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Fractionated Pyrolysis Gas Chromatography-Mass Spectrometry for the Analysis of Scented Finger Nail Polish

John R. Stuff and Jaqueline A. Whitecavage

GERSTEL, Inc., 701 Digital Drive, Suite J, Linthicum, MD 21090, USA

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Abstract
The global nail polish market was estimated at over $15 billion (USD) in 2023 and is expected to grow at a rate greater than 8% between 2024 and 2033. There are two main types of chemistry used for nail polish. The first is nitrocellulose dissolved in a solvent. The nitrocellulose hardens after the solvent evaporates. The other chemistry is based on acrylic polymers which polymerize as part of the application process. Other chemicals added to the polish may include photoinitiators, stabilizers, solvents, plasticizers, pigments, thickeners, and even fragrances.

Pyrolysis GC-MS is a valuable tool for identifying polymers and polymer additives. A sample can be thermally extracted at low temperature to identify polymer additives. The same sample can then be rerun at a higher temperature to pyrolyze it for polymer identification.

This work will identify the materials used in scented nail polishes. The GERSTEL pyrolysis system, in combination with gas chromatography-mass spectrometry, was used for the analysis.

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 scented fingernail polish using fractionated pyrolysis. In this mode, multiple thermal extractions and pyrolysis temperatures are applied to the same sample, with separate GC-MS runs at each temperature. This process allows for a clear differentiation between adsorbed volatiles (additives) and pyrolysates, enhancing the accuracy of the analysis.

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Experimental

Instrumentation

GERSTEL PYRO Core system on Agilent 8890 GC/5977B Inert Plus MSD (Figure 1).

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

Analysis Conditions PYRO Core System

Conditions Fraction 1

CIS 4	Split 20:1	
	-120 °C (0 min), 12.0 °C/s, 300 °C (5.0 min)	
TDU	Splitless	
	40 °C (0 min), 120.0 °C/min, 100 °C (5.5 min)	
Pyro	Lead Time	0.25 min
	Follow up Time	0.25 min
	Initial Time	5.00 min
	Initial Temp	100 °C

Conditions Fraction 2

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

Nail polish was applied to aluminum foil and allowed to dry for one hour. A razor knife was used to peel the nail polish from the aluminum foil.

Pyrolysis: Approximately one hundred micrograms of the sample was placed into an open-ended quartz pyrolysis tube with quartz wool. The quartz tubes were connected to pyrolysis adapters and placed into a 40-position pyrolysis tray.

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Results and Discussion

Figure 2 shows the total ion chromatogram (TIC) for the first fraction of pyrolysis for a breath mint-scented nail polish. Several large peaks, which are present in all the first fractions of the nail polishes, are seen. 2-Phenoxyethanol is used as a preservative/solvent in cosmetics. The large peaks between retention times 7-7.5 min are isomers of propylene glycol, which is used as a solvent in cosmetics. Isopropyl myristate is used as a solvent for fragrance components, and diisobutyl glutarate is used as a plasticizer.

