Poster Reprint

ASMS 2021
Poster number TP347

What Are the Compounds Released from Coffee Filter Paper?

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Introduction

Coffee is the most popular beverage in the world with more than 400 billion cups consumed every year. This popularity has provided convenient, affordable, and high-quality coffee that can be brewed at home with various types of equipment. Most techniques utilize a filter to hold the ground coffee during the brewing process, which includes, drip, pour-over, and cold brewing. In general, we always think of filters as a "removal" tool to purify substance the passes through the material. Coffee filters can reduce some of the acidity and oils from the coffee, but if they are not rinsed, negative aromas can be extracted during the brewing process. This can lead to a cup of coffee with paper, plastic and other off-odor aromas. The results presented in this poster provide information on the compounds leached from coffee filter paper and the suggestion that rinsing, before brewing, is a good idea.

The data illustrate the analytical capability of stir bar sorptive extraction and thin-film SPME as the sample preparation with an accurate mass, high resolving power GC/Q-TOF with low energy EI (Figure 1). The combination of varied ionization energies provided additional information to increase the confidence in the unknown compound detection and identification of the broad range of components released from these filters.

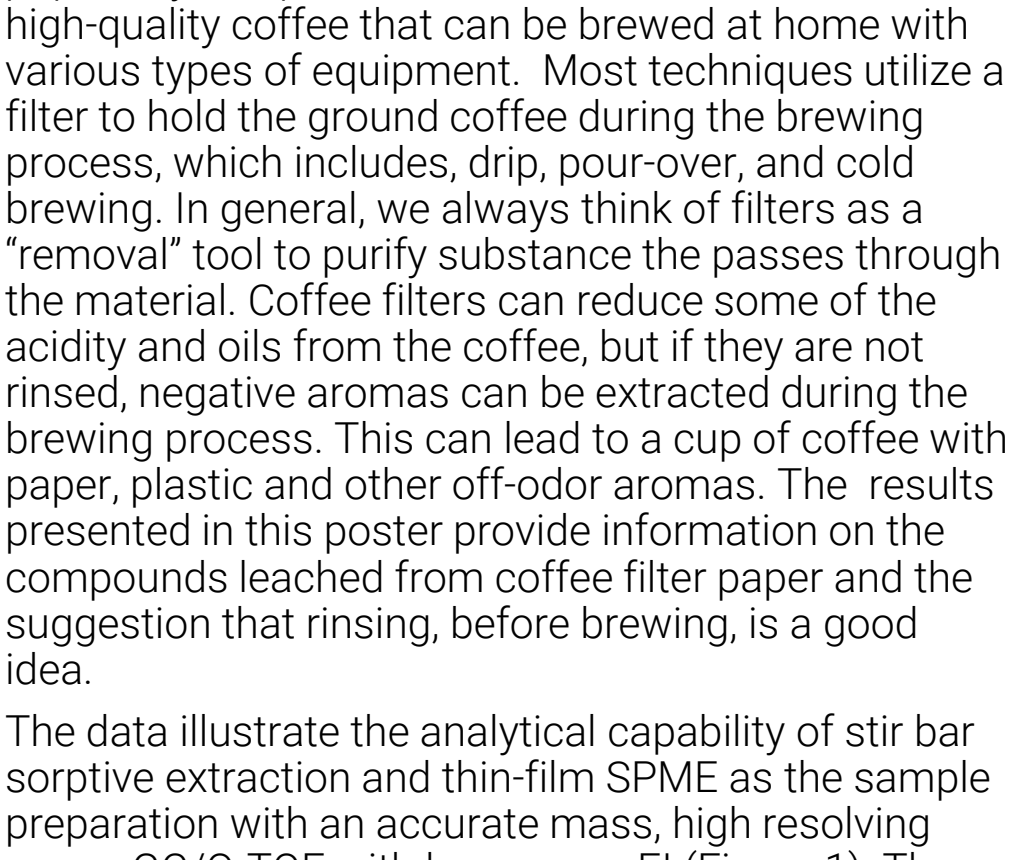

Figure 1: Agilent 7250 GC/Q-TOF with Gerstel MPS and Thermal Desorption Unit 2

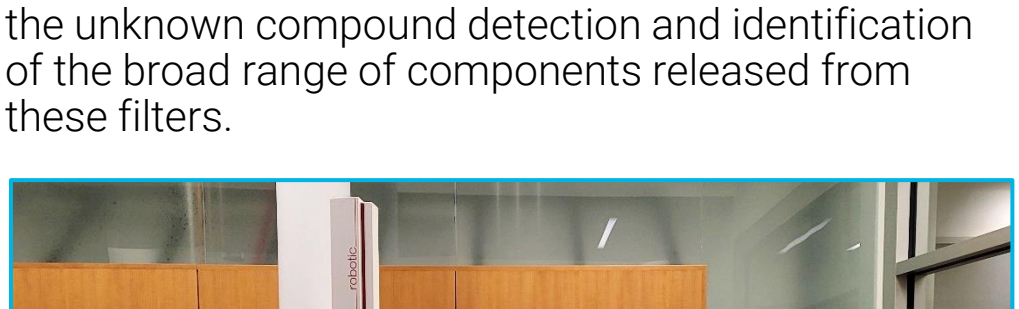

Figure 2: Three different coffee filters; two for drip and one for pour-over

Experimental

Sample Preparation:

Two solutions were used to extract the filters; LC/MS grade water and a solution of acids and oils called a model coffee. The model coffee included quinic acid, chlorogenic acid, citric acid, acetic acid, cafestol and linoleic acid. Three store bought coffee filters were selected for this analysis due to their different material, manufacturing, and different brewing techniques. 