

# Volatile and non-volatile compounds in irradiated semi-rigid crystalline poly(ethylene terephthalate) polymers

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*In this study two different semi-rigid crystalline and oriented polyethylene terephthalate materials were used and were irradiated at 25-kGy dose at room temperature by using a caesium <sup>137</sup> radiator. Volatile and non-volatile compounds present in the irradiated materials were identified and quantified. The qualitative results obtained from HS/GC/TCD/FID analysis at room temperature showed volatiles could not be identified. The HS/GC/MSD analysis performed at 106°C showed that the irradiation generated 668–742 µg/kg formic acid, 868–922 µg/kg acetic acid, 17–32 µg/kg 1,3-dioxolane, and 47–71 µg/kg 2-methyl-1, 3-dioxolane based on PET weight. The results obtained from the thermal desorption and GC/MSD performed at 200°C showed that 10–12 mg/kg acetaldehyde, 479–975 µg/kg 1,3-dioxolane, and 6.6–11.2 mg/kg methyl-1, 3-dioxolane were detected after irradiation. The concentrations of the two dioxolanes found from thermal desorption were much higher than those observed in the HS, although formic and acetic acids were not detected. It is possible that the formic and acetic acids produced by irradiation underwent further reactions with ethylene glycol during thermal desorption to form the dioxolanes. The soluble solid extracted from various PET specimens before and after irradiation were in a range of 0.67–0.78%. PET cyclic trimer is the major*

*component and is present at 0.41–0.50%, accounting for more than 50% of the percent total solid in PET. Statistically, irradiation did not increase the soluble solid and cyclic trimer. The overall results suggest that 25-kGy irradiation had a significant effect on increasing the volatile but not the non-volatile compounds detected in the PET specimens.*

**Keywords:** PET, poly(ethylene terephthalate), volatiles, non-volatiles, irradiation

**Abbreviations:** PET, poly(ethylene terephthalate); HS, headspace; GC, gas chromatograph; TCD, thermal conductivity detector; FID, flame ionization detector; MSD, mass spectrometric detector

## Introduction

Irradiation effectively reduces and eliminates food-borne pathogens in foods. Foods are packaged before irradiation to reduce the points at which pathogens are introduced into foods. During irradiation, the packaging material and any additives that were used in the package could potentially undergo chemical changes, including cross-linking and degradation. The degradation products formed upon irradiation could migrate into food during storage and pose a safety risk. Packaging materials are selected by their resistance to, or stability of, the material to chemical changes when irradiated at commercial doses. The chemical changes and migration characteristics of the degradation products formed in newer packaging materials have not been fully investigated. This has become an impediment to large-scale implementation of food irradiation.

Polyethylene terephthalate (PET) is the most commonly used polymer by the food industry because it is good barrier and can be recycled safely for food use. PET is widely used and can be manufactured into homo- and co-polymers with varying % crystallinity and orientation for many application purposes. PET

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films have already been approved by the FDA for pre-packaged irradiated foods but not the rigid structure. In this study, two semi-rigid PET materials were irradiated at ambient temperature with a 25-kGy dose by gamma radiation. The objective of this study was to determine the effects of irradiation on these materials by comparing the levels of volatile and non-volatile compounds in the materials before and after irradiation.

## Materials and methods

### *Test materials*

Crystalline and oriented semi-rigid PET homopolymer with the following properties were used: density 1.36 g/cm<sup>3</sup>, 25% crystallinity, and 0.30–0.33 mm thick. Crystalline and oriented semi-rigid PET copolymer were 1.5 mole % isophthalic acid comonomer with 1.37 g/cm<sup>3</sup> density, 30% crystallinity, and 0.28–0.30 mm in thickness. Both were supplied by Shell Chemical Company (Akron, OH).

### *Chemicals*

Reagent, HPLC grade, or the highest purity available chemicals were used. Acetic acid, 1,4-dioxane and methylene chloride were purchased from Fisher Scientific Company (Hanover Park, IL). Acetone, acetaldehyde, 1,4-dioxane, 1,3-dioxolane, and 2-methyl-1,3-dioxolane were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI).

### *Apparatus*

A six-unit extraction heater was used for extracting soluble solid from the test specimens with boiling methylene chloride solvent. A high performance liquid chromatography (HPLC) system consisting of a Waters 600E system controller interfaced with a 9100 Varian Autosampler, Waters 486 tunable UV detector and Varian Star Workstation software were used for quantification of PET cyclic trimer in the solvent extract. A Varian 3400 GC with thermal conductivity detector (TCD) and flame ionization

detector (FID) and Varian Star Workstation software, and a Hewlett Packard 5890 GC equipped with a 5970 MSD and Chemstation software were used for headspace analysis in the test specimens vials. A Perkin Elmer Thermal Desorber (Model ATD 400) interfaced with a Hewlett Packard 5890 GC and a 5972 MSD operated by Chemstation software were used to analyse volatiles in the PET specimens.