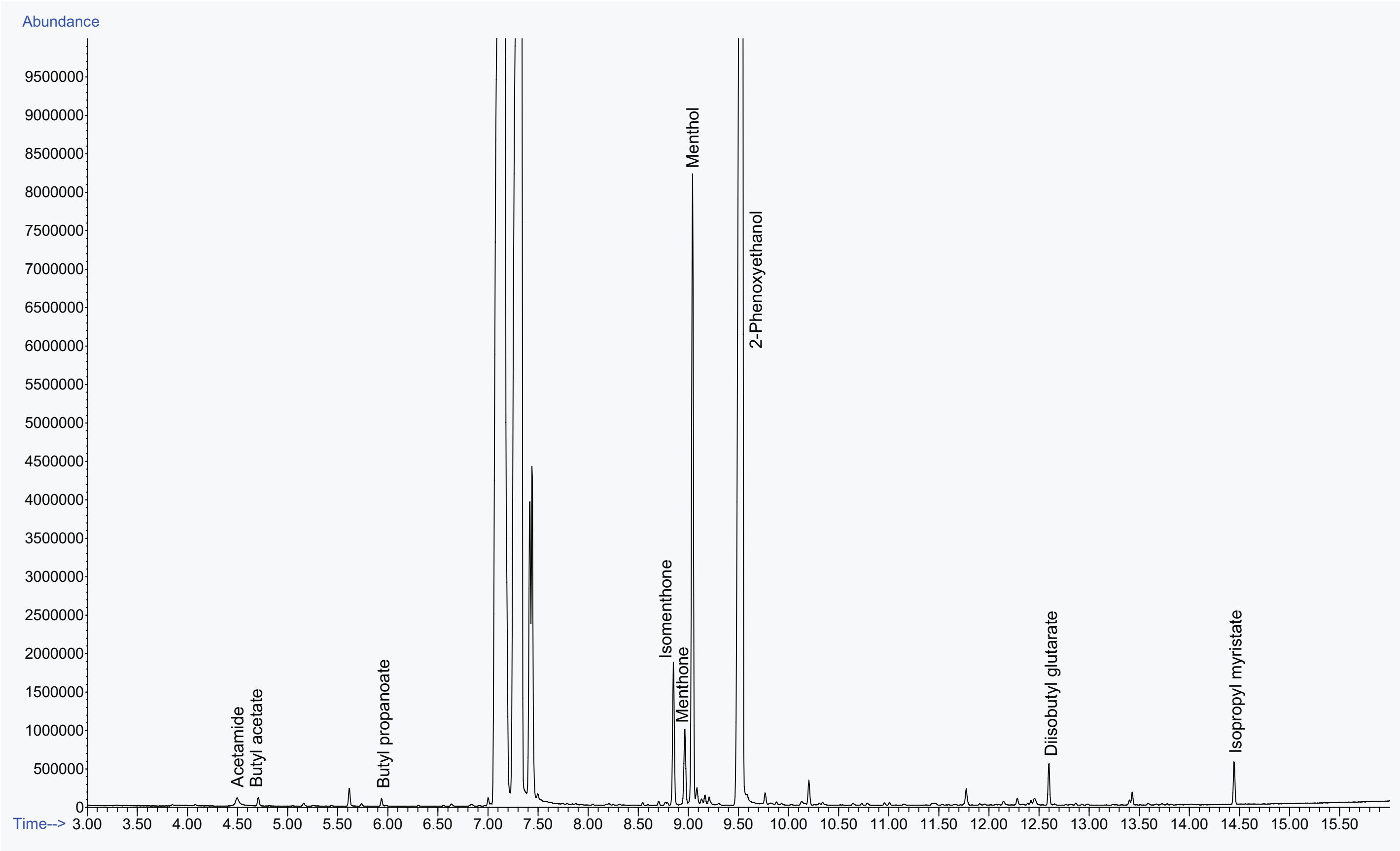

Figure 2: Total ion chromatogram for first fraction pyrolysis of breath mint scented nail polish.

The main fragrance components that compromise the mint scent are isomenthone, menthone, and menthol.

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Figure 3 shows the total ion chromatogram (TIC) for the first fraction of pyrolysis for a chocolate-scented nail polish. The 2-phenoxyethanol and dipropylene peaks are seen. A large triacetin peak is seen. Triacetin has many uses in cosmetics, including as a biocide, plasticizer, or solvent. Plasticizers diisobutyl succinate and diisobutyl glutarate are seen in the chromatogram.