53 mg for each filter were place in a 20 mL headspace vial with 10 mL of water or model coffee heated to 94 °C, an optimal temperature from medium roast coffee. After 4 mins the filter paper was removed, and the solution was allowed to cool to room temperature before transferring the solution to a 10 mL vial. The Gerstel 10 mm, 0.5 mm film thickness PDMS Twister and the 20 mm DVB TF-SPME were both conditioned before the extraction. Both were submerged in the solution for 55 mins, with constant stirring. The stir-bar and TF-SPME were dried using a stream of dry nitrogen before placing them both in a single TDU tube with glass wool. Analytical conditions for the GC/Q-TOF platform are listed in Table 1.

Software:

The data was analyzed with MassHunter Qualitative Analysis 10.0, MassHunter Quantitative Analysis 10.0, MassHunter Unknowns Analysis, and the NIST20 library.

Table 1: Agilent 7250 GC/Q-TOF; 8890B GC Parameters

GC and MS Conditions:		
Column	DB-5ms UI, 30m, 0.25mm, 0.25µm	
Injection and liner	TF-SPME and SBSE	Glass Beads
TDU (solvent vent for 1.2 mins)	40 °C for 1.2 mins	
	650 °C min^{-1} to 250 hold for 5 mins	
Inlet (CIS-4)	-39 °C for 0.2 mins	
	12 °C min^{-1} to 280 hold for 5 mins	
Solvent Vent	20 mL min^{-1} at 0.01min	
	60 mL min^{-1} per min	
	40 mL min^{-1} at 3mins	
Inlet temperature	280 °C	
Oven program	40 °C for 2 mins	
	10 °C min^{-1} to 300 °C; hold 5 mins	
Carrier gas	Helium - 1.2. mL min^{-1} const. flow	
Transfer line temperature	290 °C	
Source temperature	200°C	
Quadrupole temperature	150°C	
Spectral range	35 to 650 m/z	
Spectral acquisition rate	8 Hz, both centroid and profile	
Electron Energy	70 and 13 eV	
Emission	3µA and 0.8µA, respectively	

Results and Discussion

Filter 1 is a 100% oxygen bleached paper filter with a slight texture to aid in water flow designed for pour over brewing. Filter 2 is a generic white, basket filter for drip coffee makers. Filter 3 is a natural brown filter with a similar texture to filter 1, designed for pour over brewing. Each filter was stored in kitchen cabinets for a few years, in the original plastic packaging. In addition to extracting the filter with water and model coffee, each filter was also rinsed with 94 °C water for 30 seconds before extracting with the model coffee solution. This was performed to mimic the rinse of the filter prior to add the ground coffee before brewing. The water temperature and extraction time were set for the optimal brewing of a medium roast coffee, which is the most popular roast.

