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Aromatic Hydrocarbon Content of Common Plastic Packaging Materials

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1.0 ABSTRACT

In previous work on recycled HDPE from dairy grade bottles the presence of trace levels of aromatic hydrocarbons was detected, including benzene, toluene, 3 xylenes and naphthalenes. The source of these hydrocarbons was not related to recycling because the same compounds were found in bottles off the shelf of a supermarket. In a paper presented at the 1995 SPE Plastics Recycling Conference, it was suggested that the source of the hydrocarbons is from gasoline vapor in the air. The method of analysis is thermal desorption GC/MS (gas chromatography/mass spectroscopy). The excellent detectability is because heat is used to remove compounds rather than solvent.

Recent work has been done with other plastic packaging materials, including PET, PS and PVC. All contained readily detected levels of aromatic hydrocarbons; the highest levels were in PS. We have purged the hydrocarbons in the plastics as received using supercritical fluid extraction with carbon dioxide. Analysis confirmed the substantial freedom of hydrocarbons. The plastics were then exposed to atmosphere to allow the plastics to reabsorb the hydrocarbons from the air. The likely source is gasoline vapors because the composition and relative amounts of hydrocarbons are similar to that in gasoline.

2.0 INTRODUCTION

The initial work on the composition of volatile compounds present in plastics performed by the University of Connecticut – Institute of Materials Science was on recycled dairy grade HDPE.[1] The objective was to determine if compounds were present that might limit reuse of the recycled polymer for food contact applications. Over 100 compounds were identified that were not present in virgin HDPE. The compounds were grouped into categories as follows:

aliphatic saturated hydrocarbons w/o functional groups
aliphatic unsaturated hydrocarbons w/o functional groups
aliphatic hydrocarbons with functional groups
aromatic hydrocarbons w/o functional groups
aromatic hydrocarbons with functional groups
fragrance and flavor type compounds
others and unknowns

Functional groups include carboxyl (COOH), hydroxyl (OH), ketones (C=O), etc.

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[1] Ezrin, M. and G. Lavigne, *Analysis of Organic Compounds in Recycled Dairy Grade HDPE by Thermal Desorption Gas Chromatography/Mass Spectroscopy*, SPE Recyling Division 2nd Annual Recycling Conference, 104-110 (1995).

The category that was of most concern is aromatic hydrocarbons without functional groups. That includes benzene, toluene, xylenes and naphthalenes. Benzene is considered a highly carcinogenic compound. Quantities of the aromatic hydrocarbons are estimated at parts per billion (ppb) to low parts per million (ppm). Benzene, toluene, xylenes and styrene, all aromatic hydrocarbons without functional groups, were present in virgin HDPE and in recycled HDPE. Levels in virgin HDPE were at approximately 0.1-0.2 times the levels in recycled resin.

Since there is no reason to believe that the aromatic hydrocarbons had been introduced by the recycling process, an alternate source was considered. A HDPE water bottle from a supermarket shelf was analyzed. All the same aromatic hydrocarbons were found as in recycled HDPE, but at lower levels. Apparently the compounds are absorbed from the air. The ratio of compounds to each other is similar to that in gasoline. Vapors of gasoline are widespread in the atmosphere, coming from pumping of gas at service stations and unburned gasoline when cars and trucks are started cold. A supermarket has a large number of cars in its parking lot. For heating and cooling, air is drawn into the store, so that gasoline vapors are spread throughout the store, thus exposing packaging and other products to gasoline vapors.

The analysis of volatile compounds was extended to other plastic packaging materials and reported at SPE-ANTEC 2003.[2] Plastic packaging products analyzed were polyethylene (PE), polyvinylchloride (PVC), polyethyleneterephthalate (PET), rigid polystyrene (PS) and foam PS. Polystyrene, especially foam PS, had the highest levels of aromatic compounds.

In order to prove that the aromatic hydrocarbons came from ambient air, we sought to remove the volatiles from packaging materials, then to expose them to air for possible absorption of gasoline vapor. Heating of the plastics was not effective in completely removing the compounds. In addition, the plastics changed shape due to heat, so that using the misshapen materials for exposure to air would not be the same as the original packaging material.

Supercritical fluid extraction with carbon dioxide (CO_2) was used to remove the hydrocarbons without unduly affecting the shape and form of the materials. In this paper we report the results of extraction with CO_2 and the uptake of gasoline vapors by the CO_2-extracted materials.

The method of analysis is thermal desorption gas chromatography/mass spectroscopy (GC/MS). Heat is used to evolve the volatile compounds onto the GC column for analysis. Because solvent is not used for extraction, which results in dilution of the extracted compounds, very low levels of compounds can be determined.

3.0 PLASTIC PACKAGING MATERIALS ANALYZED

The packaging products were of the same type as those in the ANTEC 2003[2] paper as follows:

1. HDPE water bottle
2. PET water bottle
3. PVC blister pack of medication
4. PS foam cup
5. PS rigid sheet food package

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[2] Ezrin, M. and G. Lavigne, *Aromatic Hydrocarbon Content of Plastic Packaging Materials*, SPE Annual Technical Conference, 2015-2017 (2003).