### *Test specimen preparation*

Small PET sheets (1.0 cm × 6.4 cm each) were cut, blotted with hexane twice to remove any organic residues on the surface, and kept in a desiccant vacuum chamber for 24 h. For each test specimen, ten sheets were stacked longitudinally and placed in a 20-ml headspace glass vial (2.3 cm o.d. × 7.5 cm h) and purged with ultra pure nitrogen before the vial was closed with an aluminium-lined silicone septum and aluminium seal. Five replicates of test specimen were prepared for each non-irradiated (NIR) and irradiated (IR). Five empty vials were also prepared for NIR and IR.

### *Radiation source, techniques, and dosimetry*

The self-contained gamma-radiation source (a custom made irradiator) has 23 <sup>137</sup>CsCl pencils placed in an annular array around a 63.5 cm-high stainless-steel cylindrical chamber with a 22.9 cm internal diameter. The source strength at the time of this study was *ca* 117 355 Ci (4.34 PBq) with a dose rate of 0.10 kGy min<sup>-1</sup>. The dose rate was established by using National Physical Laboratory (Middlesex, UK) dosimeters. Corrections for source decay were made monthly. Routine dosimetry was performed using 5-mm-diameter alanine dosimeters (Bruker Instruments, Rjeomstettem, Germany), and the free-radical signal was measured using a Bruker EMS 104 EPR Analyzer (ASTM 1996, 1997). Samples were maintained at 25 ± 1°C during irradiation through the thermostatically controlled injection, into the top of the irradiation chamber, of the gas phase from liquid nitrogen. Sample temperature was monitored continuously during irradiation with thermocouples taped to two samples in the chamber. Based on measurements of dosimeter responses, the actual dose was 24.9 kGy within ±2% of the target dose.

### Analysis of volatile compounds

**Headspace gas chromatograph.** A few test specimen vials were subjected to headspace analysis by using a gas chromatograph equipped with a TCD and FID. One ml of HS gas was withdrawn at room temperature by using either a 2.5 or 5 ml Sample Lock gas-tight syringe (Hamilton, Reno, NV). The gas was pressurized to 0.1 ml before direct injection onto a GS-Q column (30 m, 0.53 mm i.d.) (J&W Scientific, Folsom, CA), that was connected to a TCD in series with an FID. The column temperature was programmed initially at 40°C for 4 min, increased by 15°C/min to 200°C, and held for 5 min. The temperature of both injector and detector was maintained at 220°C. The carrier gas was nitrogen, chosen to offset the nitrogen used to purge the test specimen bottles prior to irradiation. The unknown peaks were identified based on the retention times of standards.

The remaining test specimens were analysed by using a gas chromatograph interfaced with a mass spectrometer (GC/MSD) system. For these analyses, each test specimen was preheated for 20 min in a forced air oven at 106°C for 20 min, selected for quick analysis, prior to GC/MSD analysis. After preheating, two ml of HS were drawn from the test specimen by using a preheated 5-ml Pressure-Lok gas syringe (Precision Sampling Corp., Baton Rouge, LA). After drawing 2 ml of HS the test specimen was further heated again for *ca* 3 min. The needle of the syringe was left in the vial, and the valve opened to minimize any condensation of volatiles prior to injection. After reheating, the syringe valve was closed and the syringe removed from the test specimen. The HS aliquot was injected onto gas chromatograph. GC parameters were as follows: temperature (°C); injector 200, and detector interface 225. The injector was operated in the split-splitless mode with the split vent opened 1 min after injection. The volatiles were separated on an Rt<sub>x</sub>-5 FSOT column (60 m, 0.32 mm i.d., 1.5 µm) (Restek, Bellefonte, PA). The GC temperature programme was as follows: 1 min at 0°C, ramp at 25°C/min to 125°C, hold 1 min, ramp at 5°C/min to 165°C, and hold for 13 min. Total run time was 20 min. MSD parameters were as follows: MSD operated in the scan mode, scan time from 5.5 to 20 min; scan range from 40 to 300 daltons; scan rate was 1.7 scans/s. Library searches of the mass spectra identified the presence of formic acid, acetic acid, 1,3-dioxolane, and 2-methyl-1, 3-dioxolane in the irradiated PET

specimens, and acetic acid and 2-methyl-1, 3-dioxolane in the non-irradiated PET specimens.

**Quantification of volatile compounds in headspace.** The concentration of volatiles in the PET specimen vials was determined by using an external calibration procedure. Non-irradiated PET specimens were cut into sheets with the same dimension as the irradiated PET and vacuum-dried at 40°C for 48 h prior to use. Ten PET sheets were placed in an HS vial and subsequently spiked with 5 µl of a mixed standard containing acetic acid and 1,4-dioxane dissolved in methanol. The 1,4-dioxane was used for substitution of 1,3-dioxolane and 2-methyl-1, 3-dioxolane, which were unavailable at the time of testing. The vial was quickly sealed at room temperature before GS/MSD analysis by using the same conditions as the irradiated PET vials. Four different concentrations were prepared in a range of 87–686 µg/kg acetic acid and 43–174 µg/kg 1,4-dioxane. Quantification of the unknowns was based on the linear regression analyses of the acetic acid and 1,4-dioxane. The line equation for acetic acid was used to determine formic acid and acetic acid concentrations, and the equation for 1,4-dioxane was used to determine 1,3-dioxolane and 2-methyl-1, 3-dioxolane concentrations. The limit of detection (LOD) was defined as three times standard deviation of the specimen analysis. It was approximately 9 µg/kg for formic acid and acetic acid, and 18 µg/kg for both dioxolanes. No adverse effects were observed with the addition of 5 µl of methanol to the non-irradiated PET specimens.

