Analysis of Forensic Samples by Pyrolysis Gas Chromatography Mass Spectrometry

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Abstract

In this study, the GERSTEL PYRO was used for the pyrolysis of various materials that are relevant to forensic analysis applications, including paints, adhesives, and cosmetics. A GERSTEL MultiPurpose Sampler (MPS) was used in combination with GERSTEL PYRO and GERSTEL Cooled Injection System (CIS 4), enabling efficient automation of the thermal extraction and pyrolysis of complex forensic materials. Fractionated and smart-ramped pyrolysis modes followed by gas chromatography mass spectrometry (GC-MS) analysis were used to determine important volatile additives and pyrolysates (from polymers) present in a diverse set of samples.

Introduction

Forensic laboratories use a variety of instruments to analyze complex materials including rubbers, paints, fibers, printing inks, toners, cosmetics, tapes, and adhesives. Some techniques, such as infrared (IR) spectroscopy, however, do not provide a full chemical analysis of the sample. Gas chromatography mass spectrometry (GC-MS) can provide an abundance of information on a sample, but the components must be volatile to be compatible with the technique. Adding a pyrolyzer to any standard laboratory GC-MS expands those capabilities beyond volatile compounds by creating known volatile marker fragments of the polymers within the sample. Precise heating of these samples at the GC inlet yields reproducible chromatographic results, providing information on the different polymers and additives present in the sample. Pyrolysis GC-MS (Py-GC-MS) benefits from requiring very small sample sizes (microgram levels), which is integral to forensic analysis, for which only a small amount of sample may be available. Additionally, little to no sample preparation is necessary prior to pyrolysis.

Method development for traditional pulsed pyrolysis GC-MS usually requires the pyrolysis of several pieces of the same sample at different temperatures. The optimum pyrolysis temperature for that sample is then chosen based on the amount of secondary pyrolysis products (secondary pyrolysates) found in the chromatograms. This can be a sample and time-consuming process and it is not ideal for forensic analysis for which the available sample amount can be very limited.

Smart Ramped Pyrolysis (SRP), a pyrolysis mode unique to the GERSTEL PYRO system, uses a temperature ramp of 5 °C/s from 300 to 800 °C. Slow temperature ramping, relative to pulsed pyrolysis, reduces or eliminates the formation of secondary pyrolysis products, producing chromatograms that are like those obtained when pyrolyzing at optimal temperature in pulsed pyrolysis mode. As a result, little or no method development is needed and only a single sample run is required to achieve an optimized pyrogram.

Fractionated Pyrolysis (FP) involves running a single sample at multiple temperatures generating several chromatograms. FP can be used to simplify analysis and data interpretation since separate chromatograms are obtained for volatile and semivolatile components from the sample and for compounds produced by pyrolysis of the polymer.

This work shows the application of pyrolysis with the GERSTEL PYRO in combination with GC-MS for the analysis of forensic materials. Using SRP and FP modes, house paint, tape, and mascara were analyzed to determine both volatile organic compounds (VOCs) and polymers present. Sample analysis was automated using the GERSTEL MultiPurpose Sampler (MPS), while the GERSTEL Cooled Injection System (CIS 4) acted as a direct interface between the GERSTEL PYRO and the GC column (Figure 1). The CIS inlet can also act as a cold trap when the trapping of volatile pyrolysates is needed to improve chromatographic quality and separation.

Experimental

Instrumentation:

GERSTEL MultiPurpose Sampler (MPS)

GERSTEL PYRO

GERSTEL Cooled Injection System (CIS 4)

Agilent 8890 GC/5977B MSD

Analysis Conditions:

Column:	Rxi-5ms (Restek) di = 0.25 mm, df = 0.25 µm, L = 30 m
Pneumatics:	He, Pi = 7.1 psi (MSD) Constant flow = 1.0 mL/min
Oven:	40 °C (1 min), 15 °C/min, 300 °C (5 min)
MSD:	Full scan, 40 - 450 amu
CIS 4:	Split Transfer 75:1 300 °C isothermal

PYRO

Smart-Ramped Pyrolysis (Figure 2):

