# Evaluating Consumer Products for Low Level Contaminants with High Temperature Dynamic Headspace

## Application Note


## Abstract

High density polyethylene (HDPE) and polyethylene terephthalate (PET) are widely used polymers for the storage of consumer products including bottled drinks. HDPE is typically used in milk jugs while PET is typically used in soft drink and bottled water bottles. These polymers can have glass transition temperature above 250°C (482°F) and can be difficult for most headspace instruments to determine out gassing products.

This poster will present data of potential contaminants found in various high temperature polymers used for consumer products with dynamic headspace for low level detection.


## Introduction

High density polyethylene and polyethylene terephthalate are widely used polymers for the storage and cooking of consumer products. HDPE is typically used in milk jugs while PET is typically used in soft drink and bottled water. The crystalline form of PET (CPET), due to its higher temperature mechanical stability, is used for the frozen storage of foods to be instantly heated in either a microwave or conventional ovens without defrosting the food. These polymers can release organic compounds into the food that can impart a bad taste or odors to the food stored or cooked in them ,and may also be harmful to the consumer.

Numerous government agencies worldwide including, but not limited to, the U.S. Food and Drug Administration (FDA), Health Canada / Santé Canada, the Japanese Ministry of Health Labour and Welfare, the Bureau of Indian Standards, the Russian Federal Service for Supervision of Consumer Rights Protection and Human Welfare, the Chinese Ministry of Health, and the European Union have issued regulations listing the types of materials allowed for food contact. Some of these regulations also include the maximum temperatures that can be used for specific polymers.

This poster will focus on the chemical compounds released from the PET and CPET polymers currently used for freezer to microwave and freezer to oven preparation at their label cooking temperatures.

The analysis of these samples was accomplished with a Teledyne Tekmar HT3 in the both the static and the dynamic mode along with a Thermo Focus GC/DSQ II MS for the detection and preliminary identification of the organic compounds released from the samples. An EPA Method 8260 standard was used to confirm the presence of potential volatile organic compounds (VOCs) like benzene and toluene, along with other compounds regulated by the EPA method. The chemical fingerprint from the PET and CPET polymer tray and film prior to cooking will be used to determine if these compounds are detectable in the cooked food.




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## Experimental-Instrument Conditions

| HT3 Headspace Instrument Parameters | | | |
|---|---|---|---|
| Static | | Dynamic | |
| Variable | Value | Variable | Value |
| Valve Oven Temp | 200°C | Valve Oven Temp | 200°C |
| Transfer Line Temp | 200°C | Transfer Line Temp | 200°C |
| Platen/Sample Temp | 80°C (176°F) 160°C (320°F) | Platen/Sample Temp | 80°C (176°F) to 280°C (536°F) |
| Sample Equil Time | 30.00 min | Sweep Flow Rate | 75 mL/min |
| Pressurize | 20 psig | Dry Purge Time | 270°C |
| Loop Fill Pressure | 15 psig | Dry Purge Flow | 3.00 min |
| Inject Time | 1.00 min | Desorb Temp | 250 mL/min |
| | | Desorb Time | 3.00 min |
| | | Trap Material | #9 |

*Table 1: Static and Dynamic HT3™ Parameters*

| Thermo Focus GC/DSQ II MS Parameters | |
|---|---|
| Column | Retek Rtx® VMS, 20m, 0.18mm ID, 1µm; Constant Flow 0.90 mL/min |
| Oven Program | 40°C for 4 min; 16°C/min to 160°C, 25°C/min to 250°C hold for 4 min, run time 19.1 min |
| Inlet: | Split Flow 45 mL/min, Temperature 220°C, Helium Carrier Gas |
| MS | Source and Transfer Line Temp 230°C, Full Scan 35.0 *m/z* to 270.0 *m/z* Scan Rate 1492.11 |

*Table 2: Thermo Focus GC/DSQ II MS Parameters*

## Sample Preparation

A microwaveable / conventional oven frozen meal in PET tray with a film cover was obtained from a local supermarket. The entrée consisted of pumpkin filled ravioli with asparagus, apples, carrots, celery, onions and butternut squash. The label butter sage sauce ingredients consisted of salted Chablis wine, extra virgin olive oil, cane juice, tomato paste, garlic, spices, soybean oil, salt, sea salt and natural flavors. These ingredients will have flavors, fragrances and other compounds which will be detected by the headspace method.