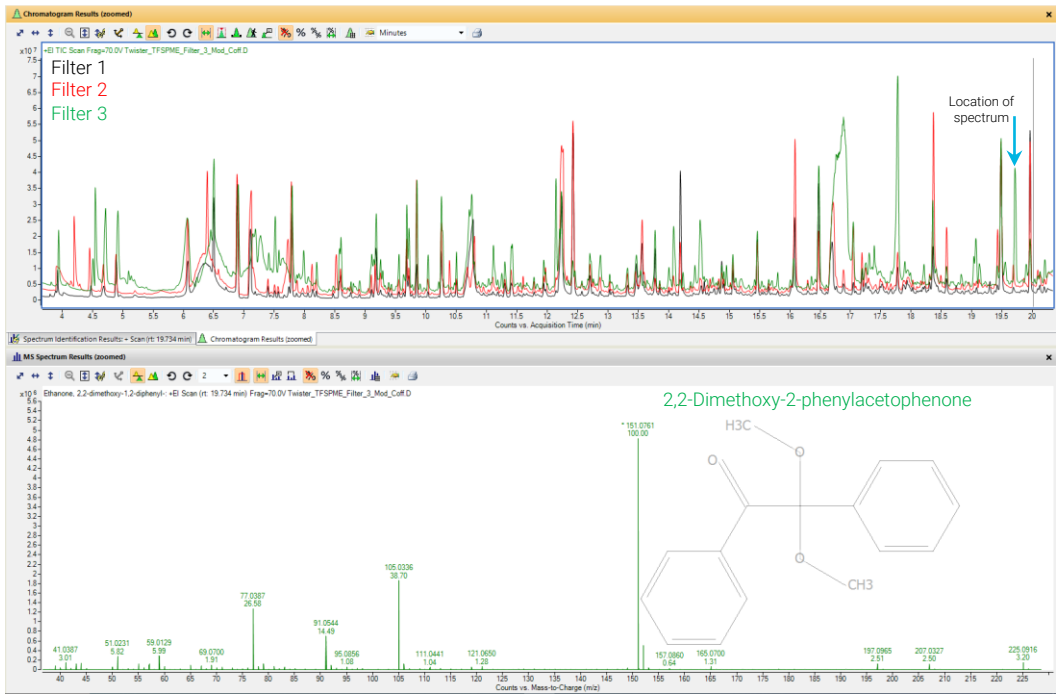

Figure 3: RTICs of the three filters with a model coffee solution. The spectrum represents a single component found at a much higher concentration in Filter 3, possibly from printing ink from the packaging.

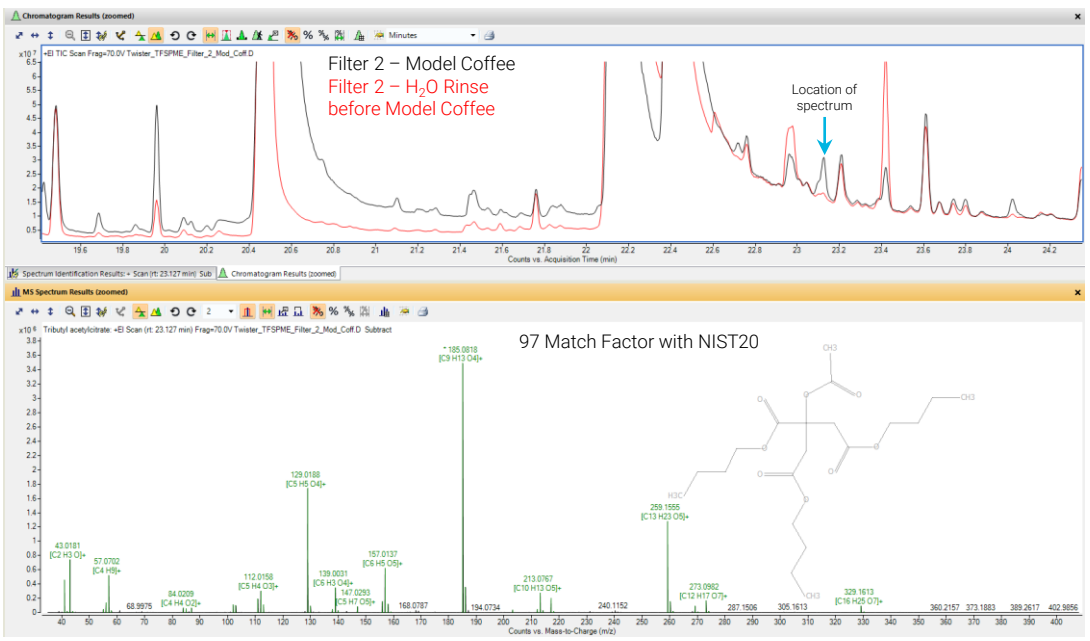

Figure 4: RTICs for filter 2 extracted with model coffee (black) and a rinse before model coffee extraction (red). The formula from the NIST entry is used for accurate mass and fragment confirmation for tributyl acetylcitrate which is used as a plasticizer for food contact surfaces.