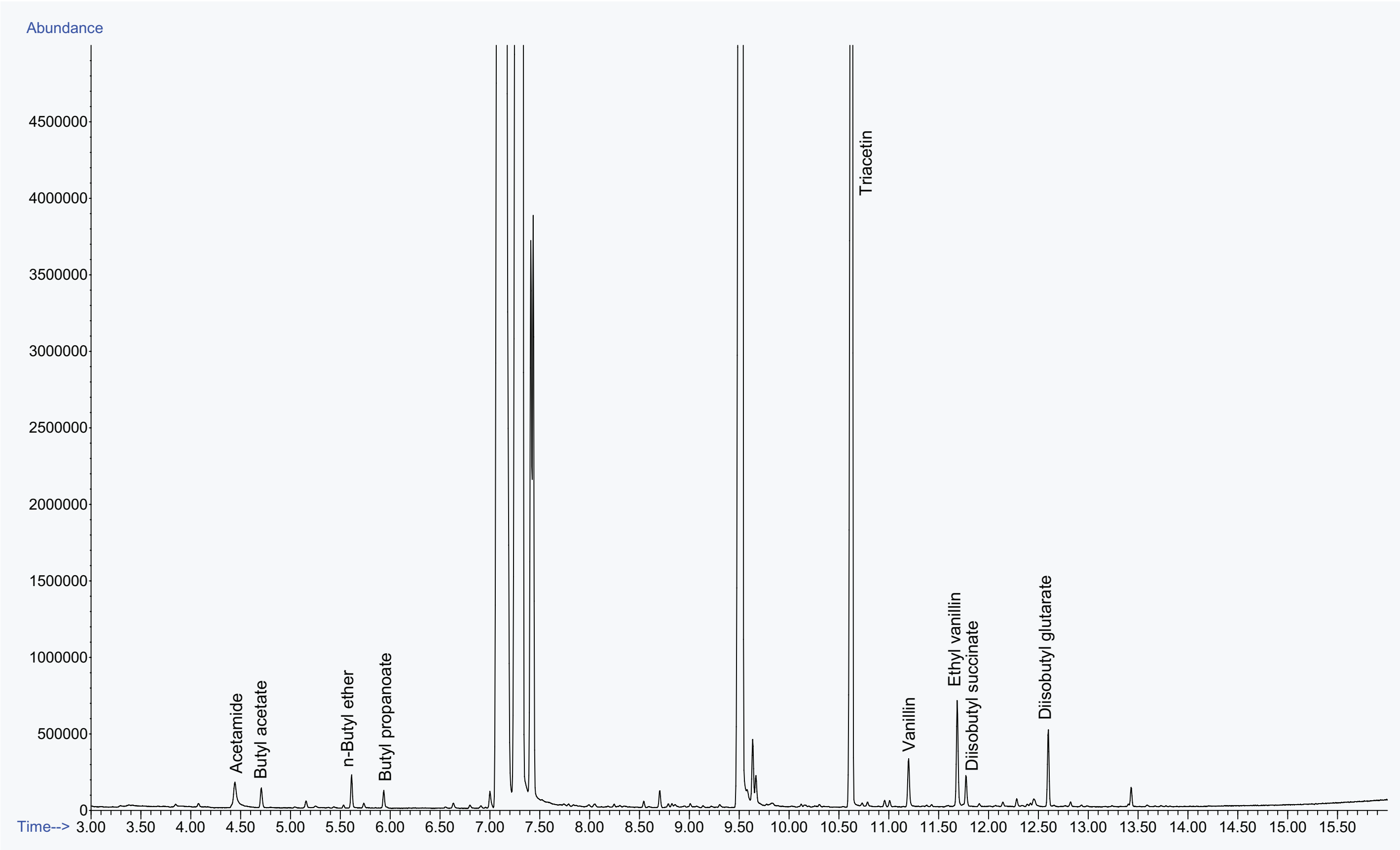

Figure 3: Total ion chromatogram for first fraction pyrolysis of chocolate scented nail polish.

The main fragrance components which compromise the chocolate scent are ethyl vanillin and vanillin.

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Figure 4 shows the total ion chromatogram (TIC) for the first fraction of pyrolysis for a fruit-flavored candy-scented nail polish. The 2-phenoxyethanol and dipropylene peaks are seen. Plasticizers diisobutyl succinate, diisobutyl adipate, and diisobutyl glutarate are seen in the chromatogram.

