Analysis of Bisphenol A and Other Food Packaging Leachates from Microwaved Food Containers Using GCxGC-TOFMS

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Introduction

Bisphenol A (BPA) is an endocrine-disrupting compound with a great deal of controversy surrounding the acceptable limitations of exposure. It is most widely known as a building block for polycarbonate plastics (Type 7 PC), and is sometimes present in other plastic types as well. A main area of concern regarding BPA is food contamination, where plastic microwavable food containers may be particularly liable to leach BPA and other plasticizers due to chemical bond breakage during heating.

Commercial microwave containers along with the food contained therein was tested using the QuEChERS sample preparation methodology followed by comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS). Because food matrices are notoriously complicated, combining the sample cleanup potential of the QuEChERS method with the large peak capacity of GCxGC and the detection/identification capabilities of the TOFMS will lead to confident isolation and detection of any BPA and other plasticizer compounds.

QuEChERS Methodology

- Homogenize food sample
- Weigh 10 g of sample into clean 50 mL centrifuge tube.
- Add 10 mL acetonitrile solvent.
- Shake vigorously for 1 min.
- Add Qsep 150 extraction salts.
- Shake vigorously for 1 min.
- Centrifuge at 3000 x g for 5 min.
- If using dSPE kit for additional cleanup, continue. Otherwise, transfer supernatant to autosampler vial and analyze.
- Transfer 1 mL of supernatant to dSPE Qsep 250 tube.
- Shake vigorously for 30 s.
- Centrifuge at 3000 x g for 5 min.
- Adjust pH using 10 µL of a 5% formic acid in acetonitrile solution.
- Transfer supernatant to autosampler vial and analyze.

Experimental Methodology

The data presented here were produced using the LECO Pegasus® 4D TOFMS, a GCxGC-TOFMS instrument, 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 acetonitrile solvent with diluting down to targeted concentrations. The 506 Calibration Mix phthalate standards, d-10 phenanthrene internal standard, and QuEChERS kits were purchased from Restek.

Two bags of each commercial food item tested (frozen broccoli florets, frozen peas, and tomato soup) were purchased at a local grocery store. These items were chosen because the bags/containers were advertised to be microwave safe, with microwaving instructions on the back. Because the microwave instructions indicated that only sealed, unopened containers should be microwaved, the non-microwaved samples came from one package while the microwaved samples came from the other package. The microwave used in this study was an Emerson MWG9111SL, operated at 1000 W.

The QuEChERS process was used to prepare the samples before analysis, as detailed previously. The dSPE kits were found not to be necessary for the samples studied.

The GCxGC-TOFMS analysis conditions are shown below in Table 1.

Carrier Gas	Helium, corrected constant flow control
Injection Volume (µL)	1
Split Ratio	Splitless
Flow Rate (mL/min)	1.0
Primary Column	30 m x 0.25 mm x 0.25 µm Rxi-1ms
Secondary Column	1 m x 0.18 mm x 0.20 µm RTX-200
Primary Oven Ramp	40°C for 0.5 min then 15°C/min to 270°C with 25 min hold
Secondary Oven Ramp	+10°C offset from primary oven
Modulator Offset	25°C
Modulation Period	4 s period (1.3 s hot)
Transfer Line Temperature	280°C
Ion Source Temperature	200°C
Mass Spec Detector Voltage (V)	1725
Mass Spec Acquisition Delay (s)	300
Mass Range (m/z)	40-650
Acquisition Rate (spectra/s)	100
Electron Energy for EI (V)	-70
Collection/Processing Software	ChromaTOF® 4.42

Table 1. Experimental conditions for the GCxGC-TOFMS analysis of QuEChERS-extracted food samples.

Results

Figure 1 displays example calibration curves of two of the standards used; BPA and di-n-butyl phthalate. The trendlines exhibit good linearity and exceed 0.999 for the R^2 value over the concentration range of 10 ppb to 1 ppm.

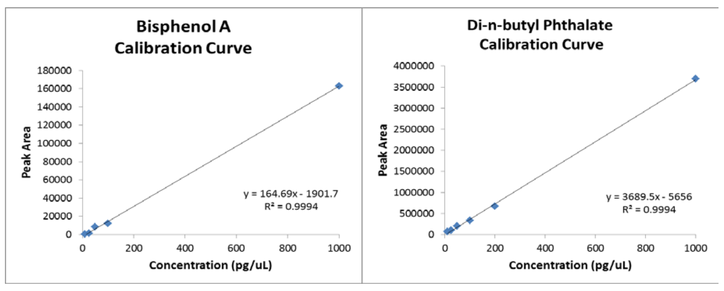

Figure 1. Example calibration curves for selected standards.

