

# IDENTIFICATION AND SEMIQUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS IN RECYCLED DAIRY GRADE HDPE

*Myer Ezrin and Gary Lavigne, University of Connecticut, Storrs, CT  
P. Dinger, American Plastics Council, Washington, DC*

## Abstract

The results of the study of the American Plastics Council/National Food Processors Association Recycled HDPE Team are reviewed for resins from four companies. Most of the 128 compounds present in recycled resin, and not in virgin resin, have been assigned to six major types of compounds. Some compounds may have been absorbed from ambient air and recycle wash water. Most compounds are present at the ppb to low ppm level. A rapid test for ranking the total volatiles contents by GC/MS and for detecting contaminants present at high levels was also developed.

## Introduction

This paper gives the results of analyses first reported at the 1994 ANTEC<sup>a</sup>. The main purpose of the 1994 paper was to report the experimental methodologies; some preliminary results were also given. The study was co-funded by the American Plastics Council and the EPA Pollution Prevention Research and Development Center at the University of Connecticut. The purpose of this study is to determine what potentially hazardous contaminants are present in post consumer recycled dairy grade HDPE resin using thermal desorption gas chromatography/mass spectroscopy (GC/MS). The present paper is the sequel to Phase 1 of the 1994 paper<sup>a</sup>. The results of Phase 2, on the kinetics of absorption and removal of contaminant simulants are reported separately<sup>b</sup>.

Commercial recycled resins taken at random from routine production of four different companies have been analyzed and two virgin HDPE resins. At least 128 compounds were detected in one or more of the recycled resins, which were not present in virgin resins. Most have been identified by MS as specific compounds or types of compounds. The compounds have been categorized by types such as aliphatic hydrocarbon, etc. Some compounds have been analyzed quantitatively. The presence of benzene, toluene, and xylenes has been demonstrated in four recycled resins. Analyses at as low as 100°C thermal desorption temperature strongly support the presence of the low boiling aromatics. Air and recycle wash water<sup>c</sup> as possible sources of some of the organic compounds are also suggested. A relatively rapid GC-MS method has

been demonstrated as a means of comparing lot-to-lot differences in volatile content as well as between recyclers.

## Experimental methods

### 1. Qualitative analysis (proc. #1)

The qualitative analysis was performed using 20'/250°C thermal desorption conditions and a SGE-BPX5 GC column, 25 meters, 1 micron film thickness, 0.22 mm ID. The head of the column was cryofocussed during thermal desorption. Sample weight was 30-35 mg cut from ten pellets. The GC/MS is Hewlett/Packard 5890II GC/5971A mass selective detector. GC temperature program is 35- 300 at 5°/min; 300-325 degrees at 15°/min; hold 15 minutes. The mass spectrometer scanned total ion abundance between 10 and 400 atomic mass units at a rate of approximately 1.8 scans per second.

Each peak was assigned a peak number. Relative peak height, as an approximate measure of content, was assigned as \*less than full scale; \*M-major peaks close to or at full scale; \*M0-major peaks off scale. The number of recycled resins in which each peak was observed was tabulated and whether the peaks were present in virgin resins, as well as the relative peak size in virgin resins. Peak identification was made from mass spectra using the Wiley collection of 130,000 spectra. In many cases the specific identification was made as to the particular compounds; in others, only compound types could be determined. In some cases, identification could not be made readily.

### 2. Semiquantitative analysis for benzene, toluene and xylenes; Quantitative analysis for BHT (proc. #2)

Sample weight--3 to 5 mg, cut from 10 pellets.

Thermal desorption--10'/325°C; cryofocus.

GC Column--see proc. #1.

GC temperature program--35° to 90° at 5°C/min., 90° to 325° at 15°/min., 325°C hold 25 min.

MS--selected ion data collection using mass 78 for benzene, 91 for toluene and xylenes, 205 for BHT. The no. of scans per second is ca. 10.

Calibration for aromatics--toluene in acetone.

Calibration for BHT--BHT in acetone.

### 3. Rapid test for comparison of total volatiles of recycled HDPE (proc. #3).

<sup>a</sup>M. Ezrin, et al., 1994 ANTEC, p. 2922-2926.