CIS Transfer Mode:	Splitless
Initial Temp:	40 °C (0 min)
Smart Ramp:	5.0 °C/s, 800 °C (0 min)
Transfer Temp:	300 °C
Post Pyro Hold:	300 °C (0.50 min)

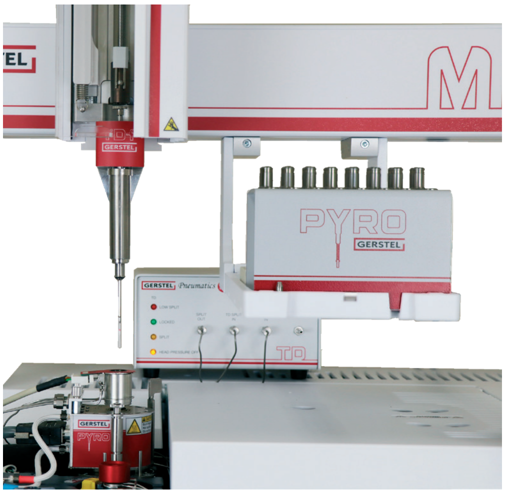

Figure 1: GERSTEL PYRO system coupled to GC-MS with automation by the GERSTEL MultiPurpose Sampler (MPS)

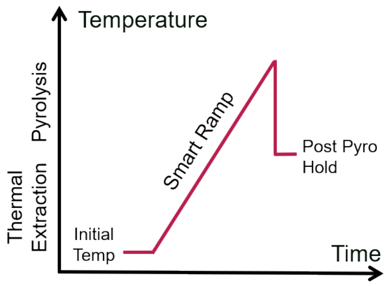

Figure 2: Temperature program for smart-ramped pyrolysis (SRP) mode

Fractionated Pyrolysis (Figure 3):

CIS Transfer Mode:	Splitless
Fraction 1 (120 °C)	
Initial Temp:	40 °C (0 min)
Temp Ramp:	60 °C/min, 120 °C (0.25 min)
Transfer Temp:	130 °C
Pulse Temp:	120 °C (1.00 min)
Post Pyro Hold:	120 °C (0.25 min)
Fraction 2 (300 °C)	
Initial Temp:	40 °C (0 min)
Temp Ramp:	160 °C/min, 300 °C (0.25 min)
Transfer Temp:	300 °C
Pulse Temp:	300 °C (1.00 min)
Post Pyro Hold:	300 °C (0.25 min)
Fraction 3 (600 °C)	
Initial Temp:	40 °C (0 min)
Temp Ramp:	720 °C/min, 300 °C (0.25 min)
Transfer Temp:	300 °C
Pulse Temp:	600 °C (0.33 min)
Post Pyro Hold:	300 °C (0.25 min)

