Introduction

Running shoe technology has come a long way since Bill Bowerman, a running coach at the University of Oregon, first made prototypes by melting rubber into treads with a waffle iron in the 1960s, starting what would become Nike. As material technology improved, along with capabilities in analyzing running kinematics and physiology, shoe designs have gotten more complex, with complicated viscoelastic cushioning, designs to correct pronation, and lightweight materials to allow greater turnover speed. A book published in 2009, *Born to Run*, started a short but passionate trend backwards towards less cushioning and more minimalistic shoes. Since then, runners have cycled back towards more cushioned designs.

In preparation for the Boston Marathon on Monday, we decided to evaluate a few pairs of running shoes, comparing and contrasting their viscoelastic properties and chemical properties. Running shoes are typically made from various types of polymers, and may provide a great deal of cushioning or very little at all! Cross-sections of the shoes we evaluated are shown in Figure 1. It is apparent that some have been used to run many miles, while others are more gently used.

Figure 1: Clockwise from upper left: Vibram, Nike, Asics, Mizuno.

Dynamic Mechanical Analysis (DMA)

CPG used dynamic mechanical analysis (DMA) to measure the ability of the materials that make up the sole of the shoe to absorb and return mechanical energy. Samples were punched from the outer soles and inner soles (where applicable) and tested using a TA Instruments RSA-G2 Solids Analyzer for characterization of storage modulus, loss modulus, and tan delta at frequencies between 0.1 Hz to 30 Hz. Storage modulus measurements are representative of the elastic portion of the stored energy, while the loss modulus measurements are representative of the viscous (or fluid like) response of the material. Tan delta values may be interpreted as a "damping ratio," characterizing the ability to which a material may absorb and dissipate energy. Figure 2 shows a comparison of the storage modulus, loss modulus, and tan delta for all shoe samples tested at a test frequency of 1Hz. Figure 3 shows frequency sweep measurements of storage and loss modulus across a range of oscillation frequencies. Most of the moduli show a gradual increase in modulus with frequency, which is typical of polymers; they become more rigid with faster impact rates.

Significant differences in storage modulus were observed among the tested samples. Generally, storage modulus values for shoe soles was significantly greater than the corresponding shoe's insole, a measure of the increased stiffness of the sole and softer, more compliant nature of the insole. Significantly higher storage modulus values were observed for the "lightly used" Mizuno sole than for the "heavily used" Mizuno sole, suggesting that the mechanical properties (and underlying materials) have degraded with prolonged use and environmental exposure, likely due to permanent compression of the porous structure in the sole.

Tan delta values (representing damping) were higher for the insole as compared to the corresponding sole, providing a measure of the ability of these components to dissipate energy during running, ensuring a more comfortable running experience—an important factor over 26.2 miles!

