PYRO CORE APPNOTE

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Identification of Materials Used in Integrated Circuit Boards using Pyrolysis Gas Chromatography-Mass Spectrometry

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Abstract
Integrated circuit (IC) boards are ubiquitous in many of the products we utilize on a daily basis. The boards contain chips, resistors, capacitors, diodes, and other devices which make up the circuitry. These devices generate heat, and the materials used to construct the IC boards must withstand high temperatures. Some of the materials contain additives for fire prevention or have fire-retardant compounds incorporated into the polymer backbone.

For IC chips, epoxy molded compounds (EMC) are commonly used, as they are chemical resistant, absorb little moisture, and can withstand high temperatures. Polymers widely used for EMCs include phenolic epoxy resins, phenol/formaldehyde polymers (Novolacs), bismaleimides, and multiaromatic resins. These polymers also contain accelerators, fillers, curing agents, and antioxidants.

With the exponential growth of consumer devices, such as VR headsets, the close proximity of IC materials to the consumer produces the need to look at off-gassing from these materials as a possible route of exposure. Also, the thermal treatment of electronic waste has become a popular method of recycling it. Lastly, if a device does catch fire, it is important to know what type of compounds are given off during combustion.

Pyrolysis GC-MS is a valuable tool for identifying polymers and their breakdown products. Pyrolysis is also helpful for identifying additives for polymers. In this study, the GERSTEL pyrolysis system, combined with gas chromatography-mass spectrometry, was used to analyze compounds from an IC board.

Introduction
The GERSTEL PYRO Core system, equipped with an advanced dual coil platinum wire, operates in various pyrolysis modes, including standard pulsed, sequential, and fractionated. Its unique heating system ensures uniform sample heating and unmatched reproducibility. The system also features an integrated GERSTEL CIS 4 inlet, serving as a cryofocusing trap for analytes or a hot split interface for direct transfer to the column. The GERSTEL MPS robotic autosampler enables complete automation of the analysis.

This study details the use of the GERSTEL PYRO system and the GERSTEL MPS robotic autosampler to analyze materials found on a printed circuit board. In Smart-Ramped Pyrolysis, a rapid, controlled temperature ramp is applied, enabling continuous pyrolysis of the sample. It produces a pyrogram in a single sample run that is equivalent to, or provides more data, compared to pulsed pyrolysis mode. This mode is ideal for unknown samples and significantly reduces method development time.

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Experimental

Instrumentation

GERSTEL PYRO Core system on Agilent 8890 GC/5977B Inert Plus MSD

Analysis Conditions PYRO Core System

CIS 4	Split 75:1	
	-120 °C (0 min), 12.0 °C/s, 300 °C (5.0 min)	
TDU	Splitless	
	50 °C (0 min), 300 °C/min, 300 °C (2.02 min)	
Pyro	Lead Time	0.00 min
	Follow up Time	0.25 min
	Initial Time	0.00 min
	Initial Temp	300 °C
	Rate	5 °C/s
	Final Temp	800 °C
	Final Time	0.10 min

Analysis Conditions Agilent 8890 GC

Column	30 m DB-5MS UI (Agilent)
	d_i = 0.25 mm, d_f = 0.25 µm
Pneumatics	He, P_i = 7.1 psi (MSD)
	Constant flow = 1.0 mL/min
Oven	40 °C (2.0 min), 15 °C/min, 300 °C (6 min)

Sample Preparation

A non-functional integrated circuit board was obtained from the GERSTEL service department. A razor knife was used to scrape a small sample from the IC chips on the board. Needle nose pliers were used to remove resistors and capacitors from the board. The razor knife was used to scrape a sample of the coating on the capacitors and resistors. The samples were placed in open-ended quartz sample tubes atop a piece of quartz wool.

Pyrolysis

The quartz tubes were connected to pyrolysis adapters and placed into a 40-position pyrolysis tray.

Results and Discussion

Figure 1 shows a picture of the instrument used in this study.

Figure 1: GERSTEL PYRO Core system mounted on an Agilent 8890-5977B GC-MS system.