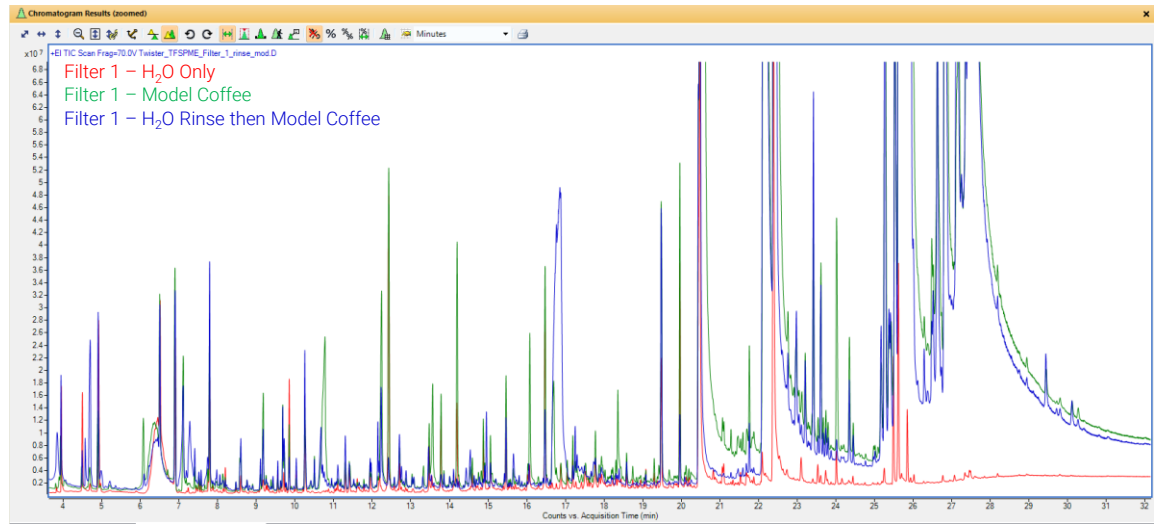

Figure 5: Overlay of the three extraction procedures for filter 1. The components after 20 mins are phthalates, long chain acids and plasticizers not removed with H_2O alone. At 16.8 mins, quinic acid is not as efficiently removed if the filter is rinsed.

