough restriction to permit the MS to maintain adequate vacuum. The Pyroprobe 6000 Series platinum filament is programmable in degrees per millisecond, second or minute, providing an extremely wide range of heating profiles. When connected this way, evolved gas mass spectral data from the polymer is produced relative to filament temperature. This technique is often called Evolved Gas Analysis, or EGA. Figure 9 for example compares the evolved gas analyses of several different polymers containing Bisphenol A.

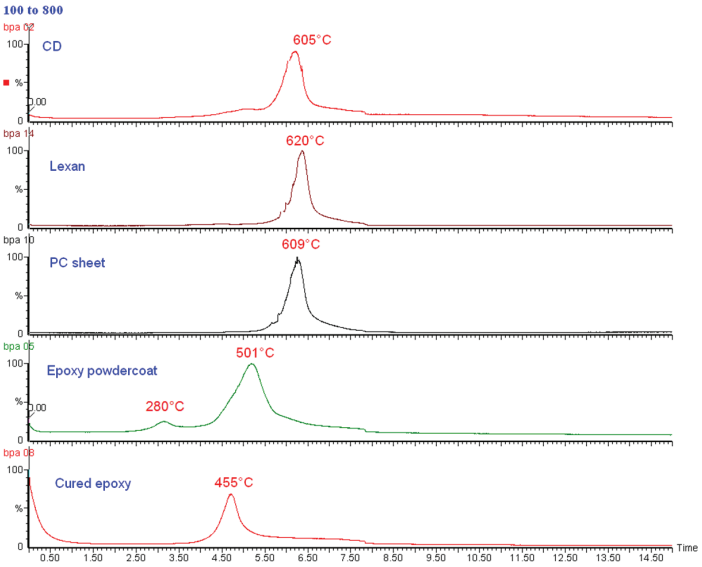


Figure 9. Evolved gas analyses of several samples containing Bisphenol A.

These polymers clearly have different thermal stabilities as indicated by the temperatures of maximum production. The epoxy powder-coat, however, also reveals an early peak which represents the evolution of semi-volatiles such as additives prior to the pyrolysis of the polymer. Examining the mass spectra at various times in the analysis can identify the types of compounds being volatilized at a certain time and the corresponding temperature. Figure 10 shows several different polymers heated to 250°C for three minutes, then ramped to 800° at 100°/minute. The initial heating at 250° vaporizes additives, such as plasticizers, allowing them to be identified before the polymer is thermally decomposed.

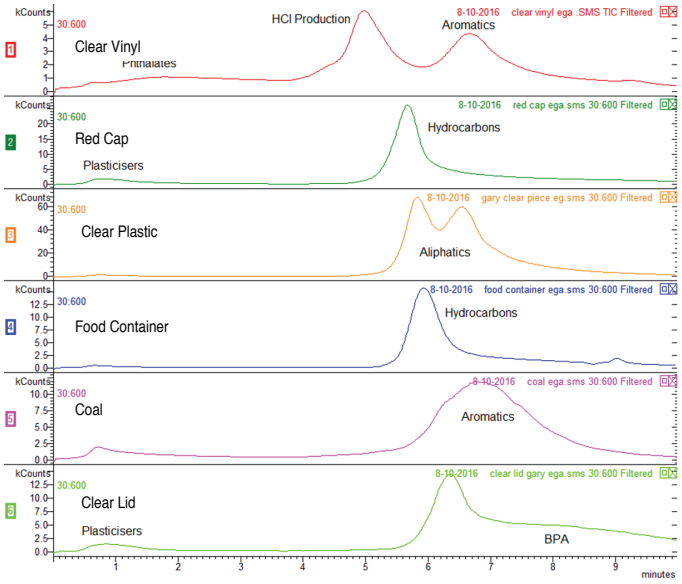


Figure 10. EGA of different materials indicating characteristic products formed.

Libraries

Because there is no chromatographic separation, all the analytical products are transferred directly to the mass spectrometer. At any point in time a spectrum could be a composite of multiple compounds entering the mass spec at that time. Averaging the spectra for the run provides a single spectrum containing information on all the products formed throughout the entire analysis. Creating these averaged spectra for a range of known polymers produces a library of spectra that can be used to identify unknown polymers. Figure 11 shows the EGA run for an unknown clear plastic. Averaging the full run and using the CDS Polymer Library of averaged spectra identifies the unknown material as PET, as shown in Figure 12.

