Comparing Additives and Other Extractables From Primary and After-Market Cell Phone Cases by High Resolution Gas Chromatography Time-of-Flight Mass Spectrometry

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Introduction

As the market for cell phone cases explodes with new forms and synthetic materials, the properties of quality and durability are paramount. At a chemical level, even small changes in the additives profile and polymer type create large differences in cost and physical properties. GC-HR-TOFMS analysis allows for non-targeted analysis of cell phone case extractables, revealing chemical profiles that can assist in assessing durability and quality of the plastics used, as well as identifying particular brand formulations.

A1 Used After-Market Consumer Favorite Hard | A2 Used After-Market Consumer Favorite Hard | A3 New After-Market Brand-Endorsed Hard | A4 New Primary Market Brand-Endorsed Hard (Medium) | A5 Used After-Market Brand-Endorsed Hard | A6 New After-Market Cheap Off-Brand Hard

B1 Used After-Market Consumer Favorite Soft | B2 Used After-Market Consumer Favorite Soft | B3 New Primary Market Cheap Off-Brand Soft | B4 New Primary Market Brand-Endorsed Soft | B5 New Primary Market Cheap Off-Brand Soft

Methods

New and used cell phone cases were cut into small pieces (2 to 4 sq. mm), placed into glass vials, and sonicated in dichloromethane for 1 hour. High resolution GC-TOFMS data (Pegasus® GC-HRT) were acquired and searched against commercial MS libraries. Analytes which were not present in or received low similarity scores against commercial libraries were verified using high resolution electron ionization TOFMS data. The general classifications of hard or soft plastic were confirmed by the presence of specific types of plasticizers and siloxanes.

GC-HR-TOFMS (Pegasus GC-HRT) Conditions	
Injection	1 microliter, Splitless, Inlet 280°C, He carrier gas
Column	Rxi-5MS, 30 m x 0.25 mm x 0.25 µm (Restek, Bellafonte, PA)
Temperatures	1.50 min at 40°C, ramp 20°C/min to 310°C and hold 30 min
MS	Collected 50-1000 m/z at source temp 280°C

Used Cell Phone Cases

Compounds found on used cell phone cases were fairly predictable. Many were from residues of skin care products like lotion, sunscreen, or even insect repellant. It was also interesting to note that most of the components were recovered from the soft parts of the cell phone cases, which must have absorbed more contaminants.

Component	Common Use	Case (s)
Dodecanoic acid	Soap/Detergent component	A5, B1, B2
Octocrylene	Sunscreen component	A5, B1, B2
Homosalate	Fingerprint oil	B1, B2
Isopropyl palmitate	Moisturizer, Thickening agent, Anti-static agent	B1, B2
Benzoic acid, tetradecyl ester	Soap/Detergent component	B1, B2
Squalene	Fingerprint oil	B1, B2
Myristyl myristate	Moisturizer, Thickening agent, Anti-static agent	B1, B2
Diethyltoluamide	Insecticide	B2
Caffeine	Component of coffee—a favorite beverage	B1, B2

Fragrance Components

Many of the plastics also contained fragrance ingredients, regardless of whether they were cheap or expensive. Soft shell cases tended to contain more fragrances, although nearly every type of cell phone case contained traces of D-Limonene, a citrus-scented cleaning solvent that removes oil from machines. Another common fragrance component found was o-Cymene, which is often used as a solvent in rubber production, in addition to being a component of the fragrant olibanum (commonly known as frankincense).