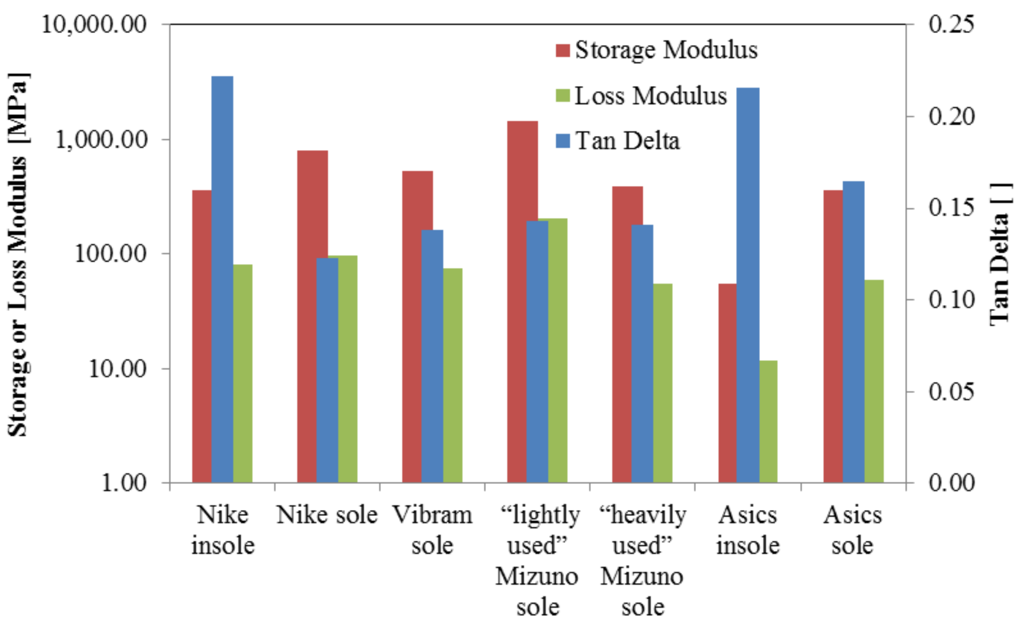

Figure 2: Summary of Storage and Loss Modulus, as well as Tan Delta, at 1 Hz for all shoe samples tested.

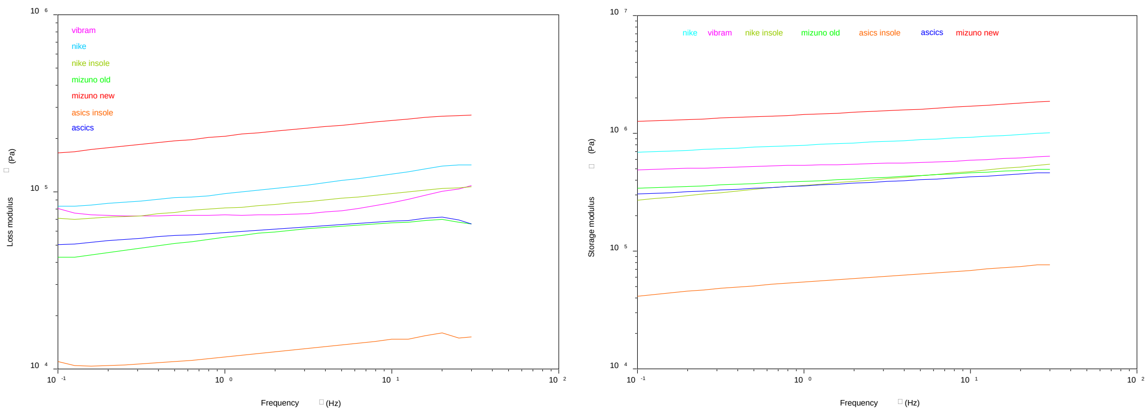

Figure 3: Loss Modulus (left) and Storage Modulus (right) overlay of shoe samples during frequency sweep from 0.1 Hz to 30 Hz.

Headspace Gas Chromatography-Mass Spectrometry (HS-GC-MS)

In order to perform a chemical comparison between the shoe samples, they were analyzed by headspace gas chromatography coupled to mass spectrometry (HS-GC-MS). Samples from shoe soles were sectioned with a clean razor blade, transferred into a headspace vial, heated at 160 °C for 60 minutes. After this period of time, the off-gassed products were transferred onto a gas chromatography column for separation on the basis of boiling point as well as affinity for the column's stationary phase. Compounds were detected by a mass spectrometer which measured a characteristic electron impact mass spectrum which was used to "fingerprint" the compound and screen it against a NIST mass spectral library.

The following shoe soles were evaluated:

1. Nike sole
2. Vibram sole
3. "Lightly used" Mizuno sole
4. Asics sole

Each sample yielded a rich amount of data, far more than can be comprehensively described here. Measured chemical may come from the constituent materials composing each sole, from environmental interferences[1] (all shoes were sampled from a mildly worn state), as well as from thermal degradation during the headspace heating and off gassing process.