**Thermal desorption.** The PET test specimens that were previously analysed by headspace and GC/MSD were subsequently subjected to thermal desorption. This analysis was performed on five of ten PET sheets contained in a specimen vial, for a total of two specimen vials. Each PET sheet was trimmed to obtain  $0.1225 \pm 0.0025$  g, cut into four small chips and loaded in a sample tube of the ATD 400 thermal desorber interfaced to the HP 5890 GC/MSD system. The loaded sample tubes were purged with helium and heated at 200°C for 5 min in the ATD 400 to thermally desorb volatile compounds from the PET. The desorbed volatiles were trapped on Tenax trap (2.75 mm i.d., 20 mm) held at –30°C. The Tenax trap was ballistically heated to 300°C, and the trapped volatiles were desorbed onto the gas chromatograph for analysis. The carrier gas was helium at a flow of 1–2 ml/min. The injection

was split at a ratio of 10:1 onto a DB-5ms capillary column (30 m, 0.25 mm i.d., 1.0  $\mu$ m) (J&W Scientific, Folsom, CA). The GC temperature programme was as follows: 5 min at 40°C, ramp at 10°C/min to 200°C, and hold for 6.5 min. Total run time was 27.5 min. MSD parameters were as follows: MSD operated in the scan mode; scan time from 1 to 27.5 min; scan range was from 30 to 300 daltons; scan rate was 2.39 scans/s. Library searches of the mass spectra confirmed the presence of acetaldehyde, acetone, 1, 3 dioxolane, 2-methyl-1, 3 dioxolane, and toluene in both irradiated and non-irradiated PET specimens.

*Quantitation of volatiles by thermal desorption.* Concentrations of the volatiles detected in PET specimens were determined via external calibration using a mixture of acetaldehyde, acetone, 1,3-dioxolane, and 2-methyl-1, 3-dioxolane, which were dissolved in pure water, and toluene in methanol. The initial concentration was 780  $\mu$ g/ml of 1,3 dioxolane, 910  $\mu$ g/ml of 2-methyl-1, 3-dioxolane, 590  $\mu$ g/ml of acetone, 2810 ( $\mu$ g/ml of acetaldehyde, and 820  $\mu$ g/ml of toluene. The mixture was further diluted with water to various concentrations to bracket the unknown concentrations. Three replicates of these solutions were used and were subjected to the same thermal desorption conditions as the PET specimens. The peak response area was recorded and used to construct a calibration curve for determining the amount of the compound desorbed from the PET specimen. The LOD was defined as three times standard deviation of the specimen analysis. It was approximately 155 ng/ml for acetaldehyde, 146 ng/ml for acetone, 35 ng/ml for 2-methyl-1, 3-dioxolane, 7 ng/ml for 1,3-dioxolane, and 2 ng/ml for toluene. Reproducibility of the standards calibration was in a range of 2–13%.

#### *Analysis of non-volatile compounds*

Non-volatile compounds were determined by using solvent extraction and measured by percent soluble solid. The extraction of soluble solids from PET specimens was performed by using methylene chloride (MC) solvent. MC was selected for its tendency to make the PET matrix swell. As a result, the extraction can be performed more rapidly than with other food-simulating solvents. It is probably the worse case when compared to all food simulants for PET (private

communication with Office of Pre-market Approval (OPA's staff).

*Soxhlet extraction.* Eight non-irradiated PET sheets (1.9 cm  $\times$  3.2 cm) of each PET were extracted with methylene chloride (MC) solvent for 24, 48, 72, or 96 h. Two replicates were used at each extraction time. The MC extract was concentrated by rotary evaporation to 2–3 ml, filtered with 0.22  $\mu$ m Teflon membrane, and dried by vacuum centrifuge (Speed Vac, Servant, MA). The MC soluble solids were gravimetrically measured to determine the percent total non-volatile extractable in the PET, and the optimum extraction time. The optimal extraction time was observed to be 24 h.

*Measure of non-volatile soluble solid extractable.* MC soluble solids extracted from non-irradiated and irradiated PET specimens were measured and used to determine percent of soluble solid. After a 24-h soxhlet extraction by using boiling MC solvent, the MC extract was filtered through a hydrophobic membrane and made up to 100 ml with pure MC. Two ml of the solution was pipetted to a 10 ml test tube (pre-cleaned, dried, and weighed), and vacuum-centrifuged to dryness. The solid was reconstituted with 0.6 ml MC solvent to limit concentration of the PET cyclic trimer in the solution in a range of 1–500 mg/l and subject to HPLC analysis. Then 98 ml of the solution was concentrated to less than 5 ml by using a simple distillation apparatus. The concentrate was subsequently dried by vacuum centrifuge before the soluble solids weight was measured and used to calculate percent of MC soluble solids based on the initial PET weight before extraction.

