Analytical Pyrolysis of Paper by a Novel Thermal Slice Technique with a Pyroprobe

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Application Note
Polymers

Abstract
This application note presents pyrolysis GC-MS of cash register paper, using a thermal slice technique to thermally remove the paper component from the analysis.

Introduction
In a previous application[1], paper which is coated with material that changes color when exposed to heat, also known as thermal paper, was analyzed with evolved gas analysis (EGA) while including a thermal slicing technique to remove the cellulosic portion of the paper but leaving the additives and polymer coating. In this application, this technique was used in conjunction with pyrolysis-GC-MS.

Experimental
Using information gathered from an EGA and multi-step pyrolysis in a previous application note[1], 100 μg of paper was analyzed with Pyrolysis-GC-MS with a "stitched method" and thermal slicing to remove the cellulose.

Pyrolysis with Thermal Slice
(Sequence of 2 methods):

Pyroprobe Method 1

GC Ready:	Enabled
GC Start:	Disabled
Thermal Slice:	None
DISC Chamber:	300°C 60s
Interface:	300°C
Transfer Line:	325°C

Pyroprobe Method 2

GC Ready:	Disabled
GC Start:	Enabled
Thermal Slice:	400°C 60s
DISC Chamber:	550°C 30s
Interface:	300°C
Transfer Line:	325°C
Valve Oven:	300°C

GC-MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium 1.25mL/min 50:1 split
Injector:	360°C
Oven:	40°C for 2 minutes 12°C/min to 320°C hold 15min
Ion Source:	230°C
Mass Range:	35-600amu

Results & Discussion
Almost all consumer products contain more than one material. Sometimes these materials can be separated thermally. For example, thermal paper contains cellulose from the paper, and also sensitizers, color developers plus a polymer coating.

In a previous application note[1], thermal paper was analyzed using evolved gas analysis, which showed 3 distinct regions of outgassing, as depicted in the top graphic of Figure 1. This indicated that the materials within the paper could be thermally separated from each other. The EGA was followed by multi-step pyrolysis, using the temperature information gained by the first step to show chromatographic detail of each of the temperature regions. Finally, a second EGA was performed, demonstrating a thermal slicing technique, in which the middle region of the EGA, the cellulose portion, was removed.

In this application note, a novel thermal slicing technique was performed using pyrolysis GC-MS instead of EGA. In this manor, the additives and polymer coating appear in the chromatogram without the interference from cellulose. Thermal slicing is accomplished by running two sequential Pyroprobe methods in one GC run, also known as a "stitched method". It is possible to "stitch" two methods together in one GC run by de-selecting the "Use GC Ready" in the second method of two methods, then running two methods in a sequence.

A traditional Pyroprobe method contains a pre-pyro delay to allow the GC inlet pressure to stabilize before pyrolysis, and a post-pyro delay to allow time for the pyrolysis vapors to leave the DISC. When the "Use GC Ready" is de-selected in the second method, the post-pyro delay in the first method and the pre-pyro delay in the second method are disabled, so the temperature ramping between method one and method two proceeds seamlessly.

To stitch 2 methods together for this application, the first method was programmed to use GC ready signal, and heat the sample to 300°C. The "Other" tab in the Method Editor shows the "Use GC Ready" is checked and the "Issue GC Start" is unchecked (Figure 2). The second method has the "Use GC Ready" unchecked, as seen in the Method Editor "Other" tab in Figure 3. This automatically removes the post pyro delay in the first method and the pre pyro delay in the second method when run in a sequence together. The "Issue GC Start" is checked and Thermal Slice is set at 400°C for 60 seconds. Method 1 and Method 2 were then added to the sequence table (Figure 4), and the sequence was run. When the sequence was started, the first method waited for the GC to become ready, then heated the sample to 300°C. After the first method completed, the second method immediately performed the thermal slice, by placing the DISC in-line with the sample vent and continuing to heat to 400°C for 1 minute. After the thermal slice was completed, the DISC was placed back online with the GC, started the GC and proceeded to the final pyrolysis temperature of 550°C. A graphical temperature display of this py-gc-ms stitched method, matched with an EGA is shown in Figure 1.