Total ion chromatograms for each sole are shown in Figure 4 through Figure 7.

Some compounds identified in the Nike sole include n-butanol, α-methylstyrene, acetophenone, and butylated hydroxytoluene (BHT). These compounds suggest the sole is composed of a synthetic rubber rather than a natural rubber, due to the presence of styrene derivatives and possible degradation products. The BHT is likely added as an antioxidant to prevent material degradation during processing and usage. The n-butanol is likely used as a processing solvent during the rubber production.

[1] A polite way of saying 'foot odor'

Some compounds identified in the Vibram sole include benzaldehyde, benzothiazole, decamethylcyclopentasiloxane, and BHT, suggesting the material contains significant silicone rubber elements. The benzothiazole is related to accelerators used for the crosslinking (vulcanization) of rubbers.

Some compounds identified in the lightly used Mizuno sole include toluene, phenol, benzothiazole, acetophenone, and BHT. The toluene may be a residual solvent from rubber processing.

Some compounds identified in the Asics sole include ethylhexanol, 1,2,3-trimethylbenzene, 2-pentyl-furan, acetophenone, 1-dodecene, 2,6-di-tert-butylbenzoquinone, and BHT. BHT is a widely used antioxidant and it is therefore not surprising to see its presence in each of the samples tested here.

As can be seen, headspace GC-MS is a valuable tool for exploring the chemical nature of polymeric samples, processing history, residual products, degradation products, and characterization of off-gassed species.

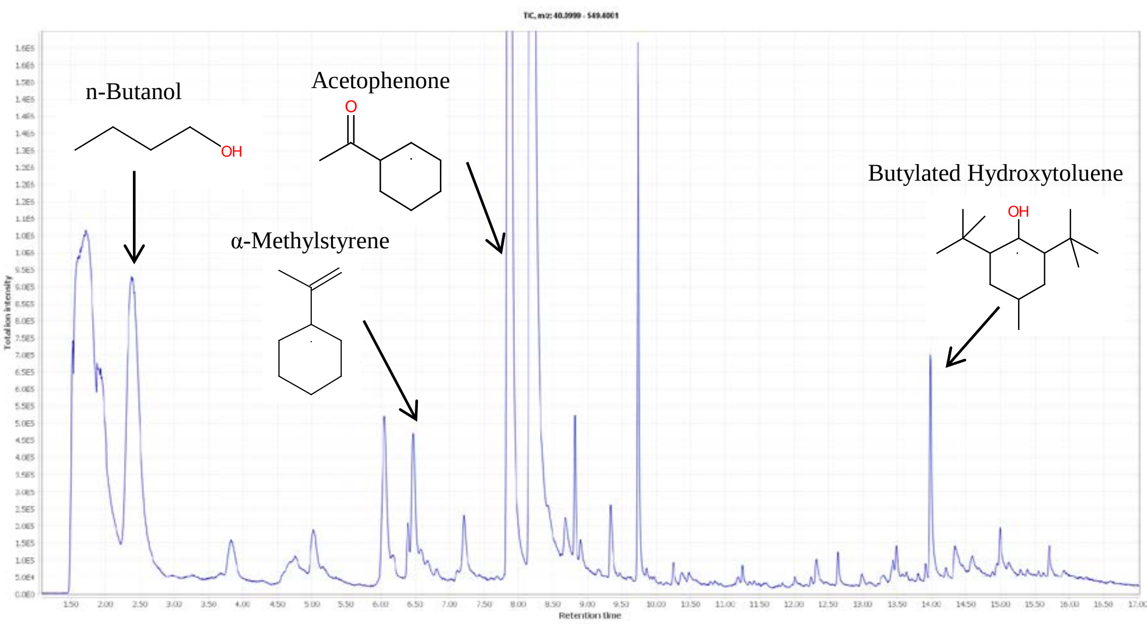

Figure 4: Total ion chromatogram for the Nike sole. A subset of the identified compounds is indicated with their chemical structures.