*High performance liquid chromatograph (HPLC).* The soluble solids in the 0.6 ml MC solvent aforementioned were analysed by using the mobile phases shown in table 1, a modification of those used by Begley and Hollifield (Begley and Hollifield 1989). An aliquot of 10  $\mu$ l of the reconstituted MC soluble solids was injected onto a C8 Zorbax column (6.5 cm, 3.9 mm i.d., DuPont, DE) to which a C8 guard column was first attached, separated and quantified by UV detection at a wavelength of 254 nm.

*Quantitation of PET cyclic trimer.* The concentration of PET cyclic trimer present in the MC soluble solids was determined by using an external calibration. Standard PET cyclic trimer was dissolved in MC at various concentrations ranging

Table 1. Mobile phases for HPLC analysis of PET oligomers.

Run time (min)	Flow rate ml/min	% Mobile phase <sup>a</sup>		
		A	B	C
0	1.0	63	18	19
1.10	1.0	63	18	19
8.0	1.0	30	57	8
14.0	1.0	30	64	6
15.0	1.0	15	85	0
26.0	1.0	15	85	0
30.0	1.0	63	18	19

<sup>a</sup> A = 100% water, B = 100% acetonitrile, C = 1% acetic acid/ water (v/v).

from 0.5 to 635 mg/l to construct a calibration curve. The curve was fitted with a line equation and used to determine the unknowns in the MC soluble solids. The limit of detection (LOD) was defined as three times the signal to noise ratio (S/N) of the peak and it was approximately 500 µg/l in the solution.

*Changes in peak areas of an unidentified compound.* The changes in peak areas of unidentified soluble PET oligomers detected by the HPLC were determined and calculated by using the integrated peak area of oligomers obtained before and after irradiation. Because the high molecular weight oligomers are less important in migration, only the low molecular weight linear oligomers were considered.

### Statistical analysis

*t*-test and one way ANOVA of SPSS Statistical Analysis and Graphics Software for Windows (SPSS, Chicago, IL) were used.

## Results and discussion

### Volatile compounds

*Volatiles by HC/GC/TCD/FID.* Representative TCD chromatograms of the GC analysis of HS aliquots sampled at room temperature from empty HS vials, and vials containing either irradiated or non-

irradiated PET are shown in figure 1. Qualitatively, both oxygen and hydrogen were present in the HS vials and co-eluted at 1.41–1.44 min, while carbon dioxide eluted at 1.87–1.90 min. The magnitude of these peak areas was relatively the same for the HS vials as for the empty vials; thus it is unlikely that the irradiation caused the generation of these gases.

Representative FID chromatograms of the GC analysis of HS aliquots sampled at room temperature from empty HS vials and vials containing either irradiated or non-irradiated PET are shown in figure 2. Qualitatively, the irradiation did not increase areas of the acetaldehyde peak at 10.3 min. The acetone peak eluted at 13.3 min and heptane peak eluted at 19.5 min and are likely inadvertent laboratory contaminants. These were previously identified by GC/MSD.

*Volatiles by HS/GC/MSD.* Preliminary headspace GC analyses of non-irradiated PET strips were performed to determine the optimum equilibration time and temperature. No volatiles were observed when the strips were analysed after exposure to 75°C for up to 1 h. Trace levels of volatiles were observed after exposure to 90°C for up to 1 h. However, when the strips were exposed to 106°C the volatiles observed were easily determined, and the levels remained constant after 15 min up to 1 h equilibration. Since acetaldehyde is the major volatile thermal decomposition product which is produced during the thermoforming processes to make PET containers the time and temperature selected for headspace sampling was selected with caution. Also, the absence of formic and acetic acid in the volatiles' chromatograms from the thermal desorption experiments suggested that other reaction processes were occurring during the heating of the PET strips. Since our objective was to determine the radiolytic products and not thermal decomposition products of PET we selected 20 min at 106°C as the headspace equilibrium conditions prior to GC/MS analysis.

Total ion chromatograms (TIC) of volatiles present in the headspace of non-irradiated and irradiated PET homopolymer and copolymer are shown in figures 3 and 4, respectively. The chromatograms indicate that the major volatile compounds that evolved from the PET specimens are formic acid, acetic acid, 1, 3-dioxolane and 2-methyl-1, 3 dioxolane. The concentrations of these compounds before and after irradiation are shown in table 2. The concentrations of