The microwave and conventional oven cooking instructions were followed. The ravioli was sliced into 1 cm strips and placed into separate 22 mL headspace vials for each cooking method and immediately capped. The vegetables were sampled into separate 22 mL headspace vials for each cooking method and immediately capped. The cover film and the tray from the 2 different cooking methods was cleaned with water and wiped dry. The film was cut into 5 cm squares and placed into separate 22 mL headspace vials. The tray material was cut into 1 cm by 6 cm strips and placed into separate 22 mL headspace vials. Similar samples of the ravioli, vegetables, film cover and tray prior to cooking were also placed into headspace vials for analysis.

The food samples along with the tray and film samples were analyzed with the static headspace parameters listed in Table 1 with the platen at 80°C (176°F) and 160°C (320°F). These temperatures are similar to the temperatures reached in the microwave (product needs to reach 74°C (165°F) to be thoroughly cooked) and the conventional oven. These temperatures were sufficient to revolatilize the compounds absorbed by the food from the polymer materials, and from the flavor components of the food absorbed by the polymers.

The uncooked film and PET tray samples were tested from 80°C (176°F) to 280°C (536°F) by dynamic headspace to determine the compounds out gassed from the polymers and to analyze the out gassing temperature profile. This higher temperature analysis was performed to determine if additional compounds were released after the polymers glass transition or melting point had been reached. These compounds could potentially migrate from the polymers into the rood during storage. The conventional oven temperature of 177°C (350°F) fell within this range.



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## Results

All sample data was compared to a 50 ppb 8260 standard to identify any known VOC compounds. The food sample chromatograms contained numerous peaks not present in the 8260 standard. These compounds were tentatively identified by the mass spectrometry software search against the NIST database. These additional compounds were not confirmed with actual standards, except acetaldehyde, ethanol and acetic acid.

A hydrocarbon similar to 2-methylpropene (2), acetaldehyde (3), acetone (6), methyl acetate (7), 2-butanone (8), a compound similar to octane (10), and toluene (11) were identified VOC's released from the tray samples. The peak areas of the compounds were plotted versus sample temperature to show their release from PET versus cooking temperature.

Figure 1 shows an overlay of the total ion chromatogram for the 100°C (212°F), 140°C (284°F), 180°C (356°F) and 200°C (392°F) dynamic sample temperatures showing the change of peak area for the identified compounds. Figure 2 presents the temperature profile plot of the acetaldehyde peak area for both the tray sample and the film sample. The other VOCs also exhibited similar profiles with an increased release of the compound after 177°C (350°F).