Figure 2 shows the total ion chromatogram (TIC) for the pyrolysis of a sample of a coating from a resistor on the IC board. The pyrogram shows a typical example for a phenolic epoxy resin with compounds such as phenol, bisphenol A, bisphenol A monoglycidol ether, and bisphenol A diglycidol ether. Triphenylphosphine oxide (TPPO) is added to the polymer as a fire retardant. Melamine is present and can be used in epoxy resins as a mold release agent, fire retardant, or crosslinking agent. Isobornyl acrylate was also found. Acrylates are also common additives to epoxy resins.

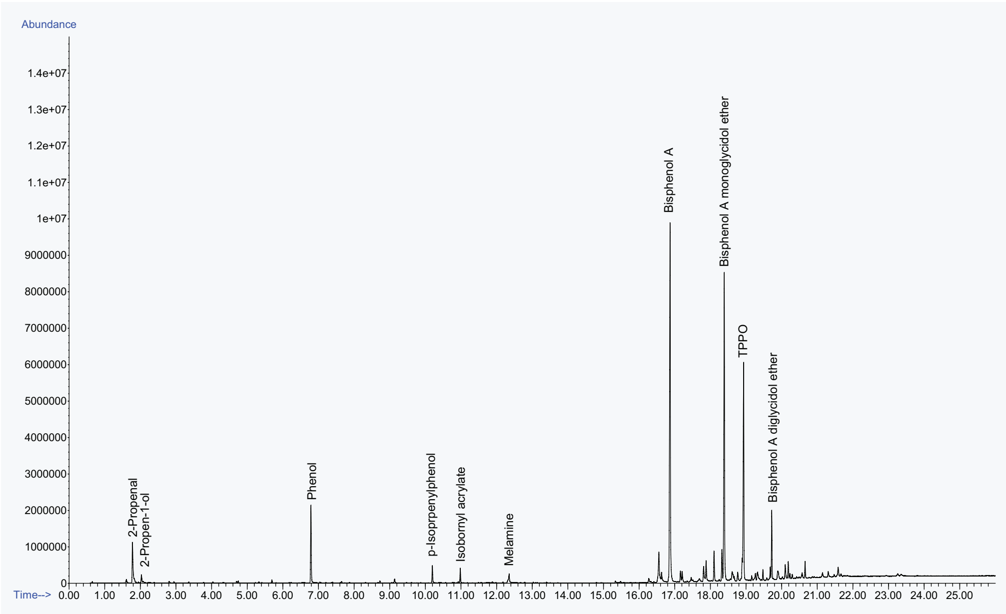

Figure 2: Total ion chromatogram for pyrolysis of a resistor coating.

Figure 3 shows the TIC for a sample scraped from the IC board edge. The pyrogram shows an example of a brominated epoxy resin. Several of the peaks are similar to those found in Figure 2, with the addition of tetrabromobisphenol A, tribromobisphenol A, and dibromobisphenol A. Other brominated compounds found in the pyrogram include bromacetone, isopropenyl bromide, and bromomethane. A large peak for tetrahydrophthalic anhydride is seen in the pyrogram. It is used as a hardener for epoxy resins.

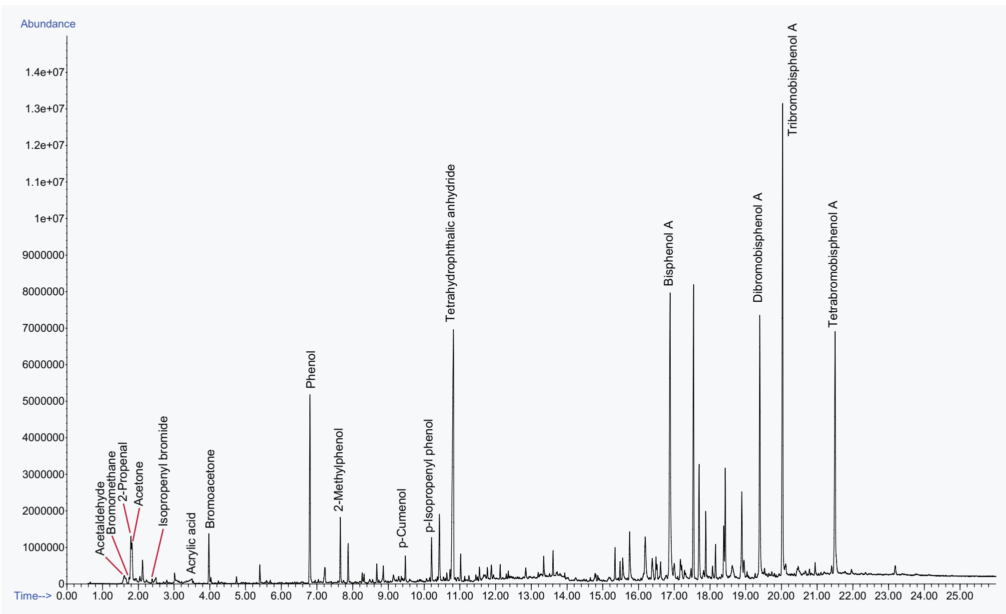

Figure 3: Total ion chromatogram for pyrolysis of an IC board edge.