Figure 5 compares single step pyrolysis of paper at 550°C to pyrolysis of the paper at 550°C with the thermal slice at 400°C

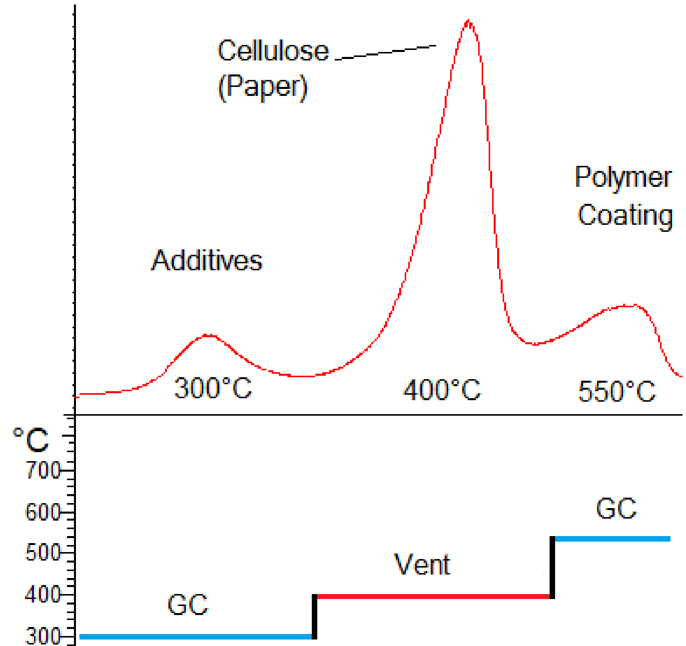


Figure 1. Paper EGA (top), and temperature profile using a stitched py-gc-ms method with a thermal slice (bottom).

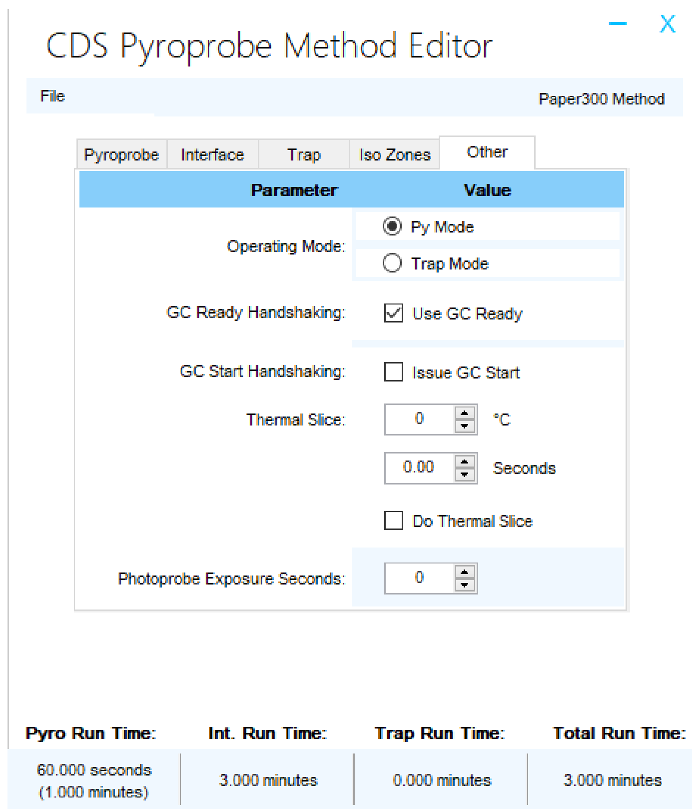


Figure 2. CDS Pyroprobe Method Editor "Other" tab of Method 1.

using the stitched method technique. Peaks 1, 3, and 6 can be contributed to the polystyrene coating. Peaks 4 and 5 are additives. Peak 2 and other small unlabelled peaks along the chromatogram are due to the contribution of cellulose. When a