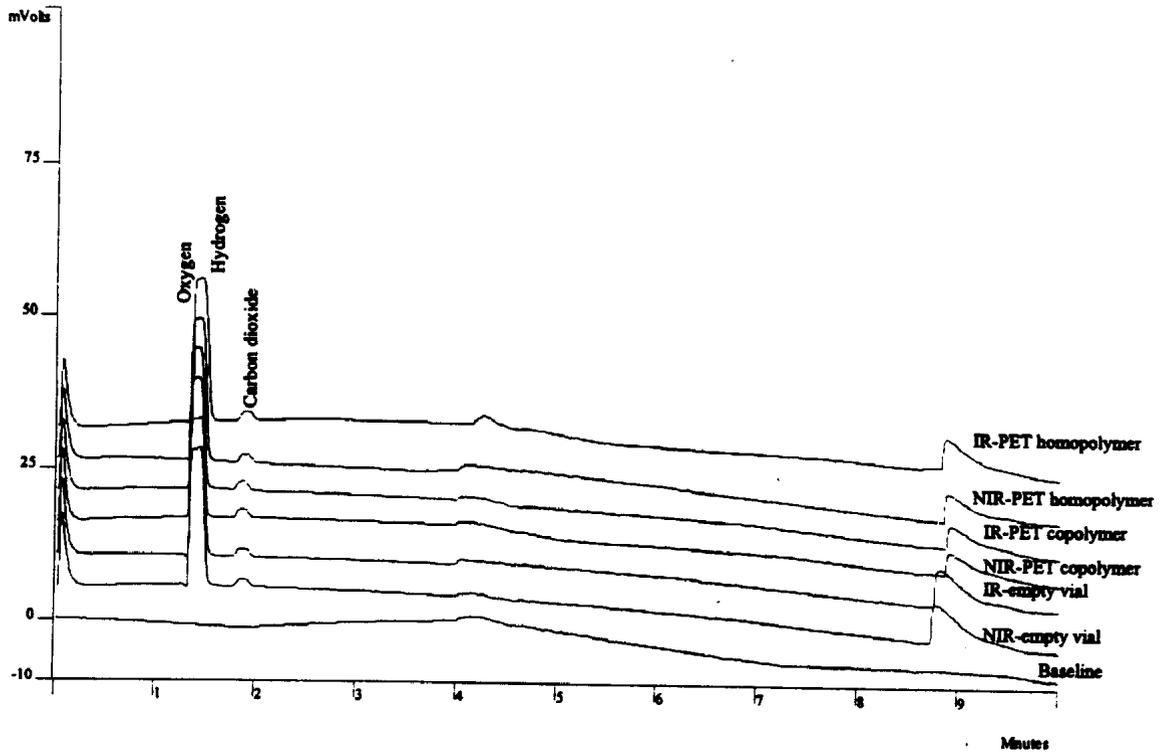


Figure 1. Gas chromatograms of headspace gas in the empty vials and vials containing PET before (NIR) and after (IR) 25-kGy gamma irradiation against baseline, detected by TCD.

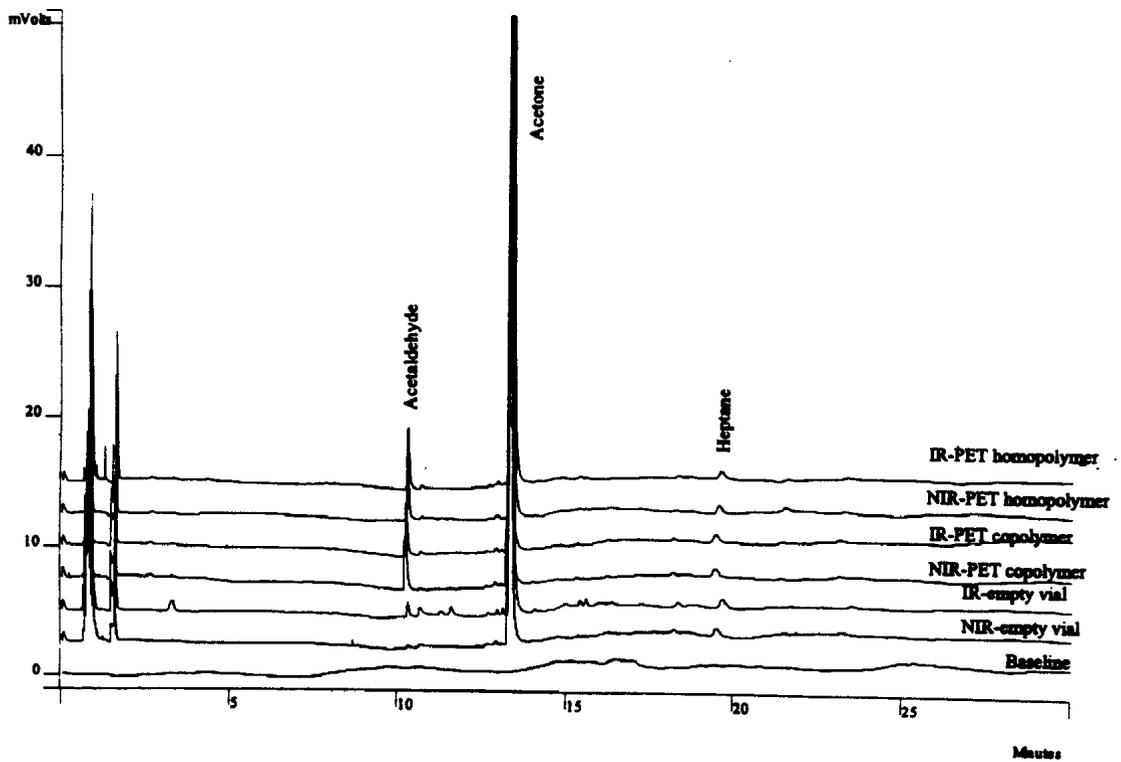


Figure 2. Gas chromatograms of headspace gas in the empty vials and vials containing PET before (NIR) and after (IR) 25-kGy gamma irradiation against baseline, detected by FID.