<sup>b</sup>E. D. Wyatt Klingelhoff, et al., 1995 ANTEC, Plastics Recycling Division.

<sup>c</sup>L. Fodor, Phillips Petroleum Co.-private communication

Sample weight--3 to 5 mg cut from 10 pellets.  
Thermal desorption--2'/250°C; cryofocus.  
GC column--100% methyl silicone, 9 m x 0.2 mm id, 0.2 micron film thickness; 24 psi pressure.  
GC temperature program--35 to 300 at 30°/min.  
Mass spectrometer - 10 to 400 atomic mass units.  
Measure of total volatiles--total ions per mg for all peaks including unresolved peaks above baseline.

## Experimental results

### 1. Qualitative Analysis

172 compounds in recycled and in virgin resins were identified or listed as unknown. Of these, 128 present in recycled and not in virgin resins were categorized as follows:

- Aliphatic Sat'd Hydrocarbons w/o Functional Groups
- Aliphatic Unsat'd 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

Table 1 gives the number of compounds in recycled HDPE by type of compound. Thirteen compounds in recycled resins, of a total of 128, are listed as unknown. Of the thirteen unknowns, only one was present as a major peak offscale (\*MO) in all four recycled resins (peak #120).

### 2. Semiquantitative/Quantitative Analysis

The average value for BHT was 41 ppm for four recycled resins. The BHT analysis is considered quantitative because practically all the BHT is evolved under the thermal desorption conditions (10'/325°C). Table 2 gives the avg. values for benzene, toluene, and xylenes under the same conditions. In their case, however, significant additional amounts were evolved with further 10 min. heating periods beyond the first. That was also the case when 250°C was used. It is uncertain if all the aromatics are present as such in PE and are not readily desorbed, even at 325°C, or if some is formed at 325°C as a product of pyrolysis<sup>6</sup>. Consequently the values in Table 2 are semi-quantitative and subject to confirmation by further analysis, possibly by an alternate method. There is no question, however, that benzene, toluene and xylenes are present in HDPE. They were detected at 150°C desorption temp.<sup>8</sup> and at 100° (Fig. 2). Table 2 also gives the relative content of toluene and xylenes, normalized to benzene as 1.

### 3. Rapid Test for Volatile Content by GC/MS

Figure 1 gives the chromatogram for V2 virgin resin and R2 recycled resin. Total time is 12' including 2' thermal desorption. The total ion count/mg is 5.7 times greater for the recycled resin. The avg. for the four recycled resins was 6.7.

### 4. Thermal Desorption at 100°C/10 min.

In order to substantiate that the low boiling aromatics are present in the HDPE, proc. #1 was performed using 10'/100°C thermal desorption with 23-24 mg. sample. Using selected ion data collection with masses specific to benzene, toluene, and xylenes, the aromatics were readily detected. Figure 2 is for recycled resin R2. Similar results were obtained for a second recycled resin. A blank run detected none of the compounds. In Fig. 2, the benzene peak is not included.

## Discussion

### 1. Types and relative amounts of compounds present in recycled HDPE

The contaminants found and their levels were substantially similar between the four recycled resins, suggesting uniformity of the composition of the containers recycled and/or similarly effective cleanup by the recycle resin manufacturers. No specific contaminants at notably high levels were found. Everything is estimated at ppb or ppm levels and typically much below the levels of the routine contaminants found in virgin resins, such as ethylene oligomers (see major peaks of virgin resin in Fig. 1). A reasonable source for most of the contaminants can be proposed based upon the typical intended uses of PE bottles. If contaminants such as pesticides were present before recycling, they were either present at very low levels, averaged over the whole batch recycled, or they were effectively removed during cleanup. Further analysis for potential contaminants of concern, such as pesticides, would be desirable using a larger set of samples from multiple suppliers. This could be accomplished using a rapid test procedure such as proc. #3, and confirmed with proc. #1 in suspect cases.

