Analysis of Coffee Packaging and Filter Leachates from Various Single-Serve Coffee Pod Suppliers Using GCxGC-TOFMS

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Introduction

Single-serving coffee brewers have become popular in recent years and can be found in millions of homes and offices. As with any food product that is stored, transported, and prepared for consumption in plastic packaging, care must be taken to ensure contaminants and package leachates are not passed on to the consumer after the coffee or other beverage has been prepared.

Commercial "pods" were evaluated by analyzing the brewed coffee after performing a liquid/liquid extraction with dichloromethane (DCM). After extraction with DCM, comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) was used to analyze the extract. The large peak capacity of GCxGC, cryofocusing effects of thermal modulation, and the detection/identification capabilities of the TOFMS leads to confident isolation and detection of extractable compounds from plastic packaging materials such as plasticizers, UV stabilizers, antioxidants, and assorted phthalates. A standard mixture of phthalates and bisphenol A were added to the brewed coffee to demonstrate detectability using this procedure.

Experimental Methodology

The data presented here were produced using the LECO Pegasus® 4D GCxGC-TOFMS, in conjunction with the ChromaTOF® software package.

The BPA standards were created by combining 10 mg of BPA granules (Sigma-Aldrich) with 10 mL of dichloromethane solvent, and diluting down to targeted concentrations. The EPA 8061A phthalate ester mix standards were purchased from Restek. Single-serving coffee pods were purchased from a local grocery store.

Brewed Coffee Analysis

Coffee was prepared with the liquid size set to 7.25 oz. (~215 mL). The spiked standards were added to one coffee sample to produce 50 ppb (v/v) per compound.

The brewed coffee was extracted with 10 mL of dichloromethane (Fisher Scientific) after cooling the coffee to room temperature. Aliquots of the dichloromethane were transferred to an autosampler vial and injected into the GC without further preparation.

The GCxGC-TOFMS analysis conditions used are detailed in Table 1.

Pegasus 4D GCxGC-TOFMS

Table 1. Experimental conditions for the GCxGC-TOFMS analysis of dichloromethane-extracted coffee samples.

Carrier Gas	Helium, Corrected Constant Flow
Injection Volume (µL)	1
Split Ratio	Splitless
Flow Rate (mL/min)	1.0
Primary Column	60 m x 0.25 mm x 0.25 µm Rxi-1ms
Secondary Column	1 m x 0.18 mm x 0.18 µm RTX-200
Primary Oven Ramp	40°C for 0.5 min then 10°C/min to 290°C with 20 min hold
Secondary Oven Ramp	+10°C offset from primary oven
Modulator Offset	15°C
Modulation Period	2 s period (0.6 s hot)
Transfer Line Temp	310°C
Ion Source Temperature	200°C
Mass Spec Optimized Voltage Offset (V)	+200
Mass Spec Acquisition Delay (s)	370
Mass Range (m/z)	40-700
Acquisition Rate (spectra/s)	100
Electron Energy for EI (V)	-70
Collection/Processing Software	ChromaTOF® 4.50

Results

Figure 1 displays a GCxGC contour plot of the dichloromethane-extracted non-spiked brewed coffee sample where 1220 peaks were detected at the 50>S/N level. The caffeine concentration was high enough to exceed the second dimension column and modulator's capacity, leading to the vertical streak.

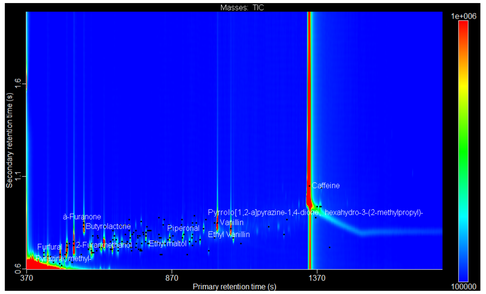

Figure 1. GCxGC-TOFMS TIC contour plot of the non-spiked brewed coffee sample.

Figure 2 displays the GCxGC contour plot of the dichloromethane-extracted phthalate and bisphenol A-spiked brewed coffee sample. The majority of analytes native to the coffee elute before the standards, although the extremely large caffeine peak's tail would likely interfere with trace phthalate detection without the second column separation. Another large peak from the coffee, ethyl vanillin, nearly coelutes with dimethyl phthalate, even with the second-dimension separation. However, the Automated Peak Detection and Deconvolution algorithms determined 163 m/z is not shared between the two compounds, and therefore dimethyl phthalate can be isolated from this interference.

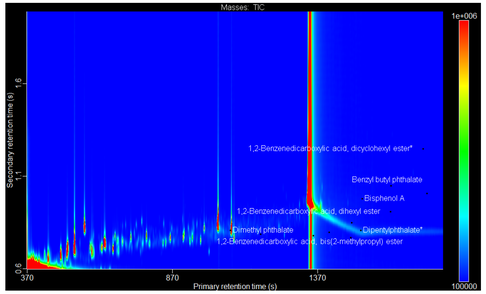

Figure 2. GCxGC-TOFMS TIC contour plot of the brewed coffee sample spiked with 50 ppb phthalates standard and bisphenol A.