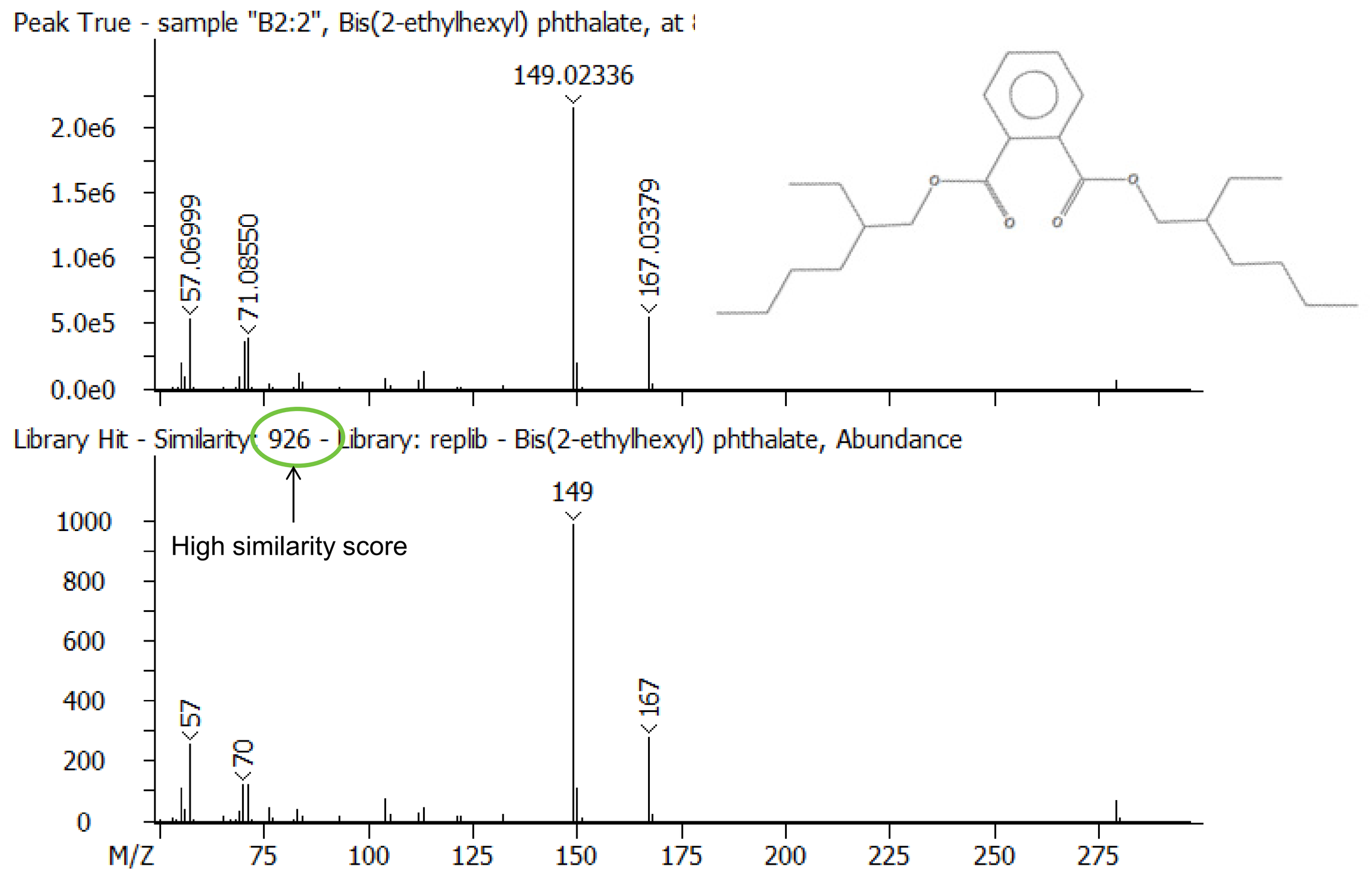
Component	Common Use	Case(s)
o-Cymene	Solvent in rubber production; Component of olibanum (frankincense essential oil)	A1, A2, A3, A4, B2, B3, B4
D-Limonene	Solvent for removing oil from machines; Citrus fragrance	A1, A2, A4, B1, B2, B3, B4
à-Phellandrene	Essential oils and plant extracts (Eucalyptus)	A3, A4, B1, B2, B3, B4
Bicyclo[3.1.0]hex-2-ene, 2-methyl-5-(1-methylethyl)-	Monoterpene in a variety of plant essential oils	A3, B1, B2, B3, B4
3-Carene	Monoterpene constituent of turpentine	A4, B2, B3, B4
Estragole	Component of basil oil and tarragon	B2, B3, B4
Cyclopentanone	Fragrance agent	A4, A5, B4
Octanal, 2-(phenylmethylene)-	Fragrance ingredient (primarily for masking)	B1, B2
Benzyl Benzoate	Dye carrier, Plasticizer, Fixative in perfumes	B1, B2