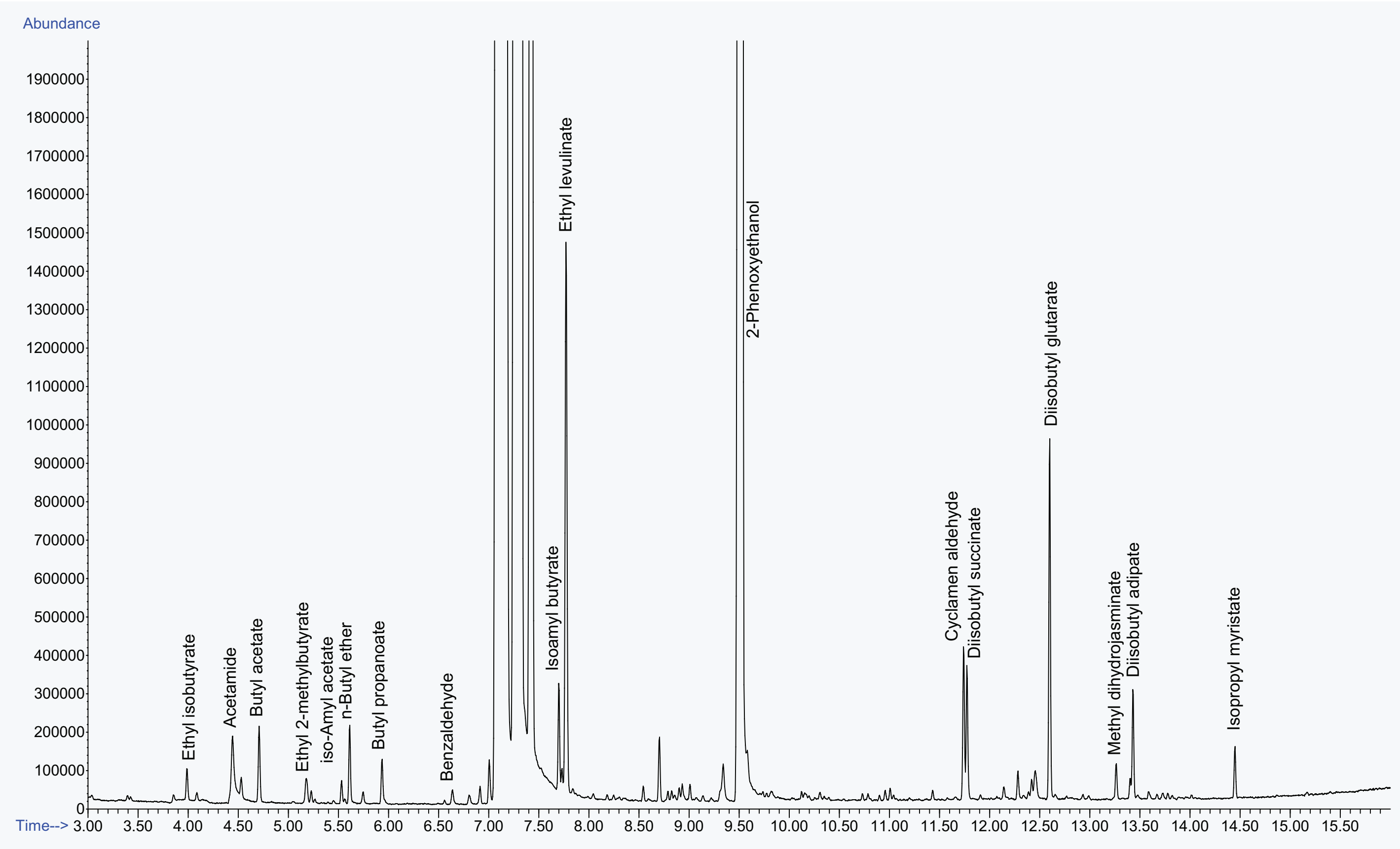

Figure 4: Total ion chromatogram for first fraction pyrolysis of fruit flavored candy scented nail polish.

Several fragrance components give a fruity scent. These include ethyl isobutyrate, ethyl methyl butyrate, iso-amyl acetate, butyl propanoate, and iso-amyl butyrate. A large peak for ethyl levulinate is seen; it is also part of the fruity scent. Floral notes added to the mix come from cyclamen aldehyde and methyl dihyrojasminate.

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Figure 5 shows the total ion chromatogram (TIC) for the second fraction pyrolysis for the breath mint-scented nail polish. The second fractions for the other scented nail polishes showed similar pyrograms. Smart Ramped Pyrolysis was used for the second fraction of the scented nail polishes. Smart Ramped Pyrolysis combines a slow heating rate with a quick transport rate to apply a broad temperature range to a sample without overheating its components. This results in an optimized pyrogram for a sample without having to determine the correct pulsed pyrolysis temperature. This is especially important for unknown samples or where the sample size is limited.