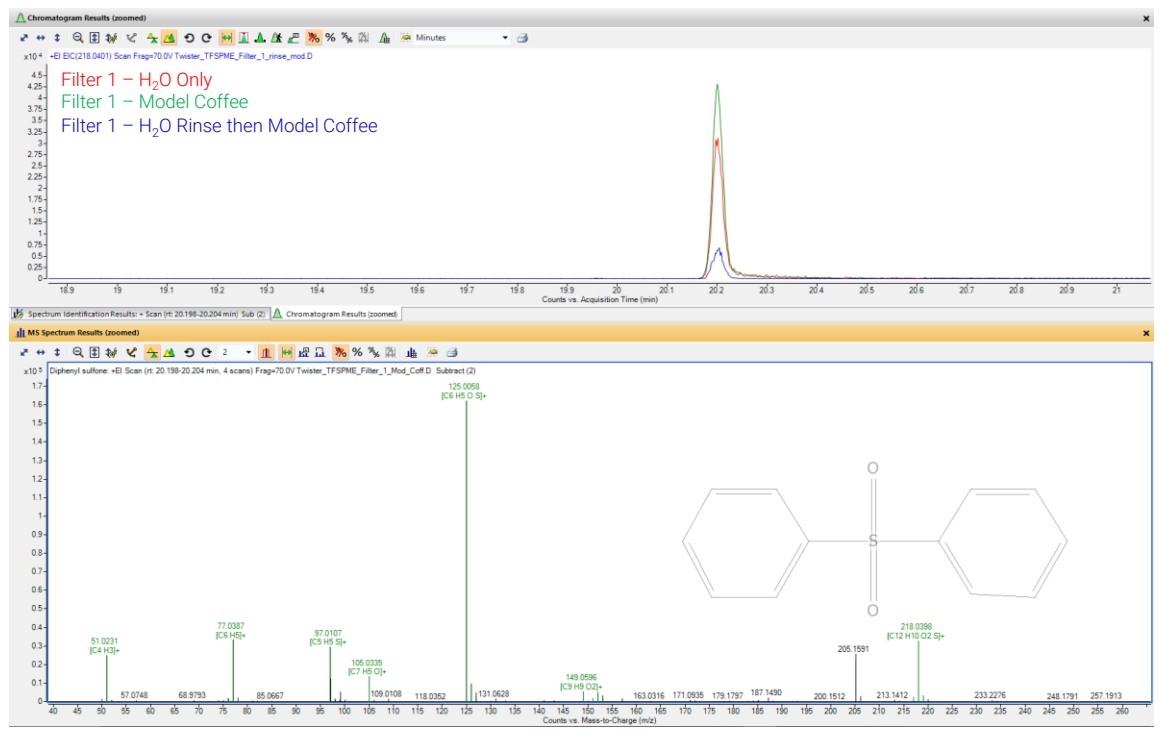

Figure 6: Reduction of diphenyl sulfone is most significant if the filter is rinsed first. This compound is being used in paper manufacturing as a replacement for bisphenol A.

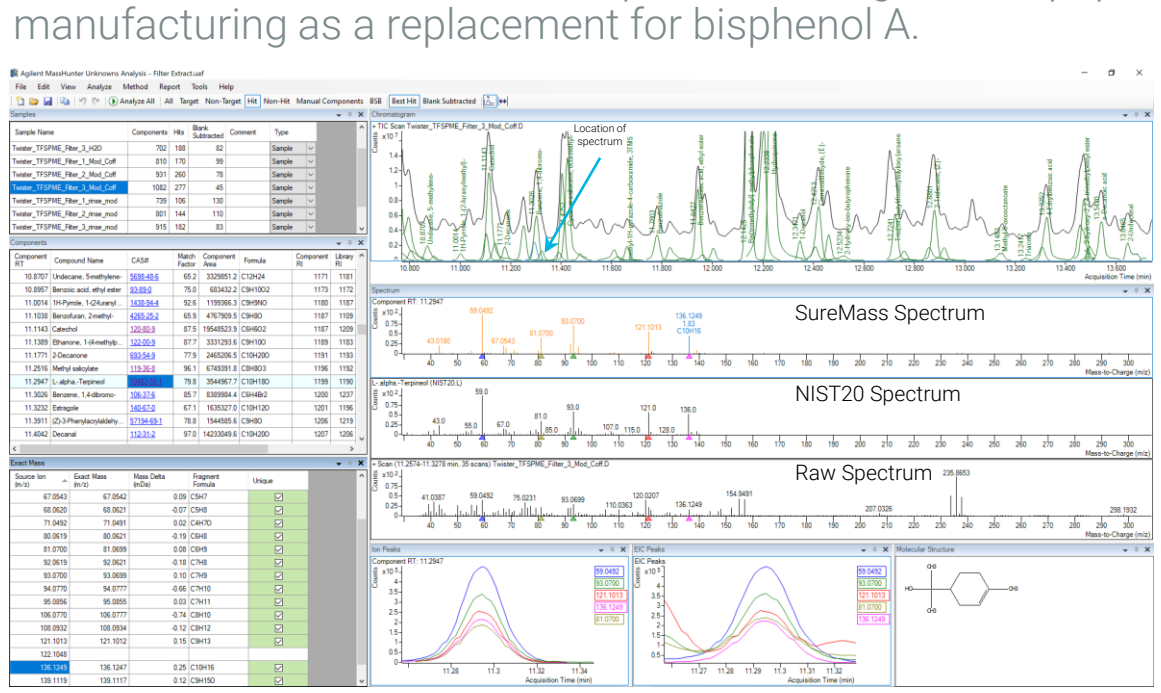

Figure 7: The filter with the most components detected was the natural/unbleached filter for all three extractions. α-Terpineol is shown with 79.8 spectral match using the SureMass feature extraction to separate this analyte from the coeluting dibromobenzene.

Results and Discussion

Table 2: SureMass found components for each filter and extraction procedure. The model coffee extracted almost 30% more components but rinsing with water first reduced total components.

Total Components	H_2O Only	Model Coffee	Rinse before Model Coffee
Filter 1	638	810	739
Filter 2	692	931	801
Filter 3	702	1082	915

Figure 9: EICs are drawn for the main fragment ion produced by phthalates. The H_2O only extract (red) has the lowest observed phthalate compounds and concentrations. Low eV provided a significant increase in the molecular ion to calculate the elemental composition.