Figure 3 further demonstrates the utility of the second-dimension separation in GCxGC. The two phthalate standards, benzyl butyl phthalate and di-n-hexyl phthalate, share a prominent 149 m/z common to many phthalates while eluting off the primary column at nearly the same time. The second-dimension separation makes it easy to differentiate the peaks and accurately measure S/N and peak area, which would be a difficult task if the two peaks overlapped.

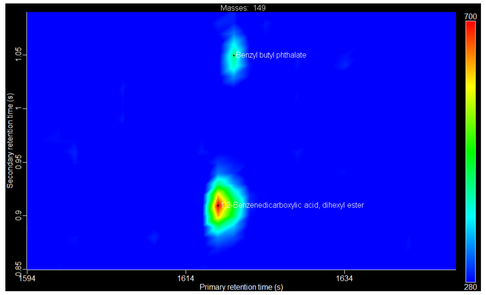

Figure 3. GCxGC-TOFMS extracted ion chromatogram for 149 m/z. Two phthalate standards that would coelute in a conventional GC analysis without the second-dimension separation are displayed.

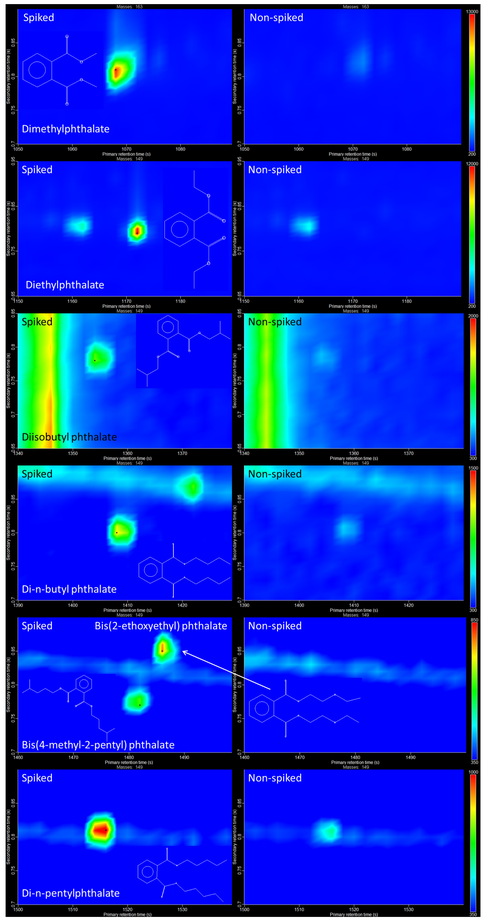

Figure 4a. GCxGC-TOFMS extracted-ion contour plot comparisons between spiked and non-spiked brewed coffee samples with the standard molecular structure displayed.

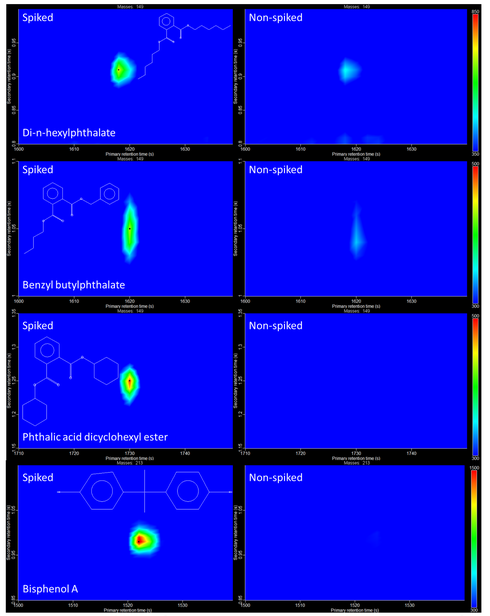

Figure 4b. Additional GCxGC-TOFMS extracted-ion contour plot comparisons between spiked and non-spiked brewed coffee samples with the standard molecular structure displayed.

Figures 4a and 4b show comparisons between the spiked and non-spiked dichloromethane-extracted brewed coffee samples. Phthalate compounds that appeared at low levels (sub-10 ppb) in the unspiked coffee include diisobutyl phthalate, di-n-butyl phthalate, di-n-pentylphthalate, di-n-hexylphthalate, and benzyl butylphthalate. The low-intensity peak appearing in the dimethyl phthalate screenshots is from the nearby ethyl vanillin peak. The combination of two-dimensional separation and use of unique ion masses clearly separates each peak from their neighboring peaks and the long caffeine tail.

Conclusions

The LECO Pegasus 4D GCxGC-TOFMS system was successfully used to analyze potential plasticizer compounds such as bisphenol A and phthalates in single-serving coffee pod products that can potentially leach into the coffee. The results show that a few of these compounds were isolated and detected after a dichloromethane extraction sample preparation process. Combining the separation power of GCxGC with the library-searchable mass spectra produced by the TOFMS leads to confident detection and isolation of both targeted and unexpected analytes.