4.0 EXPERIMENTAL METHODS

4.1 Supercritical fluid extraction with CO_2

Polymers as cut pieces of 4x4 mm were placed in an extractor vessel modified from a liquid chromatography precolumn filter. Pressurization of the extraction vessel was accomplished with CO_2 in a SFC5000 micro syringe pump pressurized to 4000 psi using a restrictor of 15 microns ID x 38 mm length. Extractable compounds dissolved in CO_2 at 60°C for 3 hours were continuously vented to the atmosphere during the extraction process. The extracted samples were analyzed by GC/MS to determine how completely the hydrocarbons had been removed. Another similar extracted group was used for exposure to air to determine if hydrocarbons are absorbed from air.

4.2 Test of ability of plastics to reabsorb aromatic hydrocarbons following extraction with CO_2

Samples that had been extracted with CO_2 were suspended in a 2 liter round bottom flask. One microliter of a mixture of benzene, toluene and xylene was placed in the bottom of the flask. The samples were left in the flask 16.5 hours. There was a control sample vial containing only quartz wool, same as in the vials with samples. The samples were analyzed by GC/MS.

4.3 Exposure of extracted plastics to ambient air

CO_2-extracted samples were placed in a residential garage seven days. Air was pumped over the samples using a small pump that circulated air at 20 ml/min. Purpose of pumping was to ensure adequate exposure to ambient air in a matter of days. The pump is SKC air sampling pump model 210-1002, designed for air sampling without introducing any compounds from the pump.

4.4 Thermal desorption gas chromatography/mass spectroscopy (GC/MS)

This method has been described in previous publications and is available on the web site http://www.ims.uconn.edu/~lavigne/gcmslab.html. It utilizes a unique thermal desorption device invented here by Gary Lavigne. The GC/MS instrument is a Hewlett Packard 6980. The GC column is J+W db-5 0.25 mm ID x 30 m 1.0 micron film. GC oven temperature program was 35 to 325°C at 15°/min. with 5 min. hold at 35°C. Thermal desorption was at 200°C for 5 min. splitless. With this device, sample is heated in the injection port, in this case at 200°C. Volatiles are continuously transferred onto the column by helium flow, where they are trapped by using liquid nitrogen cooling of the head of the column. After the heating period, the sample vial is forced out of the injection port with gas pressure.

Identifications were by mass spectra of the whole mass range. Retention times were determined for each compound. Thereafter (Table 2), levels of each were measured by selected ion data collection using an appropriate mass for each compound, as follows: benzene-78, toluene and xylenes-91, naphthalenes-128. The relative content of each was measured by peak area and normalized per mg sample weight. The amounts detected were well in excess of a blank run.

5.0 EXPERIMENTAL RESULTS

Table 1 gives normalized peak area/mg sample weight for benzene, toluene and xylenes for three conditions of the plastics – as received, after extraction with CO_2, and after exposure to a mixture of benzene, toluene and xylene (see sec. 4.2 above). The five plastics, PE, PVC, PET and PS foam and rigid, differ in their content of hydrocarbons from normal ambient air as received. PE, PVC and PET were completely purged of benzene, toluene and xylene by supercritical extraction. Both PS rigid and foam lost some hydrocarbons but not all. Apparently the hydrocarbons are strongly attached to PS and do not respond completely to extraction with CO_2 at 4000 psi and 60°C/3 hours.

Table 2 gives the hydrocarbon contents after exposure to garage air seven days (see section 4.3). The removal of hydrocarbons by SCF appears to have been less complete for this group of samples than for those in Table 1. The reason is selected ion data collection was used in the Table 2 analyses, which is more sensitive than using a broad mass range as in Table 1. There was substantial reduction in the as received samples and the increase in hydrocarbon content due to exposure to air is so great in most cases that there is no question that hydrocarbons were absorbed from air.

The blank of quartz wool after 7 days showed some benzene and naphthalene. This may be due to volatiles absorbed by dust in the air, which was circulated through the air collection pump, so that dust collected on the quartz wool would show up with hydrocarbons. Other blanks of quartz wool were negative in previous runs (Table 1).

6.0 DISCUSSION

The hydrocarbons, which appear to be absorbed from air by common plastic packaging materials, can be removed substantially using supercritical fluid extraction with carbon dioxide (Table 1). Even with that, 3 hours @ 60°C and 4000 psi was required which left some hydrocarbons unremoved on PS foam and rigid. The reductions by SCF of the as received samples were great enough to show that subsequent garage exposure caused absorption of a high content of hydrocarbons for the plastics. The greatest levels as received and after garage exposure are for foam PS.