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Figure 4 shows the TIC for the pyrolysis of a sample scraped from an IC chip. The peaks indicate the sample is from a polyester, most likely 1,4-butylene terephthalate. Several brominated compounds are seen in the pyrogram. These are most likely part of the polymer backbone added as a flame retardant.

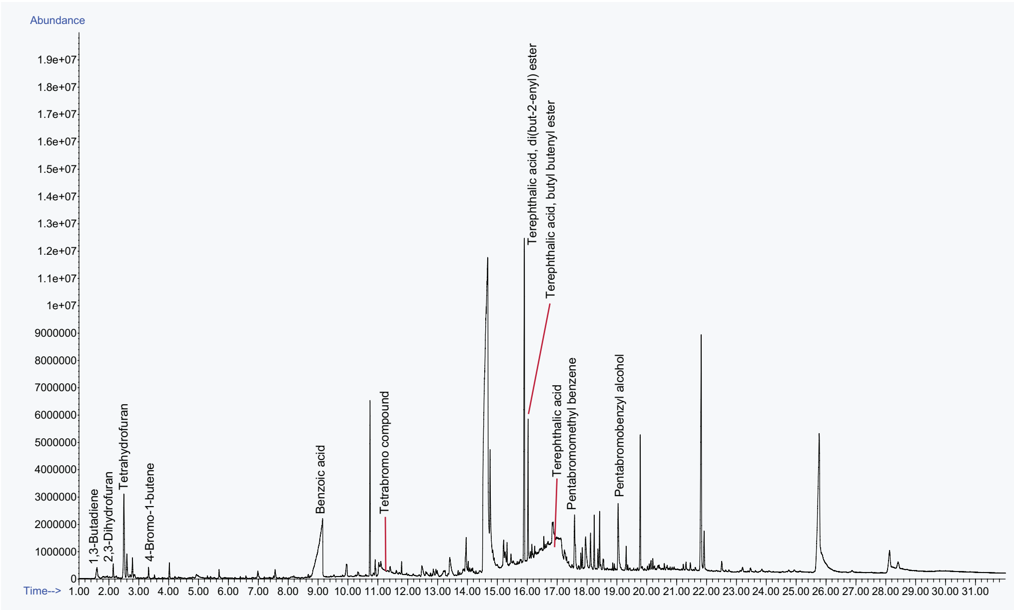

Figure 4: Total ion chromatogram for pyrolysis of an IC chip.

Figure 5 shows the TIC for a brown wrapper off a large capacitor on the IC board. The peaks for HCl, benzene, and chlorinated alkanes indicate the polymer is polyvinyl chloride. Most of the peaks after a retention time of 16 minutes are all common plasticizers added to PVC.