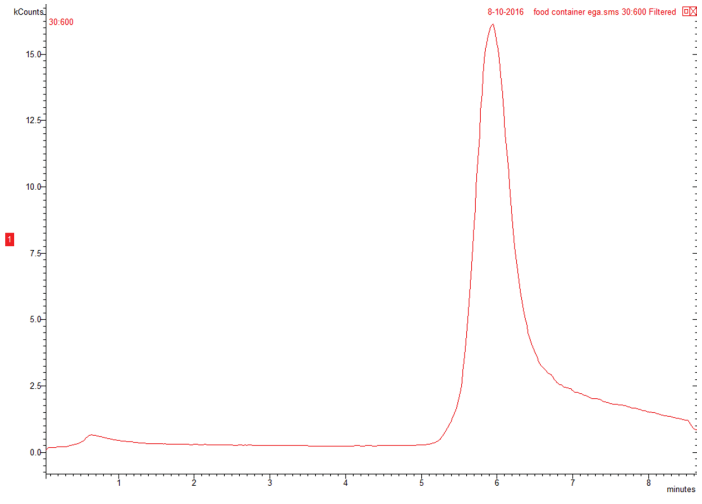


Figure 11. EGA analysis of an unknown clear plastic.

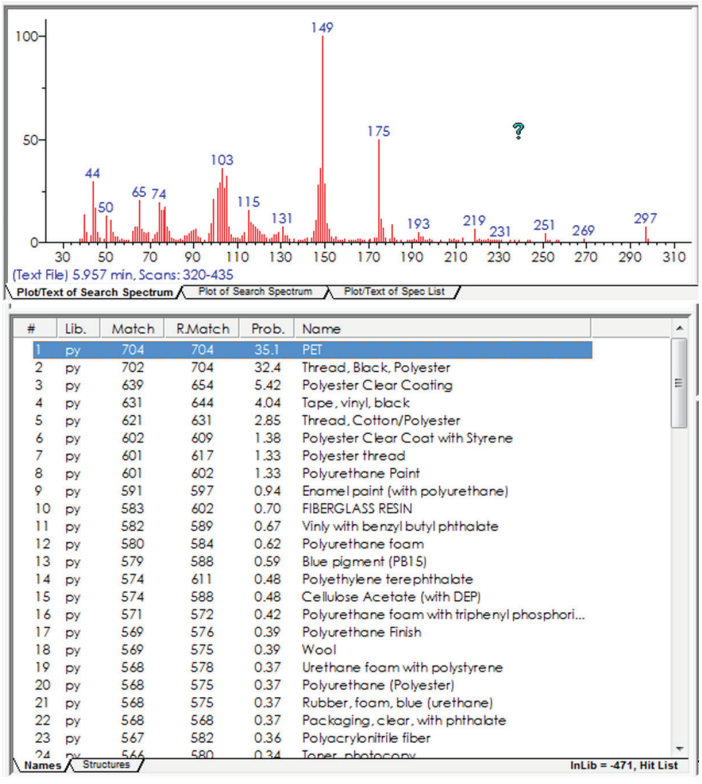
EGA Experimental Parameters

The sample was pyrolyzed in a DISC tube, using a CDS Pyroprobe 6200 Autosampler.

Pyroprobe
Initial: 250°C for 3 minutes
Ramp: 100°C/minute
Final: 800°C

Interface
Rest: 300°C
Initial: 300°C
Ramp:
Final: 300°C for 8 minutes
Valve oven: 300°C
Transfer line: 315°C