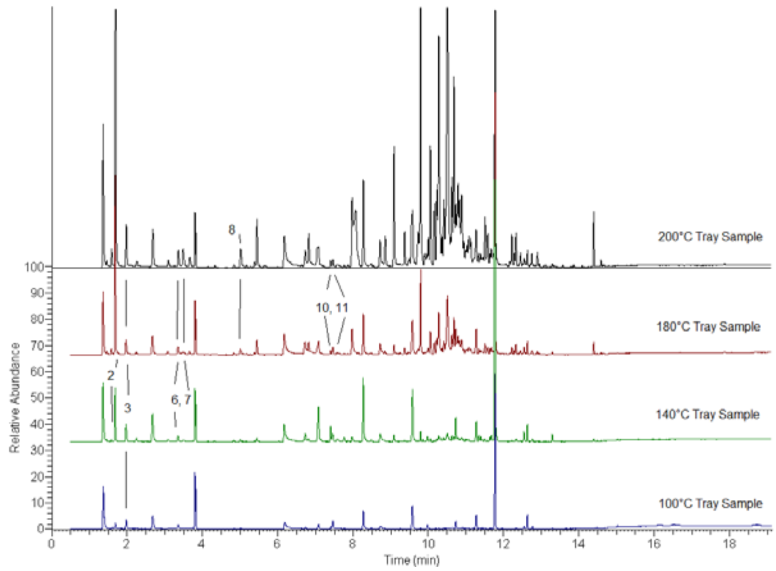


Figure 1 – Overlay of the Total Ion Current of the PET Tray Samples at 100°C (212°F), 140°C (284°F), 180°C (356°F) and 200°C (392°F) Dynamic Sample Temperatures.

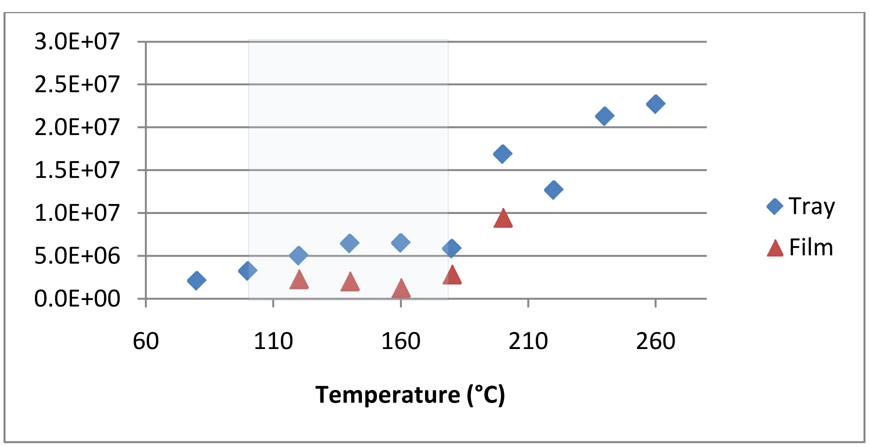


*Figure 2 – Temperature Profile Plot of the Acetaldehyde Peak Area for the Tray Sample (blue diamond) and the Film Sample (red triangle). The grey box indicates the cooking temperature range from 100°C (212°F, boiling water) to the manufacturer's upper oven limit of 177°C (350°F)*



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Chloromethane (1), acetaldehyde (3), chloroethane(4), 1,1-dichloroethene (5), acetone(6), methyl acetate (7), 2-butanone (8), methyl methacrylate (9), a hydrocarbon similar to octane (10), toluene (11), and 1,3-dichlorobenzene (12) were identified in the film samples. The peak areas of the compounds were plotted versus the sample temperature to show their release from the film versus cooking temperatures.

Figure 3 shows an overlay of the total ion chromatogram for the 100°C (212°F), 140°C (284°F), 180°C (356°F) and 200°C (392°F) showing the change of peak area for the identified compounds. Figure 4 presents the temperature profile plot of chloromethane peak area for both the tray sample and the film sample. The other VOCs except acetone, toluene and the hydrocarbon similar to octane also exhibited similar profiles with an increased release of the compound after 177°C (350°F).