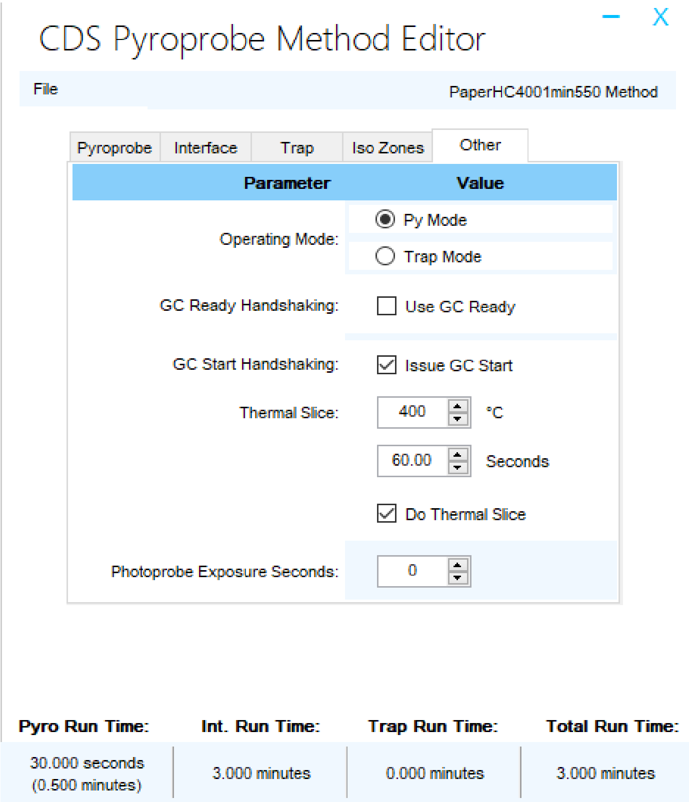


Figure 3. CDS Pyroprobe Method Editor "Other" tab of Method. 2.

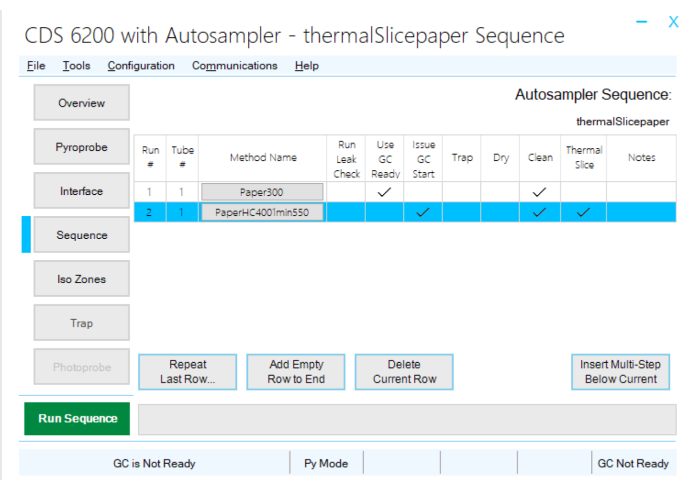
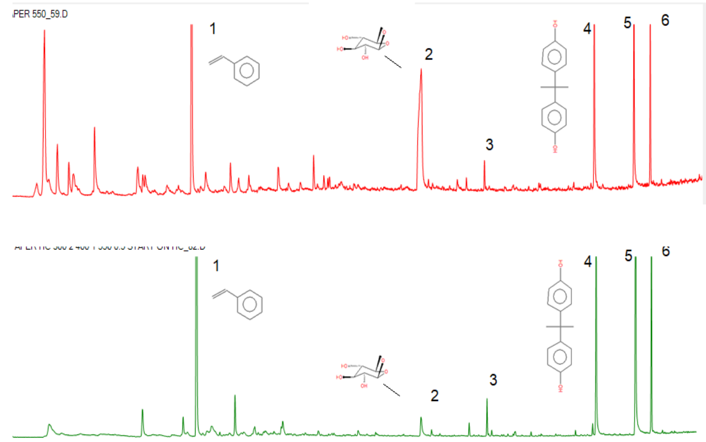


Figure 4. Stitched method Sequence Table.

thermal slice at 400°C is employed, peak 2, and other peaks for cellulose are decreased.

By removing the contribution of the cellulose, the resulting chromatogram is simpler and cleaner, so specific compounds of interest, which may be a small portion of the finished material, can be targeted by using a stitched method together with a thermal slice.



Peak	Identification	Category
1	Styrene	Polystyrene
2	Levoglucosan	Cellulose
3	Styrene Dimer	Polystyrene
4	Bisphenol A	Additive
5	Octadecanamide	Additive
6	Styrene Trimer	Polystyrene

Figure 5. Paper at 550°C (top), and Paper at 300°C and 550°C, but thermally sliced at 400°C (bottom).

Additionally, while only 100 μg of sample is preferred for pyrolysis GC-MS, these sizes can be increased with minimal concern overloading the GC-MS system as the largest portion of the sample would be thermally sliced to the vent, instead of being sent to the detector.

Conclusion

In this application note, the thermal slice option in conjuction with a stitched method technique was used on polymer coated paper to remove the cellulosic portion from the pyrogram, while keeping the additives and polymer coating. Using this technique, specific components of interest, which may be a small portion of the finished material can be targeted. In this manor, sample sizes may be increased with minimal concern overloading the GC-MS system.

References

1. Sam, K., "Evolved Gas Analysis with Heart Cutting Technique," App Note #220, CDS Analytical, 2020.