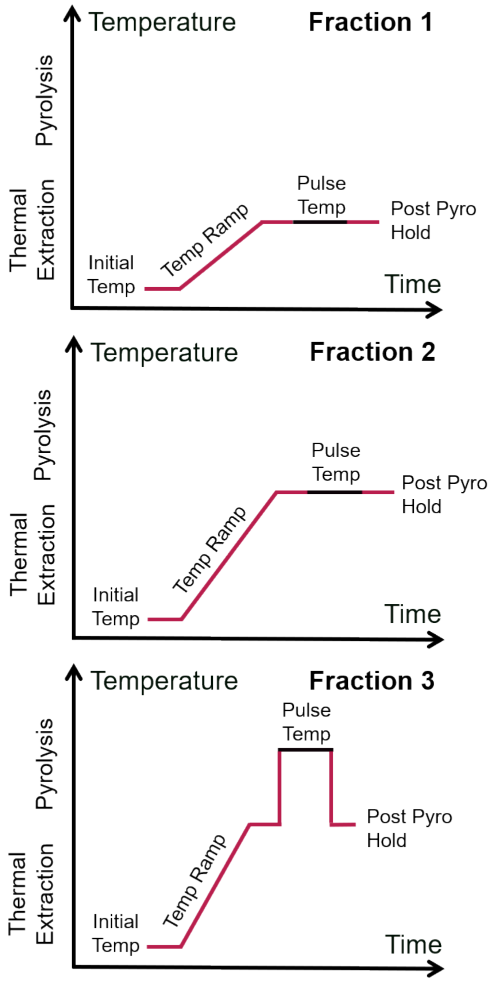

Figure 3: Temperature programs for fractionated pyrolysis (FP) mode

Sample Preparation

House paint, packaging tape, and mascara samples were obtained from local stores. For the packaging tape analysis, a small piece (less than one milligram of sample) was placed in a conditioned quartz tube on top of a small piece of quartz wool. For the mascara and the house paint analyses, a small amount of each was dabbed onto the quartz wool in individual conditioned quartz tubes. The sample tubes were then connected to PYRO transport adapters and placed into a 40 position PYRO tray.

Results & Discussion

All samples were analyzed in SRP mode, using a rapid, controlled temperature ramp of 5 °C/s from 300 to 800 °C. This method enables continuous pyrolysis of unknown samples without sample and time-consuming method development. In SRP mode, only a single sample run is required to achieve an optimal pyrogram.

Architectural and automotive paints are often characterized by Py-GC-MS as evidence at crime scenes in cases involving building or house break-in, automotive hit-and-run accidents, or vandalism. One benefit of Py-GC-MS for this type of sample is that it only requires a 10-50 microgram sample size. Typical household paint types include acrylic-, alkyd-, epoxy-, and vinyl acetate polymers. Py-GC-MS easily distinguishes between the polymers used in these paint classifications and identifies the additives used.

Figure 4 shows the pyrogram resulting from SRP of the house paint. Several monomers from acrylic polymers, the monomer from polystyrene and a few additional additives were identified. The presence of benzophenone, a UV light stabilizer, indicates that this paint was designed for outdoor use. The non-phthalate plasticizers, dioctyl maleate and diisobutyl glutarate, were also identified.