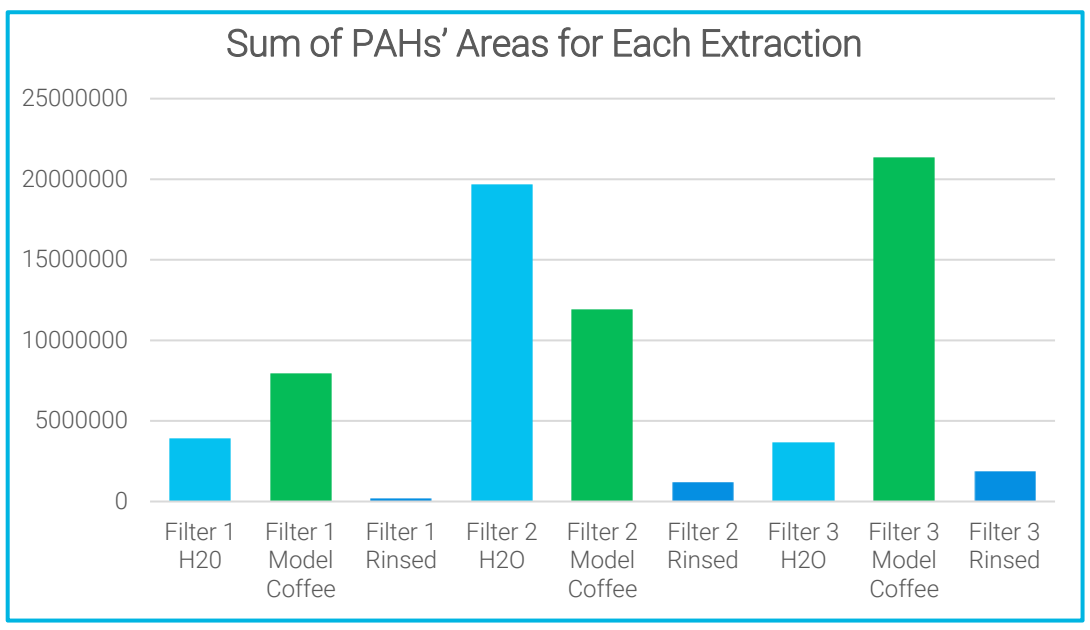

Figure 10: This graph illustrates the efficiency of the rinsing to remove PAHs before extracting. The areas for tentatively identified PAHs were summed for each filter and extraction procedure. IDs were assigned with the library match score, retention index, and accurate mass.

Both the stir bar and TF-SPME were utilized to provide a more complete coverage of polar and nonpolar components in the solution used to extract the filters. The three filters were packaged in different types of plastic bags, which are not fully resealable. Open storage allowed for environmental fragrances to adsorb to the filters efficiently. Figure 3 illustrates the differences observed from the filter material using the model coffee solution. Surprisingly, the natural/unbleached filter leached the most semivolatile compounds. Water alone might not be enough of a solvent to remove some of these components that leach from the filter, phthalates were not removed with only hot water (figure 5 & 9). Diphenyl sulfone was significantly reduced with a water rinse even though the model coffee was more efficient at extracting this compound (Figure 6). These filters are described as "real world" because they have been stored in a kitchen cabinet where coffee, spices, and other kitchen fragrances could adsorb to the filter. Vanillin, cinnamaldehyde, and Tonalid were all detected in the filters due to their proximity to vanilla extract, ground cinnamon and the kitchen being close to the laundry room. Rinsing the filter before brewing is a good first step but keeping them in a sealed container would reduce the chance of "kitchen fragrances" ending up in your freshly brewed cup of coffee. Even though the chromatograms were complex with ~800 components, high confidence in the tentative identifications was possible because the spectra represented single components using the SureMass algorithm (Figure 7).

Conclusions

High resolving power, accurate mass, and low eV provided additional information to a difficult untargeted analysis

- SureMass feature finding provided spectra that represented single compounds even when coeluting.
- Each filter had different levels of the same components with only a few being unique.
    - The more significant differences were observed from the extraction solution
- Low eV provided additional information and confirmation for fragile molecules.
- Rinsing the filter with hot water did remove some of the phthalates, fragrance, PAHs and polar compounds but also reduced the effectiveness of removing acids from the model coffee.
    - The rinsing solution might benefit from a lower pH than tap water to aid in the removal of the most compounds from the filter paper.

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DE44488.5172569444

Published in USA, October 20, 2021

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