Compounds in poly(ethylene terephthalate) polymers

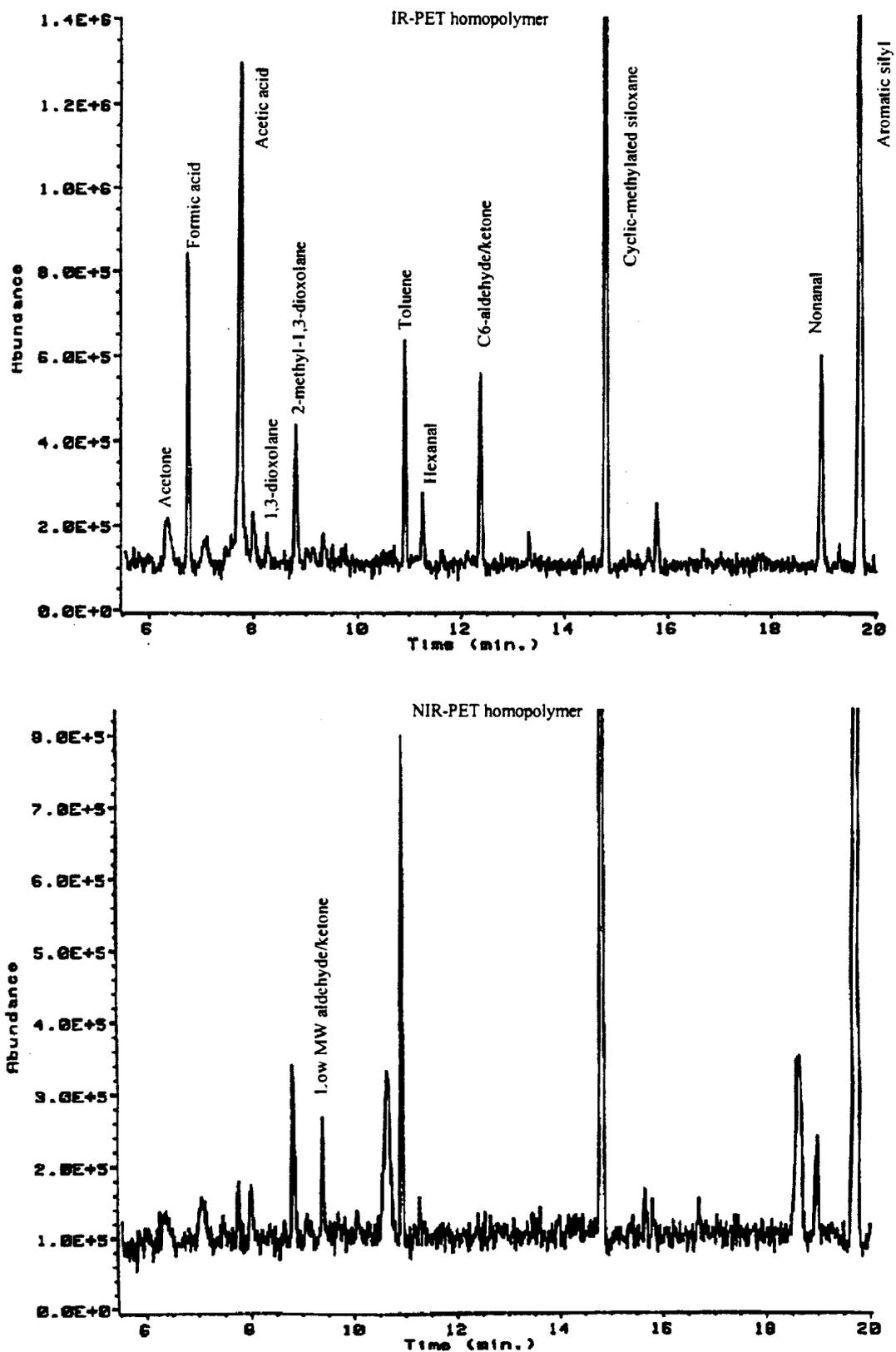


Figure 3. Total ion chromatograms of the HS gas in the vials containing irradiated (IR) (top) and non-irradiated (NIR) (bottom) PET homopolymer specimens, detected by MSD.