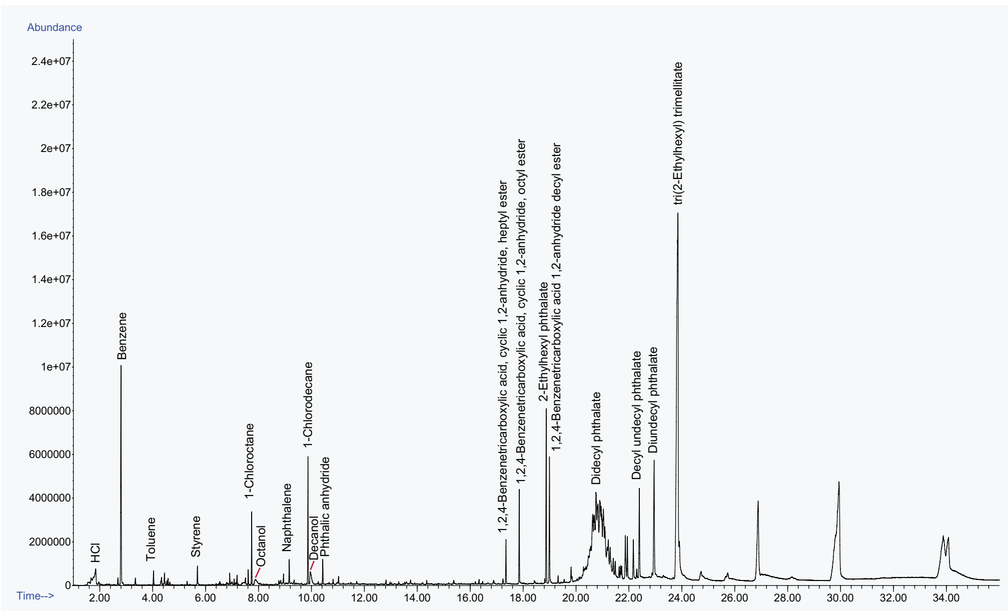

Figure 5: Total ion chromatogram for pyrolysis of a brown wrapper from a large capacitor.

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Figure 6 shows the TIC for pyrolysis from an IC chip on the board. The pattern is indicative of a brominated phenol formaldehyde resin. Triphenylphosphine oxide and triphenylphosphine sulfide are seen in the chromatogram. They are added as flame retardants. The polymer also contains nylon, as indicated by peaks for caprolactam and hexahydro-1-(2-propenyl)-2H-azepin-2-one.

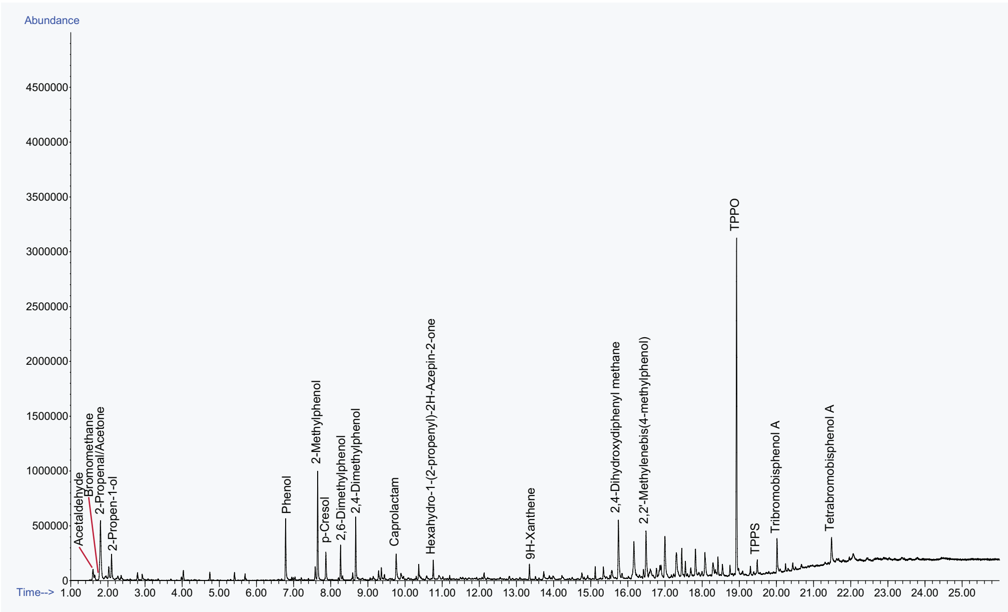

Figure 6: Total ion chromatogram for pyrolysis of a brown wrapper from an IC chip on the board.

Conclusion

This study used Smart Ramped Pyrolysis to produce an optimized pyrogram without needing method development for materials found on a printed circuit board. Several polymer types were identified in the samples. Volatile brominated compounds such as bromomethane, bromoacetone, and 4-bromo-1-butene were identified as breakdown products in some of the samples. These compounds could be off-gassed during recycling or general use of the product and may be harmful to the user. Polymer additives, such as UV stabilizers, plasticizers, and crosslinkers, can also be easily identified using pyrolysis GC-MS.

The GERSTEL PYRO Core system enables highly flexible and efficient automated pyrolysis of solids and liquids up to 1000 °C combined with thermal decomposition products using GC-MS. It provides an excellent tool for analyzing polymers and polymer additives.