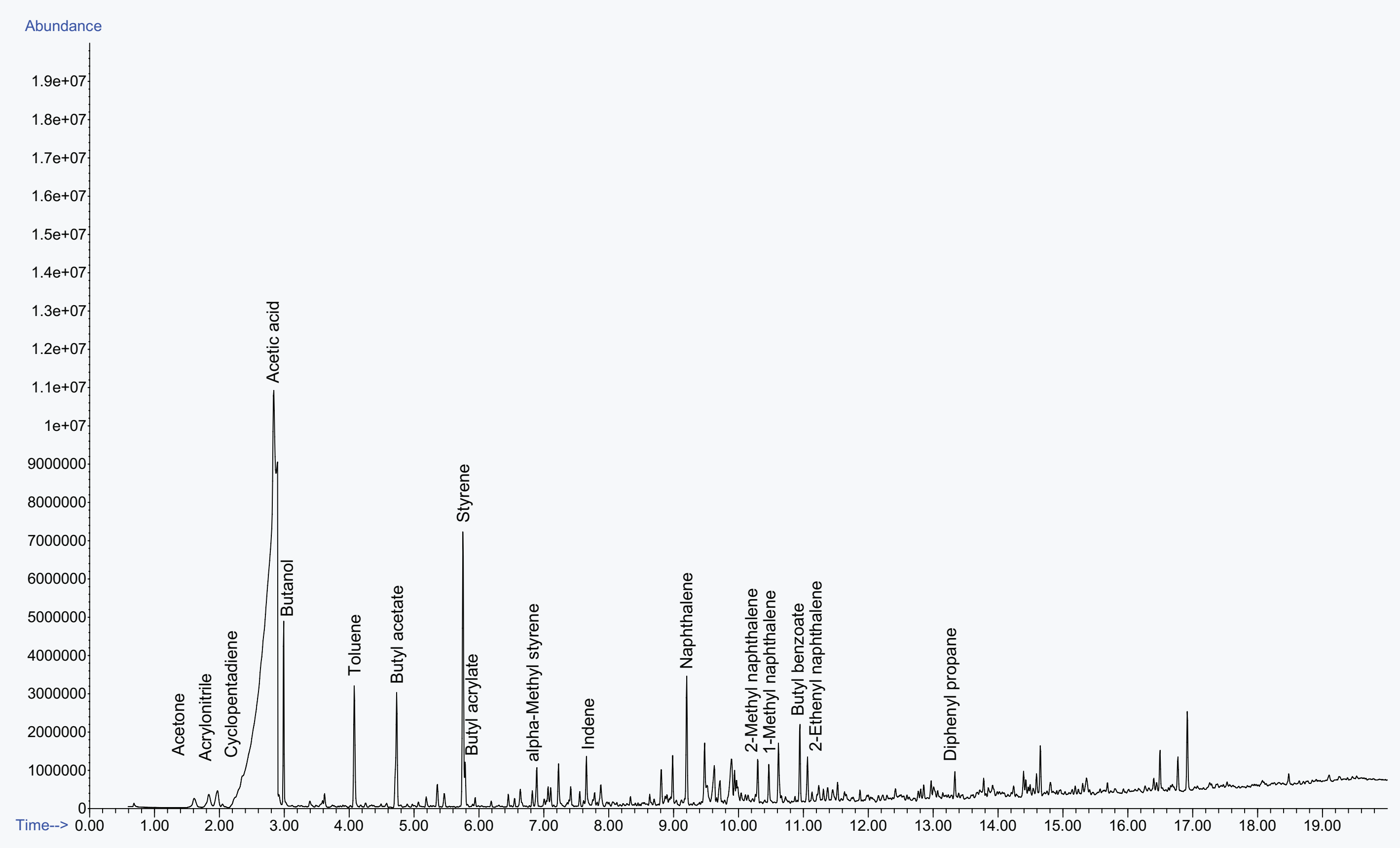

Figure 5: Total ion chromatogram for second fraction pyrolysis of breath mint scented nail polish.

The marker peaks in the chromatogram, acrylonitrile, acetic acid, styrene, alpha-methyl styrene, and butyl acrylate, identify the nail polish as an acrylonitrile-styrene-acrylate-based polymer. The large acetic acid peak is likely the result of the breakdown of acrylic acid. Acrylic-based nail polishes are fairly common and represent billions of dollars in sales.

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Conclusion

Fractioned (multi-shot) pyrolysis is an excellent technique for simplifying a pyrogram. The first fraction can remove unwanted compounds that may interfere with identifying low molecular weight pyrolysis compounds. The first fraction can also be used to thermally extract adsorbed compounds from the sample or additives to the sample, such as fragrance compounds, solvents, plasticizers, UV additives, and a host of other compounds added to polymers.

This study used fractionated pyrolysis to identify fragrance compounds in scented fingernail polishes. The second fraction was used to determine the type of polymer.

Smart Ramped Pyrolysis was used in the second step to produce an optimized pyrogram without needing method development.

The GERSTEL Pyrolysis 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.