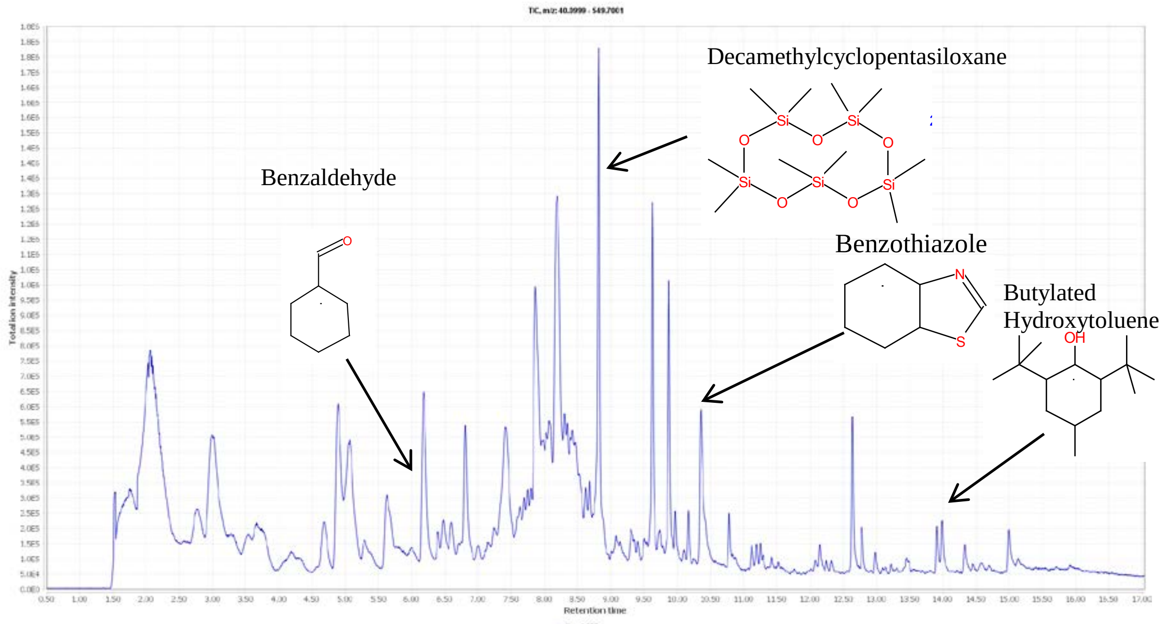

Figure 5: Total ion chromatogram for the Vibram sole. A subset of the identified compounds is indicated with their chemical structures.