Of the six major categories of compounds, the one of greatest concern is aromatic hydrocarbons without functional groups. Benzene is considered highly toxic. Three naphthalene compounds identified may also be of concern. This category amounts to 10.2% of the compounds in recycled resin. Only one compound (peak 52) is present in one recycled resin as a major peak at or close to full scale. All the other compounds are at less than full scale and are probably at the ppb to low ppm range. From the semi-quantitative values of Table 2, the total avg. content of benzene, toluene and xylenes in the 4 recycled resins is 1300 ppb (1.3 ppm). Using an estimate of ca. 0.3-0.5% volatiles content for recycled resins (based on weight loss at 200°C), the volatiles in ppm is ca. 3000-5000 ppm. Accordingly, 1.3 ppm of low boiling aromatics corresponds to <0.1% of total volatiles. Furthermore, the compatibility with PE is so high that the aromatic compounds would not be likely to migrate out of the HDPE readily.

Compared to the potential hazard that aromatic hydrocarbons without functional groups represent, that for the other 5 categories of compounds is low to negligible. The presence of functional groups on aromatic compounds, which includes such compounds as BHT, benzoic acid, phthalates, acetophenone, etc., significantly lowers the toxicity relative to benzene. Even the presence of aliphatic groups such as methyl (toluene and xylenes) and longer chain groups also lowers the toxicity.

To further put in perspective the question of the potential hazard that the low boiling aromatic compounds represent, should any be transferred to food, consider the likely source of these compounds, i.e., the air we breathe. Table 3 gives the composition of air at a gas station and in a parking lot for 5 aromatics. Other studies<sup>4</sup> report the presence of such compounds in indoor air as well as outdoors. Clearly, the low boiling aromatic compounds are being breathed as part of our air supply day in and day out. While no attempt has been made to estimate the average intake of benzene, etc. from the air, it seems clear that their intake by people, averaged over a lifetime, must be many times more than the very small amount that might be ingested occasionally from food contained in recycled HDPE. This study is one of the first to point out that a possible source of contaminants in recycled HDPE, in addition to contact with liquids and solids, is the air.

The source of some of the organics found may be absorption from the wash water used in recycling, which has been reported to contain significant amounts of organics<sup>5</sup>.

The finding of benzene, toluene, and xylenes in recycled HDPE resin using 100°C desorption temperature (Fig. 2) provides strong evidence that these compounds are present in HDPE. In addition to identification by mass spectra, the GC retention times have also been confirmed with known compounds. It should also be noted that these compounds have been detected in virgin resin at 0.1-0.2 times the levels in recycled resin (Table 2 and Ref. a). In the same way as for the amounts found for recycled resins (Exp. Results, section 2), the values for virgin resin are also semi-quantitative and subject to confirmation.

In the category "fragrance and flavor type compounds," the largest compound is d-limonene present as offscale peak in all four recycled resins.

Of 29 compounds not classified in any of the categories above, 13 are unknown (approx. 10% of 128 compounds). Only one of the unknowns (peak 120) is present as a major peak in all four recycled resins. Five compounds are furans.

## 2. Rapid test procedure (proc. #3)

The test time could be further reduced to ca. 5 min. or

less with changes in the GC conditions. A mass spectrometer need not be used. The integrated total peak area by hydrogen flame ionization detector would serve the purpose as well if only the total volatiles is being monitored.

## Conclusions

(1) This study has furnished a picture of typical content of recycled HDPE, using four resins, by thermal desorption GC/MS. 128 compounds have been detected in some or all of four recycled dairy grade HDPE resins that are not present in typical virgin resin. 115 of these 128 compounds present only in recycled resin have been identified as to type or specific compound.

(2) The compounds identified by GC/MS have been grouped by type of compound in six major categories. Aliphatic hydrocarbons with and without functional groups account for 49.2% of the 128 compounds present in recycled resin. These compounds are not likely to be potentially hazardous contaminants. That is also the case for flavor/fragrance compounds which comprise 7.8%. The major potentially hazardous contaminants are the aromatic hydrocarbons without functional groups, which amount to 10.2% of compounds found only in recycled resins. The 10.2% of aromatic compounds with functional groups, for the most part, are much less toxic than the aromatic compounds without functional groups. Of the remaining 22.6%, 12.5% were identified as to specific compounds or type of compound, of unknown toxicity. Of 13 (10.2%) that could not be identified, only one is present at a relatively large content in all four recycled resins (off scale peak).