The main objective of this paper has been achieved, i.e., to demonstrate that the aromatic hydrocarbons present in packaging materials of PS, PVC, PET and PE are absorbed from the air. The composition of the hydrocarbons resembles that of gasoline. Gasoline vapors in the air are the most likely source of absorbed hydrocarbons.

To put the toxicological consequences in perspective, people breathe the same air containing hydrocarbons and other pollutants 24 hours a day, 365 days a year. The hydrocarbons, including benzene, which is carcinogenic, are brought directly into the body. With packaging materials, the hydrocarbons tend to be retained by plastic tenaciously. If the food product is aqueous, such as water, carbonated beverage, milk, fruit juice, etc., substantial extraction of hydrocarbons into the liquid is not likely. Temperature at or below room temperature limits transfer to the liquid. To the extent that extraction occurs, the hydrocarbons are diluted by the beverage. In any case, there is no comparison of the very low levels that may be ingested from a packaged liquid over a lifetime to that being absorbed by breathing every minute of every day.

Transfer to packaged contents may be greater if the contents are hot, such as coffee or soup, or a food heated in a microwave oven. Foam PS cups are used for hot drinks. PET is used as trays for microwaveable food. PET has lower hydrocarbon content than the other plastics.

7.0 CONCLUSION

Since it was disclosed in 1995 that polyethylene bottles for milk or water contain aromatic hydrocarbons of benzene, toluene, xylenes and naphthalenes, it has been speculated that their origin is from gasoline vapors in air. For the first time now, plastic packaging materials of PS, PET, PVC and PE were substantially purged of their aromatic hydrocarbons as a basis for exposing the plastics to air, specifically in a residential garage. The same aromatic hydrocarbons noted above were present in the purged plastics after exposure to air in the garage. That they originated in air in the garage is certain. It seems very likely that the origin of the hydrocarbons is from gasoline vapors in the air in view of their similarity to gasoline aromatic hydrocarbons. The highest content of aromatic hydrocarbons before supercritical extraction and after subsequent exposure to air is foam PS.

Table 1 – Benzene, Toluene and Xylene Content of Packaging Materials As Received, Purged by SCF and After Exposure to Hydrocarbon Mixture

		Normalized Peak Area/mg		
Sample	**Sample wgt., mg**	**Benzene**	**Toluene**	**Xylenes**
PS foam as rec'd	3.25	1,010,000	443,000	5,420,000
SCF clean	3.57	250,000	39,200	67,200
BTX exp	3.25	23,170,000	35,690,000	47,080,000
PS rigid as rec'd	4.45	73,900	672,000	33,000
SCF clean	4.71	6,990	74,300	5,730
BTX exp	4.64	16,360,000	3,125,000	3,660,000
PET as rec'd	14.61	869	719	7,050
SCF clean	14.28	0	0	0
BTX exp	14.34	837,000	544,000	767,000
PVC as rec'd	6.56	24,700	9,330	45,700
SCF clean	7.44	0	0	0
BTX exp	7.59	1,000,000	191,000	250,000
PE as rec'd	21.84	582	1,340	1,190
SCF clean	22.34	0	0	0
BTX exp	22.41	6,340,000	4,460,000	9,420,000

1. SCF clean – after supercritical fluid extraction
2. BTX exp – after exposure of SCF extracted material to benzene, toluene and xylene vapor in 2 liter flask.
3. Metaxylene is not included with ortho and para xylene because it overlaps ethylbenzene.
4. Mass spectra peak areas were for the mass range 50-150 daltons.

Table 2 – Aromatic Hydrocarbon Content After Exposure of SCF-Purged Plastics to 7 Days in a Garage

		Normalized Peak Area/mg			
Sample	**Sample wgt., mg**	**Benzene**	**Toluene**	**Xylenes**	**Naphthalene**
PS foam as rec'd	3.37	919,000	376,000	3,356,000	14,900
SCF clean	3.27	309,000	78,000	100,000	1,420
garage	3.48	445,000	1,658,000	1,305,000	365,000
PS rigid as rec'd	4.67	91,100	728,000	35,000	4,980
SCF clean	4.54	8,590	77,100	7,710	0
garage	4.20	45,200	381,000	136,000	45,700
PET as rec'd	13.81	744	395	3,730	434
SCF clean	14.26	119	147	33	38
garage	14.15	1,770	20,400	19,100	13,700
PVC as rec'd	7.23	18,500	9,960	11,560	4,610
SCF clean	6.94	447	0	0	0
garage	7.27	14,700	11,700	9,350	4,810
PE as rec'd	21.01	392	1,325	1,596	812
SCF clean	21.75	285	317	115	0
garage	21.19	6,470	149,000	293,000	113,000
Blank quartz garage	1.30	4,460	0	0	654

1. As received values are averages of duplicates.
2. SCF values for foam PS are averages of duplicates.
3. Metaxylene is not included with ortho and para xylene because it overlaps ethylbenzene.
4. Mass spectra peak areas were by selected ion data collection.