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Application Note

Paper & Ink

The toner materials used in laser printers and photocopiers are frequently a combination of organic polymers or copolymers and inorganic materials like metal oxides used as pigments. It may be of interest to analyze these toners alone, for manufacturing and quality control purposes, or to analyze them after they have been printed onto paper, as in questioned document investigations. In either case, pyrolysis-GC or pyrolysis-GC/MS offers a simple and effective technique for unraveling such a complex sample.

When paper (which is essentially cellulose) is pyrolyzed, it produces CO2, water, oxygenates like furans and aldehydes, small hydrocarbons and levoglucosan. Figure 1 shows a pyrogram of a standard white paper used with laser printers, without toner. When a piece of the same paper which contains toner is pyrolyzed, the pyrogram includes all the cellulose pyrolysate peaks plus peaks from the organic material used in the toner. In this case, the toner was made using a copolymer of styrene and butyl acrylate, and the monomer peaks are easily seen in Figure 2. In fact, the styrene monomer peak is by far the largest peak, and styrene dimer and trimer may be seen as well.

The first ten minutes of these pyrograms have been expanded for easier comparison in Figure 3. Other toner formulations may include additional monomers, such as other acrylics, which are also readily identified using pyrolysis-GC/MS.

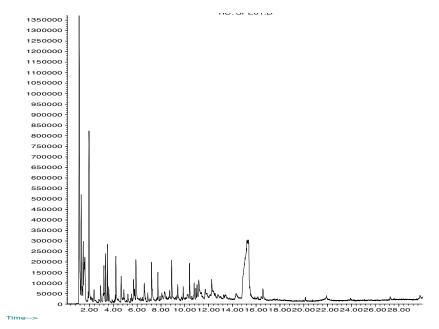


Figure 1. Paper without toner.

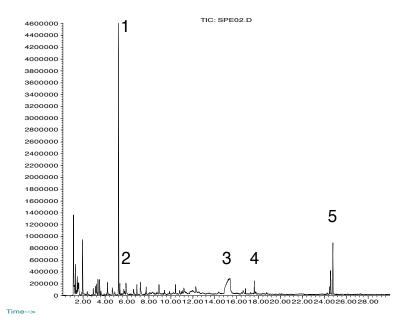
Instrument Conditions

Pyroprobe Autosampler

Valve Oven:	300°C
Temperature:	750°C
Rate:	10°C/ms
Time:	15 seconds

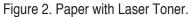
GC/MS

Column:	5% phenyl (30m x 0.25mm x .25μm)
Carrier:	Helium, 50:1 split
Injector:	300°C
Oven:	40°C for 2 minutes
	6°C/min to 295°C hold 10 min



TIC: SPE01.D

4.66



1300000 1200000 1100000 1000000 900000 800000 700000 1. Styrene monomer 600000 500000 2. Butyl acrylate monomer 400000 300000 3. Levoglucosan (from cellulose) 200000 4. Styrene dimer 100000 5. Styrene trimer Tim e --> Abundance TIC: SP 02.0 4500000 1 4000000 3500000 3000000 2500000 2000000 1500000 2 1000000 500000 <u>~~</u>

Figure 3. Upper - paper only, lower - paper with toner.

FOR MORE INFORMATION CONCERNING THIS APPLICATION, WE RECOMMEND THE FOLLOWING READING:

J. Zimmerman, D. Mooney and M. Kimmett, Preliminary Examination of Machine Copier Toners by Infrared Spectrophotometry and Pyrolysis Gas Chromatography, J. Forensic Sci., 31, 2, (1986) 489.

T. Wampler and E. Levy, Applications of Pyrolysis Gas Chromatography/Mass Spectrometry to Toner Materials from Photocopiers, J. Forensic Sci. 31, 1, (1986) 258.

Peak Identification for Figures 2 and 3