(3) BHT is present at ca. 40-50 ppm in recycled resin.

(4) Benzene, toluene, and xylenes, at levels of the order of approximately 0.1 to 1 ppm each in recycled resin may have been absorbed from the air. These compounds were also found in virgin resin pellets at approximately 0.1 to 0.2 times the levels in recycled resins. The finding of these compounds using thermal desorption temperature of 100°C strongly suggests that the compounds are present in HDPE. The amounts reported are only semi-quantitative and subject to confirmation. Recycle wash water is also a possible source of some organics.

(5) Compared to the total lifetime intake of benzene, toluene, and xylenes that people constantly breathe from the air, the potential amount that may be released into food from packages made with recycled HDPE is very low.

(6) Commercially available recycled dairy grade resin does not appear to present significant contamination problems and is quite suitable for its application in the non-food contact uses currently being served. It may also be suitable for use in some direct food contact applications.

(7) A rapid test has been demonstrated for the measurement of total volatiles by thermal desorption GC/MS

<sup>4</sup>Short Path Thermal Desorption Application Note No. 16, Feb. '93, Scientific Instrument Services, 1027 Old York Rd., Ringoes, NJ 08851

that could also be done using a flame ionization detector.

(8) Consideration is being given to use of thermal desorption GC/MS for other food contact polymers, such as PET and PS. Analysis by supercritical fluid extraction/chromatography (SFE/SFC) as an alternate to thermal desorption is being considered also.

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Sample	Parts per billion* (ppb)			Ratio normalized to Benz.=1	
	Benz.	Tol.	Xyl.	Tol.	Xyl.
Virgin HDPE V1	48	87	37	1.8	0.8
V2	66	97	89	1.5	1.3
Virgin Avg.	57	92	63	1.6	1.1
Recycled HDPE R1	215	700	583	3.3	2.7
R2	350	825	475	2.4	1.4
R3	125	398	204	3.2	1.6
R4	239	838	288	3.5	1.2
Recycled Avg.	232	690	388	3.0	1.7

\*averages of duplicate determinations in most cases. Values are based on calibration with toluene. The amounts are for that released in 10' @ 325°C.

Table 1\* Does not include benzene, toluene, xylene and styrene which are also present in virgin resin.

Compound Type	No./%
aliphatic saturated hydrocarbons without functional groups	36/28.1
aliphatic unsaturated hydrocarbons without functional groups	7/5.5
aliphatic hydrocarbons with functional groups	
acids	8
aldehydes	3
amines	1
esters	2
ketones	6
TOTAL	20/15.6
aromatic hydrocarbons without functional groups	13/10.2*
aromatic hydrocarbons with functional groups	
acids	1
alcohols	1
aldehydes	2
esters	5
ketones	1
phenols	2
sulfonamides	1
TOTAL	13/10.2
fragrance and flavor type compounds	10/7.8
compounds not classified above	
knowns identified as specific cpds.	6/4.7
identified only as to class of cpd.	10/7.8
unknowns	13/10.1
TOTAL	29/22.6
<b>TOTAL OF TYPES</b>	<b>128/100.0</b>