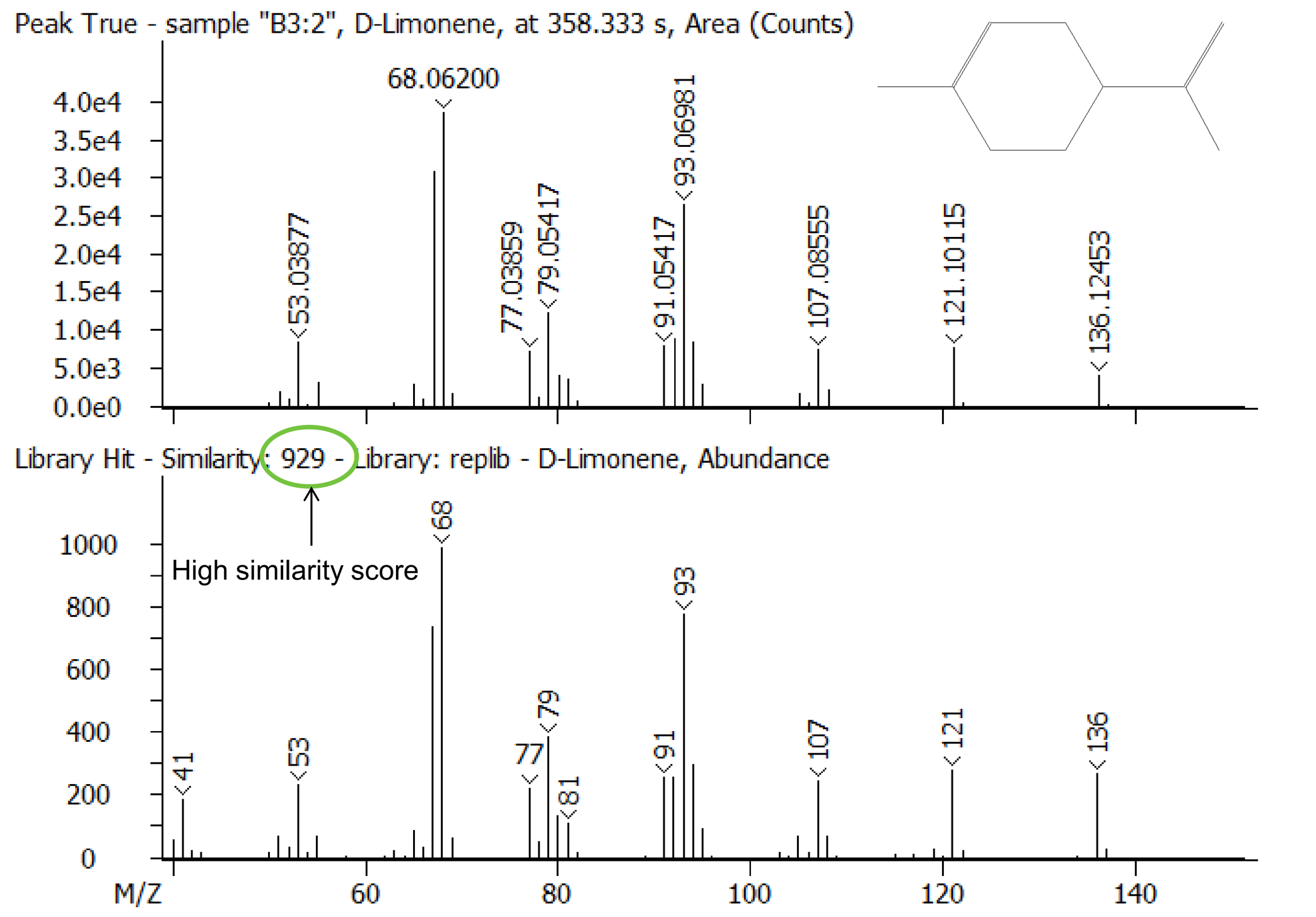
Plasticizers and other Additives

Plasticizer	Common Use	Case(s)
Triphenyl phosphate	Plasticizer, Flame retardant	A4, B1, B2, B5
Phthalic acid, cyclobutyl heptyl ester	Plasticizer	A1, A4
Isophorone diisocyanate	Plasticizer used for resistance to abrasion and degradation	B4
Diethyl Phthalate	Plasticizer	B1, B2
Tributyl acetylcitrate	Biodegradable plasticizer	B1, B2
Benzyl butyl phthalate	Plasticizer (BBP)	B1, B2
Hexanedioic acid, bis(2-ethylhexyl) ester	Plasticizer for flexible vinyl	B1, B2
1,2-Ethanediol, dibenzoate	Flexible plasticizer (Benzoflex)	B1, B2
Benzene, 2,4-diisocyanato-1-methyl-	Linking agent for carbamate/urethane (TDI)	B4
Diisooctyl phthalate	Common plasticizer (DIOP)	A4
Caprolactam	Polyurethane cross-linking agent	B2
Bis(2-ethylhexyl) phthalate	Common plasticizer (DOP, DEHP)	A5, B1, B2