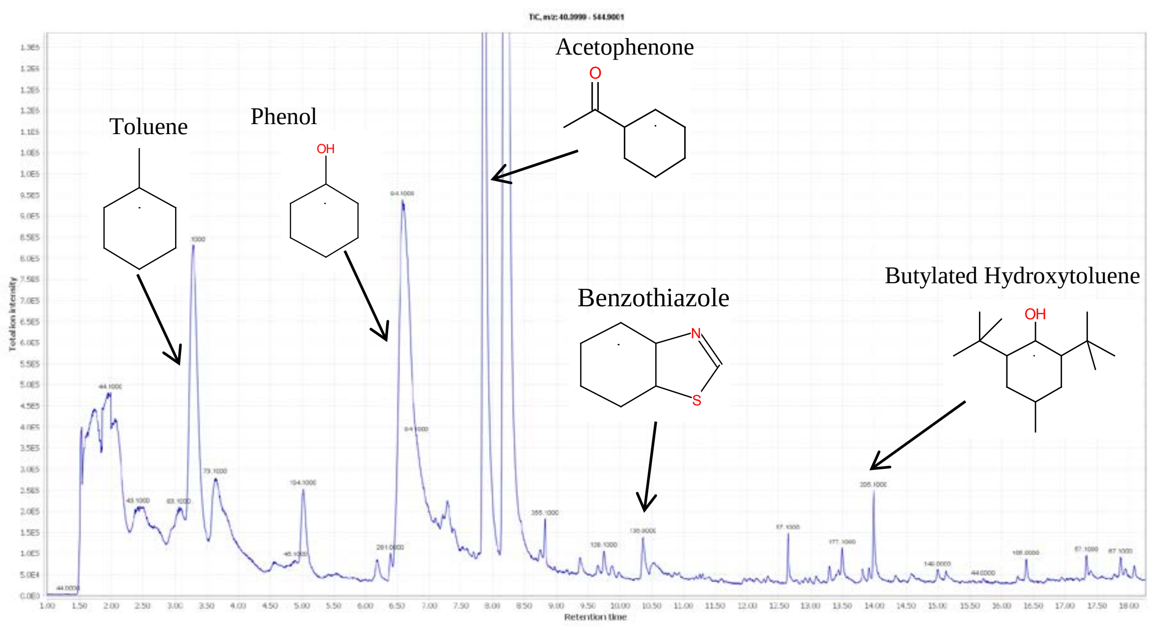

Figure 6: Total ion chromatogram for "lightly used" Mizuno Sole. A subset of the identified compounds is indicated with their chemical structures.

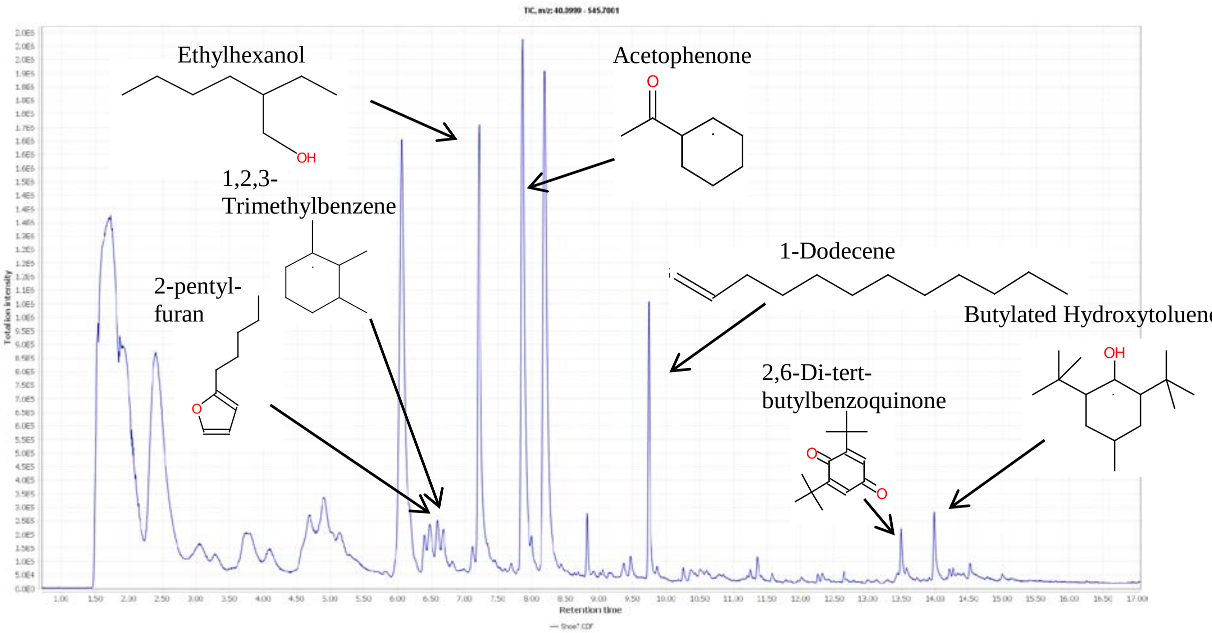

Figure 7: Total ion chromatogram for Asics sole. A subset of the identified compounds is indicated with their chemical structures.