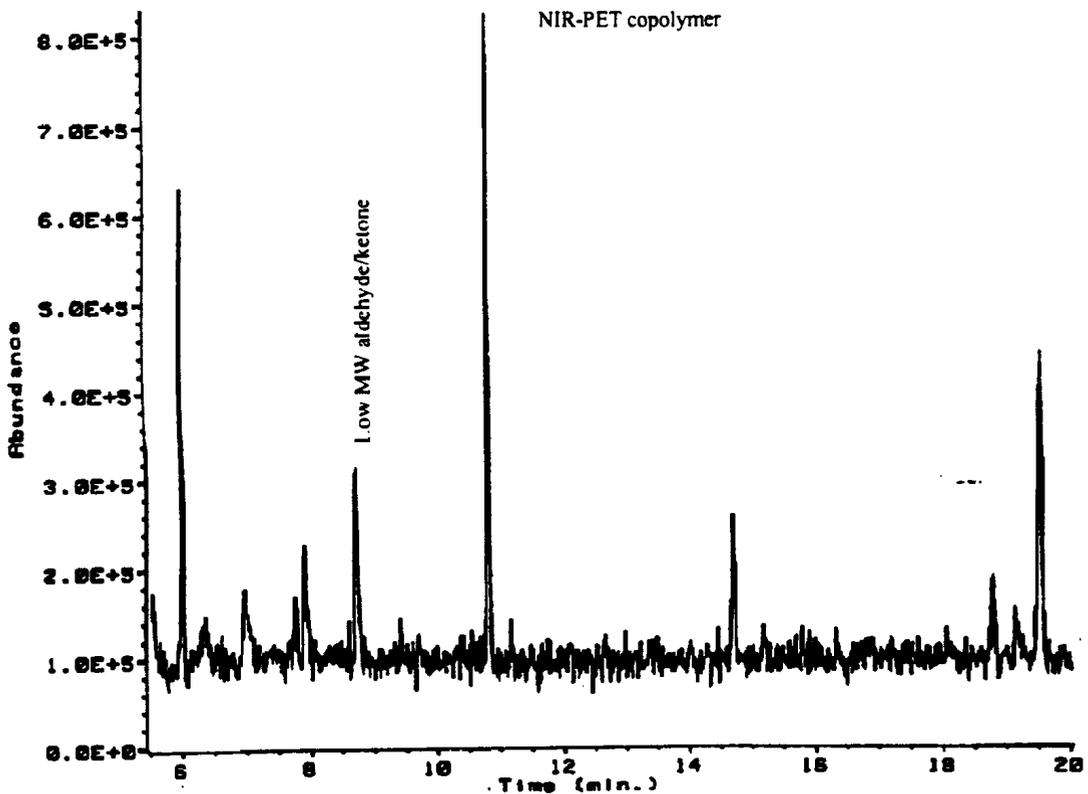
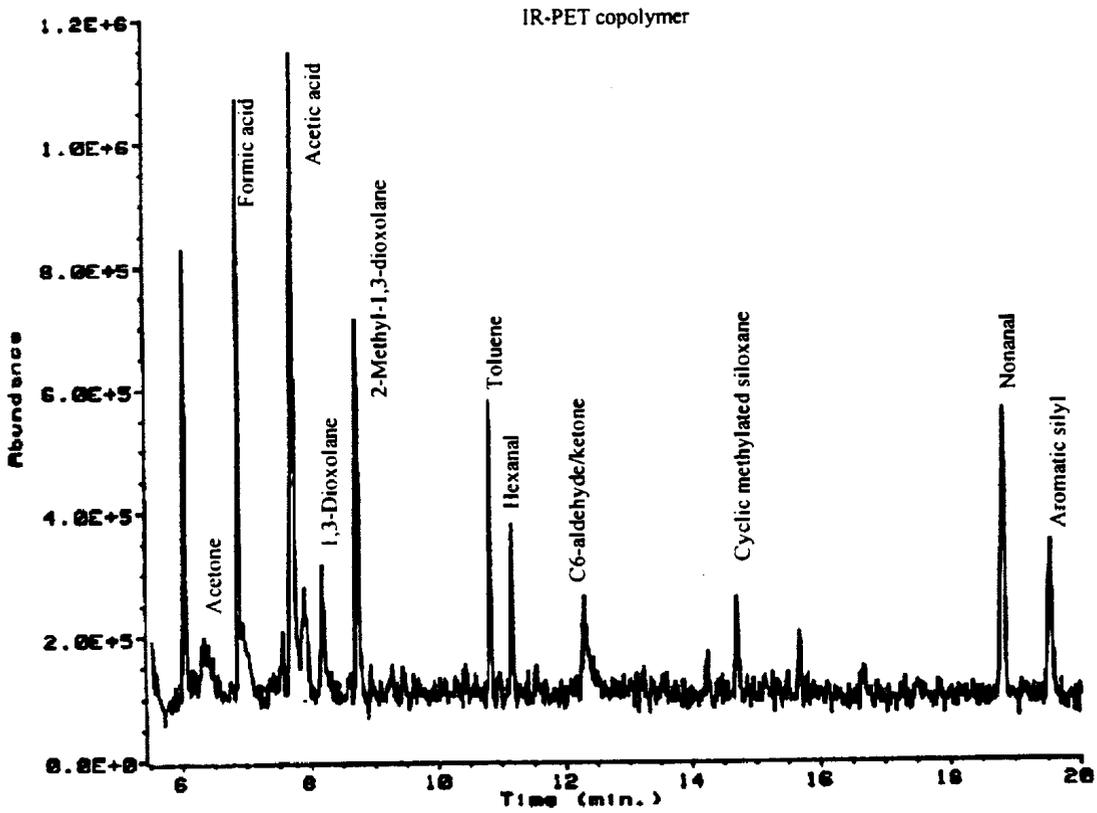


Figure 4. Total ion chromatograms of the HS gas in the vials containing irradiated (IR) (top) and non-irradiated (NIR) (bottom) PET copolymer specimens, detected by MSD.