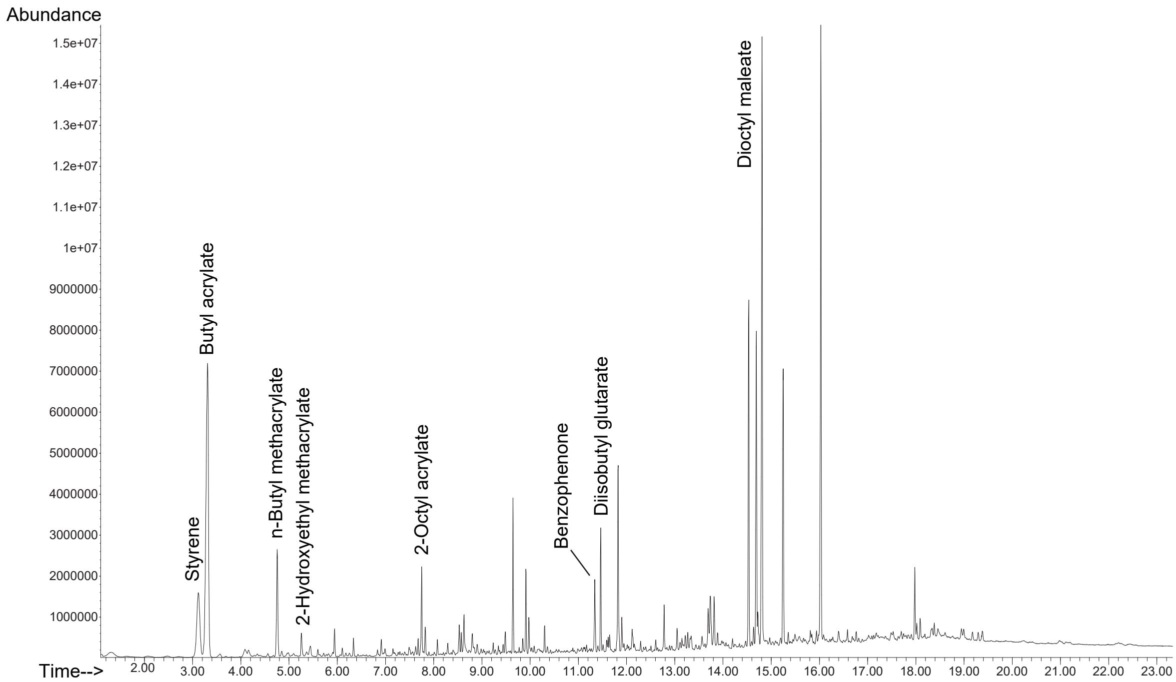

Figure 4: Total Ion Chromatogram resulting from SRP of house paint sample

Tapes and adhesives are typically used in the construction of improvised explosive devices (IEDs). In many cases, trace samples of the adhesives and tapes used are available to the forensic scientist as evidence from the bomb debris. The identification of these samples can provide information valuable in the search for a suspect. Adhesives are also used in fraudulently resealed packages, which can be examined for the presence of foreign adhesives used.

Commercial tapes are normally manufactured using up to four main types of materials, including a polymer film, the adhesive, fibers for strength, and additives, especially plasticizers, for flexibility. The tape film itself may be a polyolefin (usually polyethylene or polypropylene), paper, cellulose acetate, polyvinyl chloride, or other polymer. The adhesives can be natural rubber (polyisoprene), synthetic rubber (styrene/butadiene or styrene/isoprene) or acrylic (frequently a polyoctyl acrylate). The pyrolysate peaks from all four categories can be quite distinct and offer the forensic scientist the ability to differentiate materials from different manufacturers of these products.

Figure 5 shows the pyrogram resulting from SRP of a packaging tape. From the presence of polypropylene oligomers and a main marker peak, 2,4-dimethyl-1-heptene, it can be concluded that this tape is produced from a polypropylene-based film. A styrene/isoprene adhesive is indicated by the presence of styrene and α-methylstyrene from the pyrolysis of polystyrene and two isomers of limonene from the pyrolysis of polyisoprene.

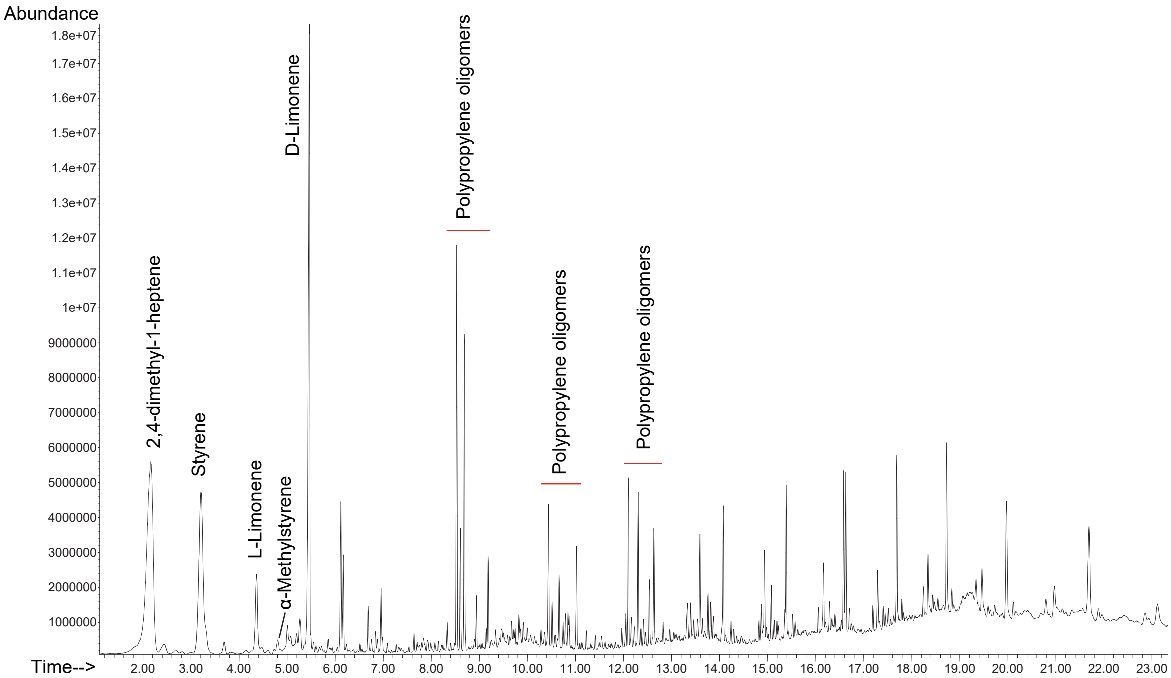

Figure 5: Total Ion Chromatogram resulting from SRP of packaging tape sample

Traces of cosmetics, such as mascara, lipstick, face creams and body lotions, can often provide valuable information to link a suspect to a victim found at a crime scene. Proper identification of a cosmetic stain on a suspected assailant's clothing, for example, can deliver a valuable piece of evidence in solving the crime. Because cosmetics contain a combination of oils, additives and polymers, Py-GC-MS can be used to provide a qualitative match of a clothing stain.