The tables below show the detected concentrations of the BPA and phthalate target compounds found in the three food samples. The acronyms used in the tables are as follows: BPA = Bisphenol A; DMP = Dimethyl phthalate; DEP = diethyl phthalate; DBP = di-n-butyl phthalate; BBP = benzyl butyl phthalate; B2A = bis(2-ethylhexyl)adipate; B2P = bis(2-ethylhexyl)phthalate; DOP = di-n-octyl phthalate; ND = Not detected; BLC = Detected but below lowest calibration level.

A number of these compounds were detected in the water blanks, indicating that either the plastic centrifuge tubes or inner linings of QuEChERS salt packets can contribute to these signals.

Concentrations Detected (ppb)				
	Unique Mass	*Water Blank*	*Non-microwaved*	*Microwaved*
BPA	213	28	58	888
DMP	163	ND	ND	ND
DEP	149	25	22	22
DBP	149	17	16	25
BBP	149	BLC	BLC	BLC
B2A	129	BLC	BLC	BLC
B2P	149	25	23	27
DOP	149	ND	ND	BLC

Table 2. List of target components with unique mass and detected concentrations in the frozen and microwaved pea samples.

Concentrations Detected (ppb)				
	Unique Mass	*Water Blank*	*Non-microwaved*	*Microwaved*
BPA	213	42	45	69
DMP	163	ND	ND	ND
DEP	149	47	70	182
DBP	149	BLC	31	37
BBP	149	BLC	24	24
B2A	129	BLC	BLC	BLC
B2P	149	23	22	21
DOP	149	ND	ND	ND

Table 3. List of target components with unique mass and detected concentrations in the frozen and microwaved broccoli samples.

Concentrations Detected (ppb)				
	Unique Mass	*Water Blank*	*Non-microwaved*	*Microwaved*
BPA	213	BLC	33	18
DMP	163	ND	ND	ND
DEP	149	34	BLC	BLC
DBP	149	BLC	BLC	BLC
BBP	149	ND	19	19
B2A	129	BLC	BLC	BLC
B2P	149	14	13	15
DOP	149	ND	ND	ND

Table 4. List of target components with unique mass and detected concentrations in the frozen and microwaved tomato soup samples.

Figure 2 displays the TIC contour plot for the GCxGC-TOFMS analysis of the frozen, non-microwaved pea sample. Peaks of interest, including target plasticizers and natural compounds such as phytosterols, are highlighted with black peak markers. In the pea sample, BPA, diethyl phthalate, di-n-butyl phthalate, and bis(2-ethylhexyl)adipate were detected in the 20 ppb range.

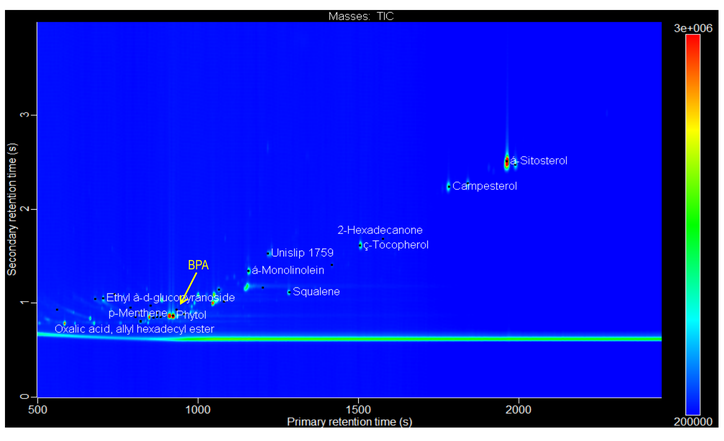

Figure 2. GCxGC-TOFMS TIC contour plot of the non-microwaved peas sample.

Figure 3 displays the TIC contour plot for the GCxGC-TOFMS analysis of the microwaved pea sample. Peaks of interest are highlighted with black peak markers. Compared to the non-microwaved pea sample, the BPA peak increased by a large amount, while diethyl phthalate, di-n-butyl phthalate, and bis(2-ethylhexyl)adipate either did not increase or increased very slightly. A closer look at the BPA peaks are shown in Figure 4.

One compound that exhibits a large increase in concentration due to the microwave action is β-monolinolein at t_r'=1156 s, t_r''=1.370 s. The peak has a strong presence in non-microwaved peas at 4,300 S/N, but after microwaving, swells to a S/N of 20,000. It is likely to be a degradation product of more complex phytosterols.