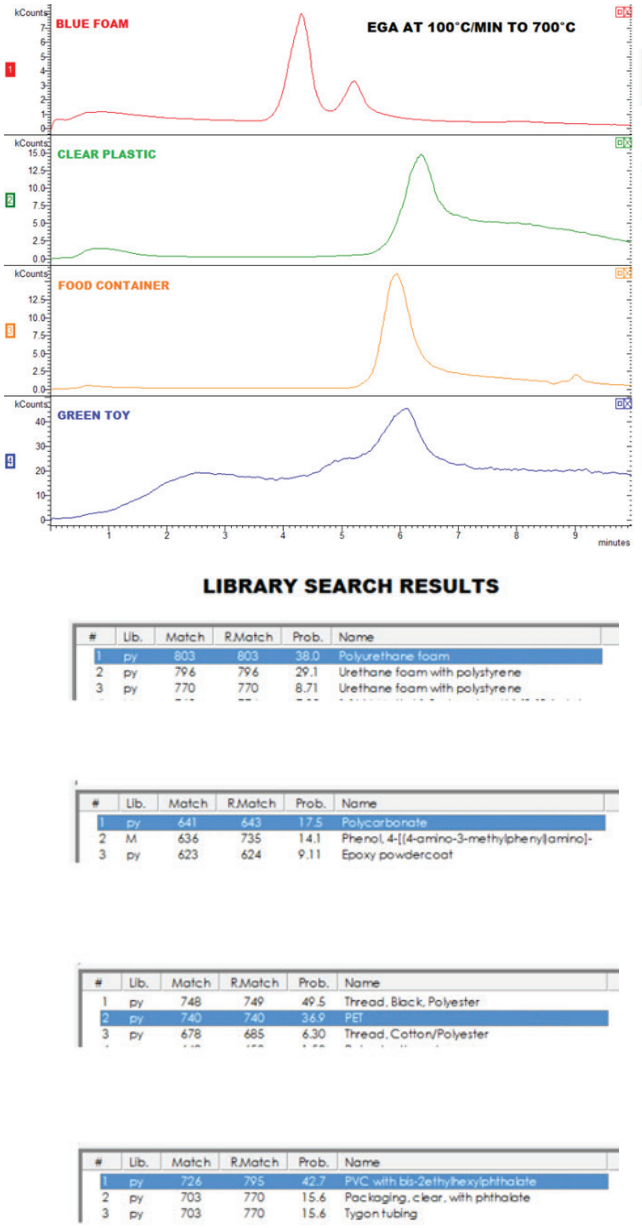
GC/MS
Column: 1 m x 0.1 mm uncoated
Carrier: Helium
Split: 100:1
Oven program:
275°C isothermal for 10 minutes



#	Lib.	Match	R.Match	Prob.	Name
1	py	704	704	35.1	PET
2	py	702	704	32.4	Thread, Black, Polyester
3	py	639	654	5.42	Polyester Clear Coating
4	py	631	644	4.04	Tape, vinyl, black
5	py	621	631	2.85	Thread, Cotton/Polyester
6	py	602	609	1.38	Polyester Clear Coat with Styrene
7	py	601	617	1.33	Polyester thread
8	py	601	602	1.33	Polyurethane Paint
9	py	591	597	0.94	Enamel paint (with polyurethane)
10	py	583	602	0.70	FIBERGLASS RESIN
11	py	582	589	0.67	Vinly with benzyl butyl phthalate
12	py	580	584	0.62	Polyurethane foam
13	py	579	588	0.59	Blue pigment (PB15)
14	py	574	611	0.48	Polyethylene terephthalate
15	py	574	588	0.48	Cellulose Acetate (with DEP)
16	py	571	572	0.42	Polyurethane foam with triphenyl phosphori...
17	py	569	576	0.39	Polyurethane Finish
18	py	569	575	0.39	Wool
19	py	568	578	0.37	Urethane foam with polystyrene
20	py	568	575	0.37	Polyurethane (Polyester)
21	py	568	575	0.37	Rubber, foam, blue (urethane)
22	py	568	568	0.37	Packaging, clear, with phthalate
23	py	567	582	0.36	Polyacrylonitrile fiber
24	py	566	580	0.34	Toner, photocopy

Figure 12. Library search identifying the unknown material in Figure 11 as Polyethylene Terephthalate (PET).

Further examples are shown for several common polymers including a polyurethane foam and a vinyl toy containing phthalate plasticizers (Figure 13).



#	Lib.	Match	R.Match	Prob.	Name
1	py	803	803	38.0	Polyurethane foam
2	py	796	796	29.1	Urethane foam with polystyrene
3	py	770	770	8.71	Urethane foam with polystyrene

#	Lib.	Match	R.Match	Prob.	Name
1	py	641	643	17.5	Polycarbonate
2	M	636	735	14.1	Phenol, 4-[(4-amino-3-methylphenyl)amino]-
3	py	623	624	9.11	Epoxy powdercoat

#	Lib.	Match	R.Match	Prob.	Name
1	py	748	749	49.5	Thread, Black, Polyester
2	py	740	740	36.9	PET
3	py	678	685	6.30	Thread, Cotton/Polyester

#	Lib.	Match	R.Match	Prob.	Name
1	py	726	795	42.7	PVC with bis-2ethylhexylphthalate
2	py	703	770	15.6	Packaging, clear, with phthalate
3	py	703	770	15.6	Tygon tubing

Figure 13. Identification of unknown polymers using EGA and the CDS Polymer Library.

Polymer screening with the Polymer Library can also be used with traditional Pyrolysis-GC-MS by averaging the mass spectra of the entire pyrogram.

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, effective EGA polymer screening and a polymer matching system to reveal a wealth of information on all your polymer samples.