The analysis of mascara using SRP resulted in a complex pyrogram with some important peaks being obscured (Figure 6). To simplify the resulting pyrograms and improve data interpretation, the mascara sample was further analyzed in FP mode. In this mode, an aliquot of the sample was analyzed three times at increasing temperatures, resulting in three separate pyrograms. For this analysis, temperatures of 120, 300, and 600 °C were applied.

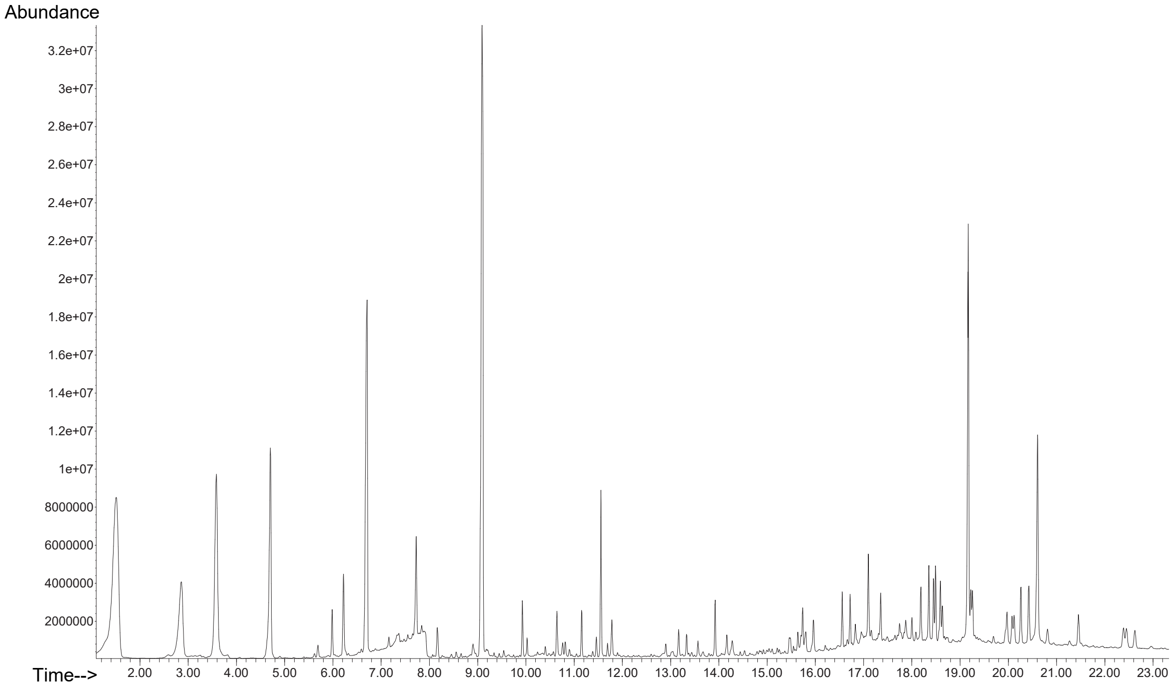

Figure 6: Total Ion Chromatogram resulting from SRP of mascara sample

Figure 7 shows a stacked view of the three pyrograms obtained at these temperatures. At the lowest temperature, glycerin was identified, which is a well-known humectant added to mascara to aid in moisture retention. Also identified at this temperature were dehydroacetic acid and 2-phenoxyethanol, preservatives that prevent growth of micro-organisms, as well as stearyl ethylhexanoate, ethyl palmitate and ethyl stearate, which are emollients. At 300 °C, several alcohols including lauryl and cetyl alcohol were identified, which are mainly used as emulsifiers. Glyceryl palmitate and stearate are esterification products of glycerin and palmitic or stearic acid, respectively. They serve as emollients, surfactants, and emulsifiers. Pyrolysis of the mascara sample at 600 °C resulted in a series of monomers from acrylate polymers, cyclosiloxanes from polysilicone, and N-vinylpyrrolidone from polyvinylpyrrolidone, all of which are film formers and waterproofing polymers.