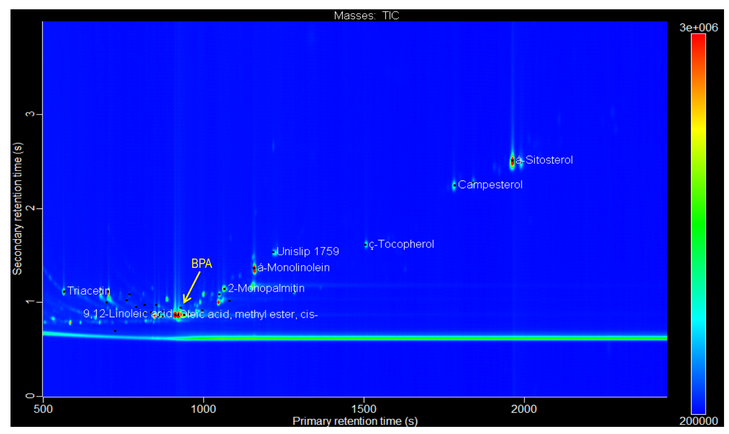

Figure 3. GCxGC-TOFMS TIC contour plot of the microwaved pea sample.

Figure 4 displays zoomed-in GCxGC-TOFMS contour plots using m/z 213, the unique ion assigned to BPA for these analyses. The left-side plots show results from the pea sample and the right-side plots show results from the broccoli sample. Plots A and B show the water blank analyses, plots C and D show the non-microwaved sample analyses, and plots E and F show the microwaved sample analyses.

The pea sample show a large increase in BPA presence due to the microwaving process, with a 15 times increase in peak area. The increase in peak area for broccoli's BPA peak was much smaller, being about a 50% increase.

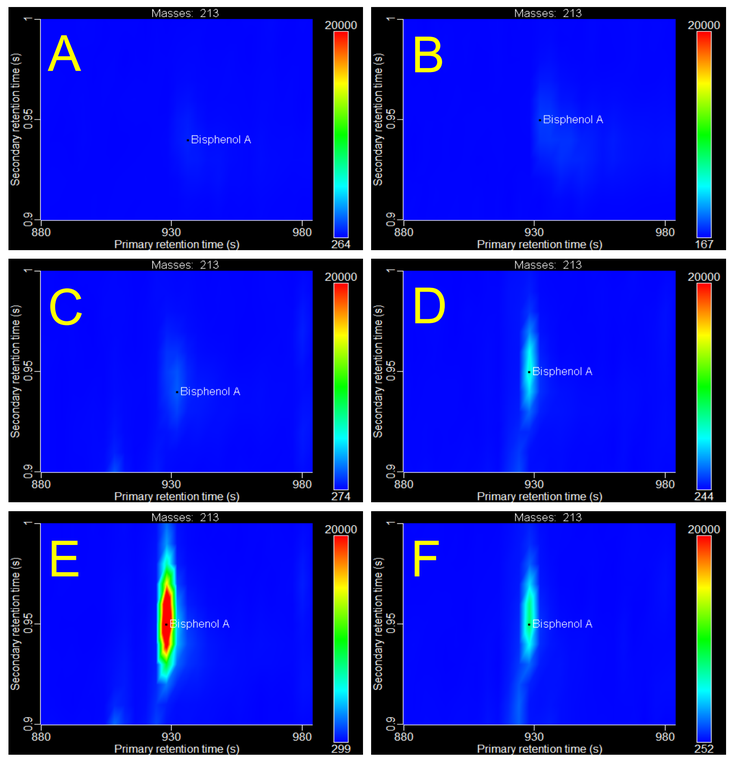

Figure 4. GCxGC-TOFMS zoomed contour plots emphasizing BPA peaks using m/z 213. Plots A, C, and E represent the peas sample water blank, non-microwaved sample, and microwaved sample, respectively, while plots B, D, and F represent the same for the broccoli sample.

Conclusions

The LECO Pegasus 4D GCxGC-TOFMS system was successfully used to analyze BPA and phthalate plasticizer compounds that can potentially leach into food products. The results show that these compounds can be isolated and detected in conjunction with the QuEChERS sample preparation process. BPA was found in the frozen pea and frozen broccoli samples and with increased concentration after microwaving the food samples. Phthalates found in low concentrations in the samples tended to be similar to water blank levels, indicating that they are likely sourced from the preparation method and not the food, although diethyl phthalate in the broccoli is an exception.