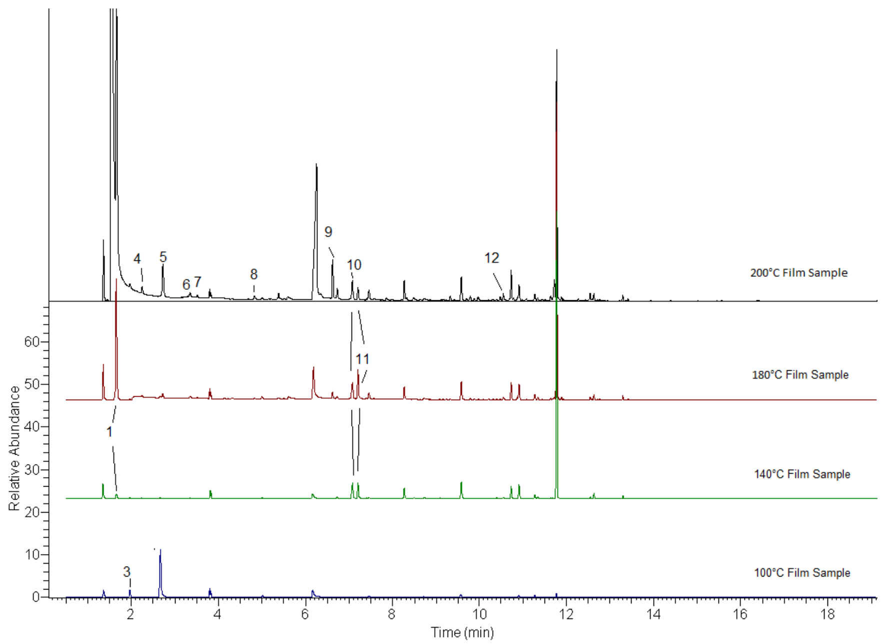


Figure 3: Overlay of the Total Ion Current of the Film Samples at 100°C (212°F), 140°C (284°F), 180°C (356°F) and 200°C (392°F) Dynamic Sample Temperatures.

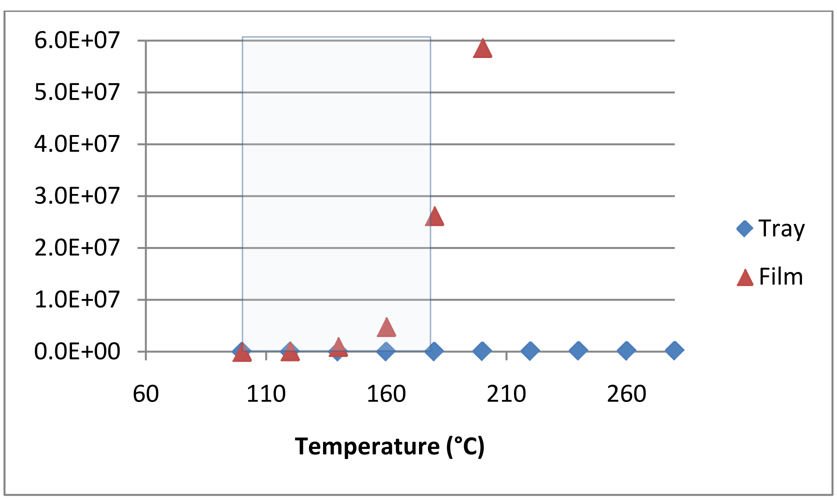


*Figure 4: Temperature Profile Plot of the Chloromethane Peak Area for the Tray Sample (blue diamond) and the Film Sample (red triangle). The grey box indicates the cooking temperature range from 100°C (212°F, boiling water) to the manufacturer's upper oven limit of 177°C (350°F)*

The food samples were evaluated for the presence of the compounds found from the dynamic headspace testing of the PET tray and the film cover. The film cover was left on the tray during the cooking process following the package cooking instructions. All of the compounds identified in the dynamic headspace analysis of the tray and the film sample were not detected in the static analysis of the tray, film and food samples. The peak areas for the found compounds are presented in Table 3 and Table 4. The compounds identified in the polymers with dynamic headspace not found in the tray, film or food samples by static headspace are included in this static headspace table.