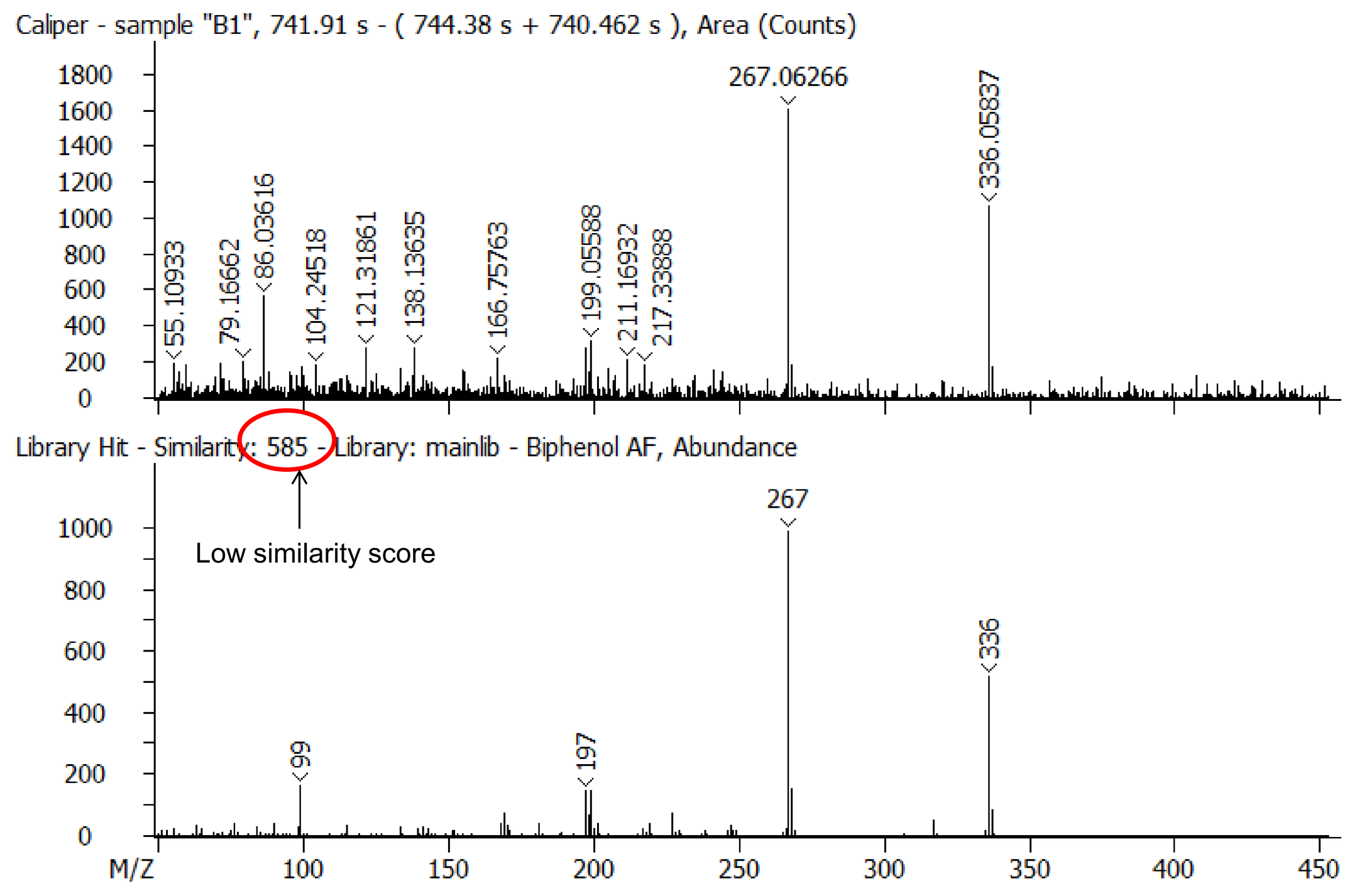
Additive	Common Use	Case(s)
Phenol	Slimicides (disinfectant/anti-septic)	A3, A5
Ethane, 1,2-dichloro-	Hardener additive,	A1
Phthalic anhydride	Scorch inhibitor and flame retardant	A5
Ethanol, 1-(2-butoxyethoxy)-	Softener for cellulose acetate plastics and styrene/acrylate binders	B1, B2, B4, B5
Anethole	Anti-microbial against bacteria, yeast, and fungi	B2, B3, B4
Benzophenone	Photo-initiator in UV-curing applications; Boosts UV resistance	B1, B2
Metilox	Antioxidant; Deodorizer	A4, B5
Phenol, 4-(1,1-dimethylpropyl)-	Stabilizer; Antioxidant (Pentaphen)	A3, A4
Hexane, 1,6-diisocyanato-	UV and abrasion resistance (HDI)	B4
Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate	Non-discoloring stabilizerr for organic substrates; prevents thermo-oxidative degradation (Irganox 1076)	A3, B1, B2, B3, B4
2-Propenoic acid, 2-methyl-, 1-methylethyl ester	Used for heat-activated, water-resistant film	B4