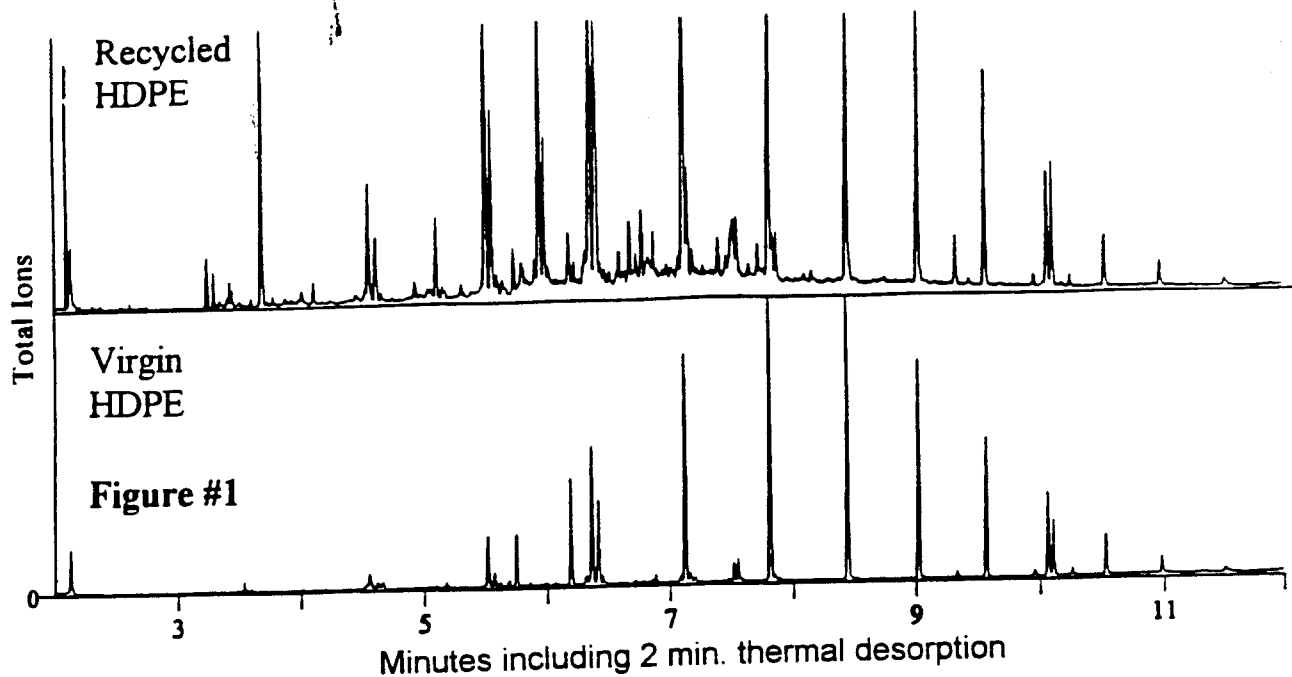


Figure 1 - Rapid GC/MS test for relative volatiles content

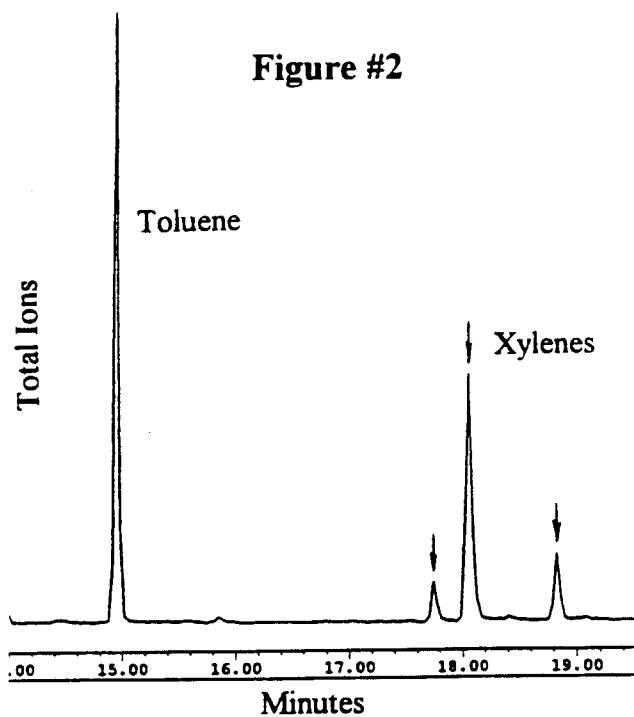


Figure 2 - Selected ion data collection mass spectral chromatogram for toluene and xylenes evolved from recycled HDPE resin using 10°/100° C thermal desorption

TABLE 3 TYPICAL CONCENTRATIONS OF LOW BOILING AROMATICS IN AIR AROUND AUTOMOBILES*		
	Gas Station 200 ml injection ppbv**	Parking Lot 200 ml injection ppbv***
Benzene	177.64	132.58
Toluene	296.65	164.68
Ethylbenzene	19.83	27.10
m/p-Xylene	81.42	98.95
o-Xylene	25.78	51.99

\*Analytical results of University of Connecticut Environmental Research Institute

\*\*2 replicates; \*\*\*3 replicates; parts per billion by volume