| | Tray | | | Film | | |
|---|---|---|---|---|---|---|
| | Cold | Microwave | Oven | Cold | Microwave | Oven |
| Chloromethane | 206883 | 227228 | 298384 | 23768964 | 22139351 | 10218123 |
| 2-Methylpropene | 3085264 | 3071339 | 3580295 | 1213575 | 3332035 | 971634 |
| Acetaldehyde | 1963293 | 2186791 | 2176159 | 1265675 | 10272642 | 4241584 |
| Chloroethane | | | | | | |
| 1,1-Dichloroethene | | | | | | |
| Acetone | 53071 | 52745 | 63528 | 162260 | 1469011 | 432558 |
| Methyl Acetate | | | | | | |
| 2-Butanone | | | | | | |
| Methyl Methacrylate | | | | | | |
| Octane | | | | | | |
| Toluene | ND | ND | ND | 1378470 | 970445 | 12018 |
| 1,3-Dichlorobenzene | | | | | | |

Table 3: Peak Area Data for the Compounds Detected in the Tray and Film Samples by the Static Method at a Sample Temperature of 160°C (320°F). The compounds identified in the polymers with dynamic headspace not found in the tray, film or food samples by static headspace are included in this static headspace table.

| | Vegetable and Sauce | | | Ravioli | | |
|---|---|---|---|---|---|---|
| | Cold | Microwave | Oven | Cold | Microwave | Oven |
| Chloromethane | ND | ND | 195723 | ND | 218913 | 1212796 |
| 2-Methylpropene | ND | 21114 | 139108 | ND | 182909 | 238769 |
| Acetaldehyde | ND | 55129 | 44808595 | ND | 17791448 | 165364859 |
| Chloroethane | | | | | | |
| 1,1-Dichloroethene | | | | | | |
| Acetone | 254486 | 83052 | 1822836 | ND | 1123675 | 4989781 |
| Methyl Acetate | | | | | | |
| 2-Butanone | | | | | | |
| Methyl Methacrylate | | | | | | |
| Octane | | | | | | |
| Toluene | ND | 2062 | 206395 | ND | 38988 | 295540 |
| 1,3-Dichlorobenzene | | | | | | |

Table 4: Peak Area Data for the Compounds Detected in the Food Samples by the Static Method at a Sample Temperature of 160°C (320°F). The compounds identified in the polymers with dynamic headspace not found in the tray, film or food samples by static headspace are included in this static headspace table.

## Conclusions

Nine EPA Method 8260 VOCs were identified in the PET tray and the film of a frozen microwavable/conventional oven food by dynamic headspace. These compounds are chloromethane, chloroethane, 1,1-dichloroethene, acetone, methyl acetate, 2 butanone, methyl methacrylate, toluene and 1,3-dichlorobenzene. These compounds typically were held in the plastic until well above the package cooking temperature of 177°C (350°F).

A compound similar to 2-methylpropene, acetaldehyde, and a compound similar to octane were also identified in the PET tray and the file of a frozen microwavable / conventional oven food by dynamic headspace. Acetaldehyde is found in natural products including ethanol and PET. Additional work would need to be performed to confirm the identity of the two additional compounds.

Only 3 of the 9 EPA Method 8260 VOCs were identified in the vegetables and sauce and the ravioli when prepared by microwaving or conventional oven. These are chloromethane, acetone and toluene. The conventional oven cooking process had greater concentrations of these compounds present when compared to the microwave prepared samples. Acetone was the only compound observed in the frozen food and may have been related to the Chablis wine listed on the label.

A compound similar to 2-methylpropene and acetaldehyde were also identified in the vegetables and sauce and the ravioli when prepared by microwaving or conventional oven. The acetaldehyde amount was greater in the food and the microwave film sample than could be accounted for in the cold tray and cold film sample analysis. This additional amount was postulated to have been released from the food and the sauce components. Additional work would need to be performed to confirm this.

The HT3™ headspace instrument provided a single instrument that allowed for high temperature dynamic determination of compounds out gassing from the PET tray and the film used by the manufacturer past their glass transition/ melting temperatures and the determination of these compounds present in the food by a static method. This poster clearly indicates that food manufacturers, along with the world regulator agencies uses the thermal release profile of the PET tray and film plastic to minimize the release of these compounds into the food. Exceeding the package cooking instruction could expose the consumer to unreasonable amounts of compounds.



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