High Similarity Scores with Commercial Libraries



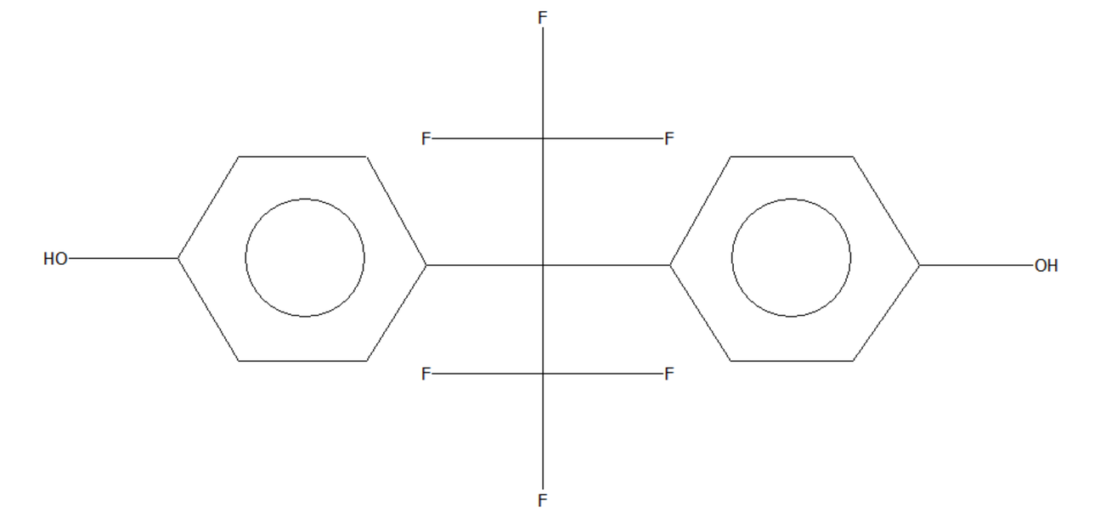


Confident Identification Using Accurate Mass



Formula	Exact Mass	Observed Mass	Mass Accuracy	Type
$C_{15}H_{10}F_6O_2$	336.05849	336.05837	-0.357 ppm	Molecular Ion
$C_{14}H_{10}F_3O_2$	267.06251	267.06266	0.562 ppm	Fragment (-CF_3)

Mass accuracies less than 1 ppm allow for confident identification of this component as Biphenol AF.