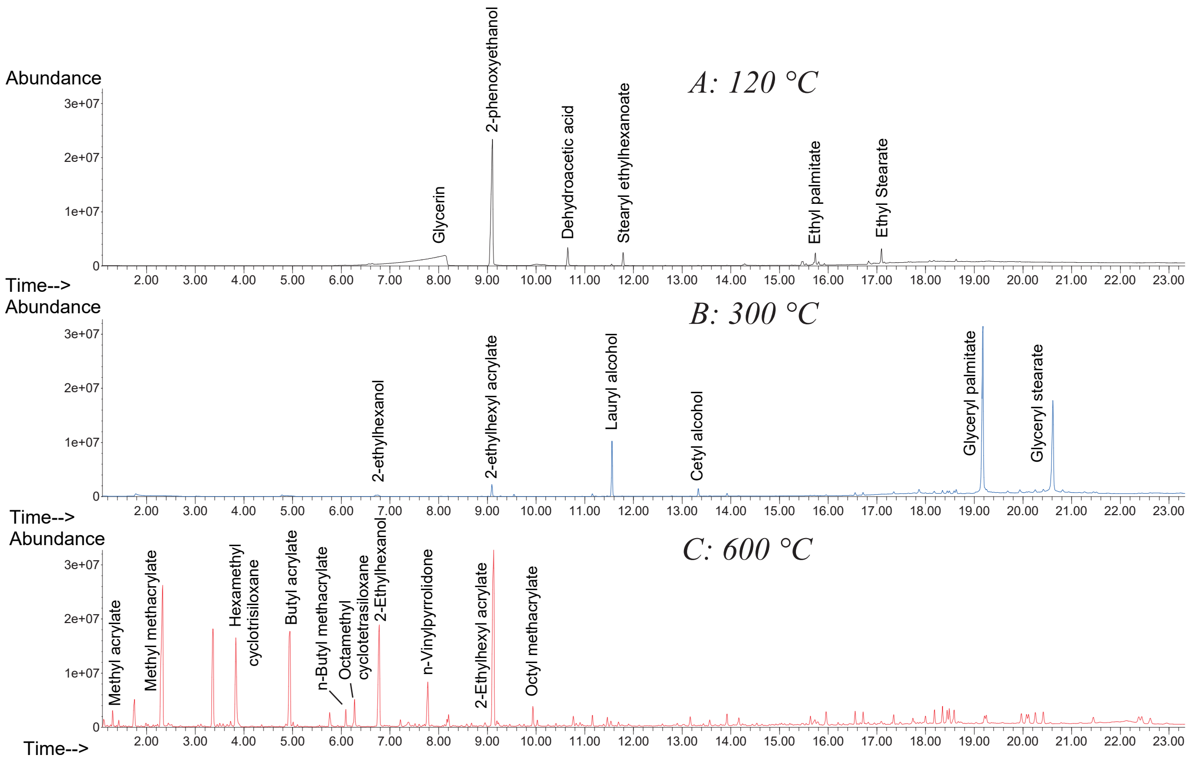

Figure 7: Stacked view for FP of mascara sample at (A) 120 °C, (B) 300 °C and (C) 600 °C.

Conclusions

The GERSTEL PYRO in combination with the MPS, CIS, and GC-MS can be used for the determination of additives and polymers present in various complex materials for the purpose of forensic analysis. Pyrolysis is an important instrumental technique for forensic analysis to obtain a full chemical analysis of a sample. SRP mode can be used to simplify method development, especially for unknown samples of which only a limited amount is available. FP mode enables the separation of compounds from complex samples into multiple chromatograms, simplifying interpretation and identification of additives and polymers in commercial products.

GERSTEL AppNote

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