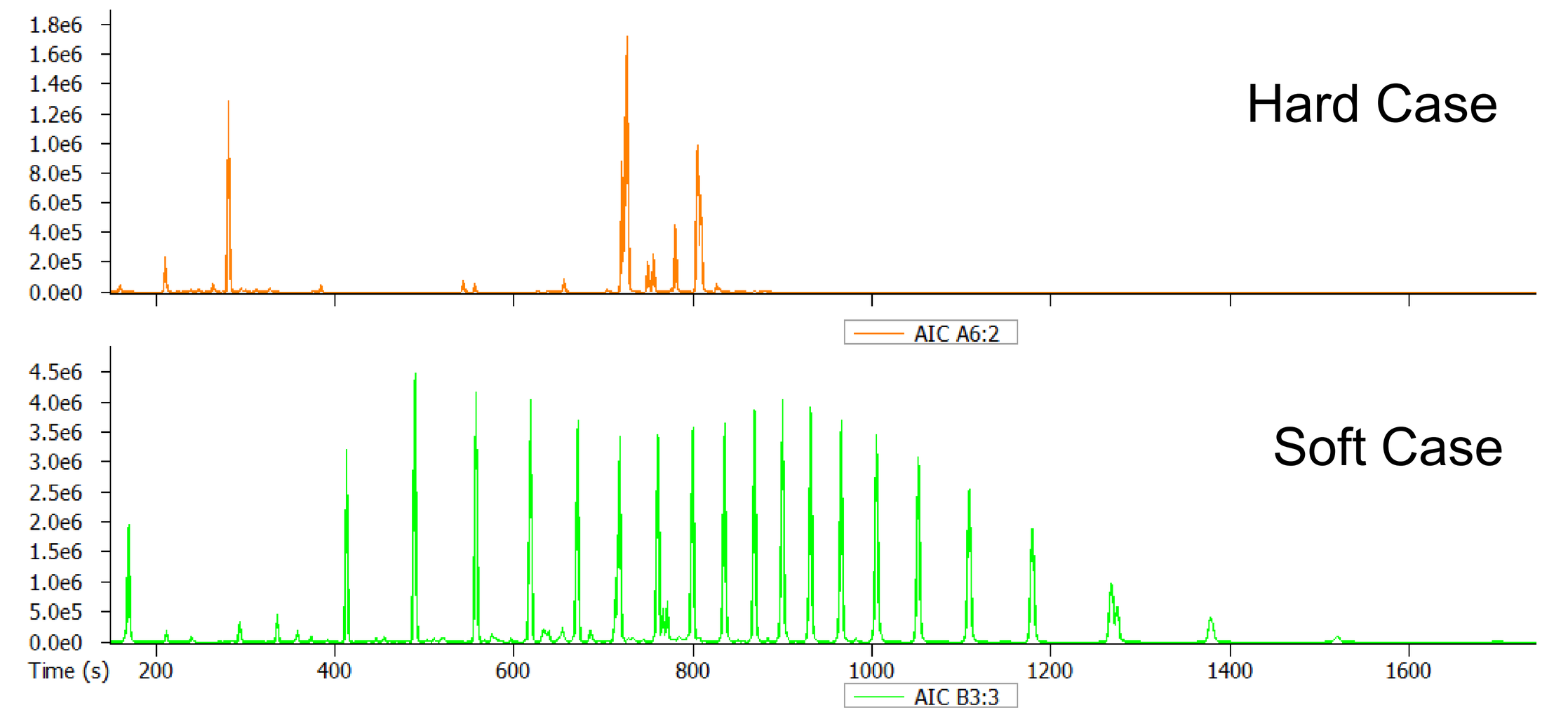


Primary and After-Market Cell Phone Cases

There were no significant differences in the components found in primary and after-market cell phone cases. Depending on the case manufacturer, there were different additives with interesting properties, such as abrasion or UV degradation resistance. Some even contained traces of antifungal or antibacterial compounds, like anethole. Of all the cell phone cases tested, the newest primary-market, brand-endorsed, soft cell phone case (B4) had the greatest number of expensive plasticizers and additives to improve durability.

So what makes a difference?

The most apparent differences were found, unsurprisingly, between hard and soft cases. Hard cases had more hardening additives and fewer extractables, while soft cases tended to have more plasticizers and surface treatments. The chromatograms below illustrate the stark difference in number of extractable analytes.



Conclusions

High resolution GC-TOFMS on the Pegasus GC-HRT allowed for quick and easy non-targeted screening of extractables from a common consumer product: the ubiquitous cell phone case. Most components could be identified with high similarity scores against commercial libraries. However, even when faced with low similarity scores against commercial libraries, such as in the case of Biphenol AF, the ability to rely on high mass accuracy allowed for confident identification of components.

Special thanks to Joe Binkley and Lorne Fell for donating their used cell phone cases for this study.

Image credits:
1. http://www.otterbox.com/apple-iphone-4s-cases/apple-iphone-4s-cases,default,sc.html
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