Compounds in poly(ethylene terephthalate) polymers

Table 2. Concentrations ( $\mu\text{g}/\text{kg}$ ) of volatiles evolved from non-irradiated (NIR) and irradiated (IR) PET specimens heated at  $106^\circ\text{C}$  into HS analyzed by GC-MSD.

PET	Rep	Average concentrations $\pm$ SD			
		Formic Acid	Acetic acid	1,3-dioxolane	2-Methyl-1,3 dioxolane
<i>Homopolymer</i>					
NIR	1	< LOD	< LOD	< LOD	34
IR	2	668	922	17	47
<i>Copolymer</i>					
NIR	3	< LOD	< LOD	< LOD	$31 \pm 5$
IR	3	$(742 \pm 5)^{\text{S}}$	$(868 \pm 77)^{\text{S}}$	$(32 \pm 6)^{\text{S}}$	$(71 \pm 7)^{\text{S}}$

SD = Standard deviation.

LOD = Limit of detection ( $9 \mu\text{g}/\text{kg}$  for both acids,  $18 \mu\text{g}/\text{kg}$  for both dioxolanes).

<sup>S</sup>Significant at  $P < 0.05$ .

formic and acetic acids in both non-irradiated PETs are below LOD ( $9 \mu\text{g}/\text{kg}$ ), but those in both irradiated PETs are approximately  $700 \mu\text{g}/\text{kg}$  formic acid ( $668\text{--}742 \mu\text{g}/\text{kg}$ ) and  $900 \mu\text{g}/\text{kg}$  acetic acid ( $868\text{--}922 \mu\text{g}/\text{kg}$ ). The concentration of 1,3-dioxolane in both non-irradiated PETs is below LOD ( $18 \mu\text{g}/\text{kg}$ ), but the concentration in the irradiated PET copolymer is approximately double that of PET homopolymer (32 versus  $17 \mu\text{g}/\text{kg}$ ). The concentration of 2-methyl-1, 3-dioxolane before irradiation is relatively the same magnitude ( $31\text{--}34 \mu\text{g}/\text{kg}$ ) in both PETs but the concentration in the irradiated PET copolymer is almost twice the level seen in the homopolymer (71 versus  $47 \mu\text{g}/\text{kg}$ ). The source of the other peaks shown in the TICs of figures 4 and 5 is laboratory contamination; they were not associated with the PET specimens, and no quantitation was attempted. It should be noted that acetaldehyde, a thermal degradation product formed during PET processing, is generally present in PET (Dong *et al.* 1980) but was not detected because the HS-GC-MSD conditions used were not adequate for the determination.

*Volatiles by thermal desorption.* Total ion chromatograms (TIC) of volatiles present in non-irradiated and irradiated PET homopolymer and copolymer specimens are shown in figures 5 and 6, respectively. The chromatograms indicate that acetaldehyde, acetone, 1,3-dioxolane, 2-methyl-1, 3-dioxolane and toluene were detected in the PET specimens. The concentration of the volatiles desorbed from the non-irradiated and irradiated PET specimens was determined and is shown in table 3. After irradiation the concentration of acetone increased from approximately  $138 \mu\text{g}/\text{kg}$  to  $322 \mu\text{g}/\text{kg}$  while those of toluene are relatively the same magnitude at approximately  $20 \mu\text{g}/\text{kg}$ . The acetone and toluene are likely inadvertent contaminants

because they are commonly laboratory solvents. They were quantified to offset their presence along with other volatiles in the PET test specimens. Acetone was previously detected in irradiated PET films (El Makhzoumi 1994), but not in work recently reported by Demertzis and co-workers (Demertzis *et al.* 1999). In table 3 the concentrations of acetaldehyde in homopolymer are relatively unchanged at approximately  $10 \text{mg}/\text{kg}$  after irradiation, but those in the copolymer decreased from  $24.1 \text{mg}/\text{kg}$  before irradiation to  $12.3 \text{mg}/\text{kg}$  after irradiation. Formic and acetic acids were observed in the HS but not after thermal desorption. These acids may react with ethylene glycol to form the dioxolanes, resulting in higher concentrations of the dioxolanes than those observed in the HS. After irradiation the concentrations of 1,3-dioxolane increased from  $12.7 \mu\text{g}/\text{kg}$  to  $479 \mu\text{g}/\text{kg}$  in homopolymer, and from  $15.6 \mu\text{g}/\text{kg}$  to  $975 \mu\text{g}/\text{kg}$  in copolymer. After irradiation the concentrations of 2-methyl-1, 3-dioxolane increased from  $3 \text{mg}/\text{kg}$  to  $6.6 \text{mg}/\text{kg}$  in homopolymer, and from  $2 \text{mg}/\text{kg}$  to  $11.2 \text{mg}/\text{kg}$  in copolymer.

Thermal desorption is a rapid technique to qualitatively identify the volatile and semi-volatile compounds present in the polymer. This technique has been recently utilized for analysis of irradiated polymers used in medical devices (Buchalla *et al.* 1999). Because the test specimen is heated quickly to desorb VOCs, heating the PET tends to have a great effect on the production of VOCs, and their potential interaction(s) with existing compounds in the polymer. This technique should be further investigated to determine if there are any induced reactions between pre-existing or radiolysis compounds in the test specimen during analysis.

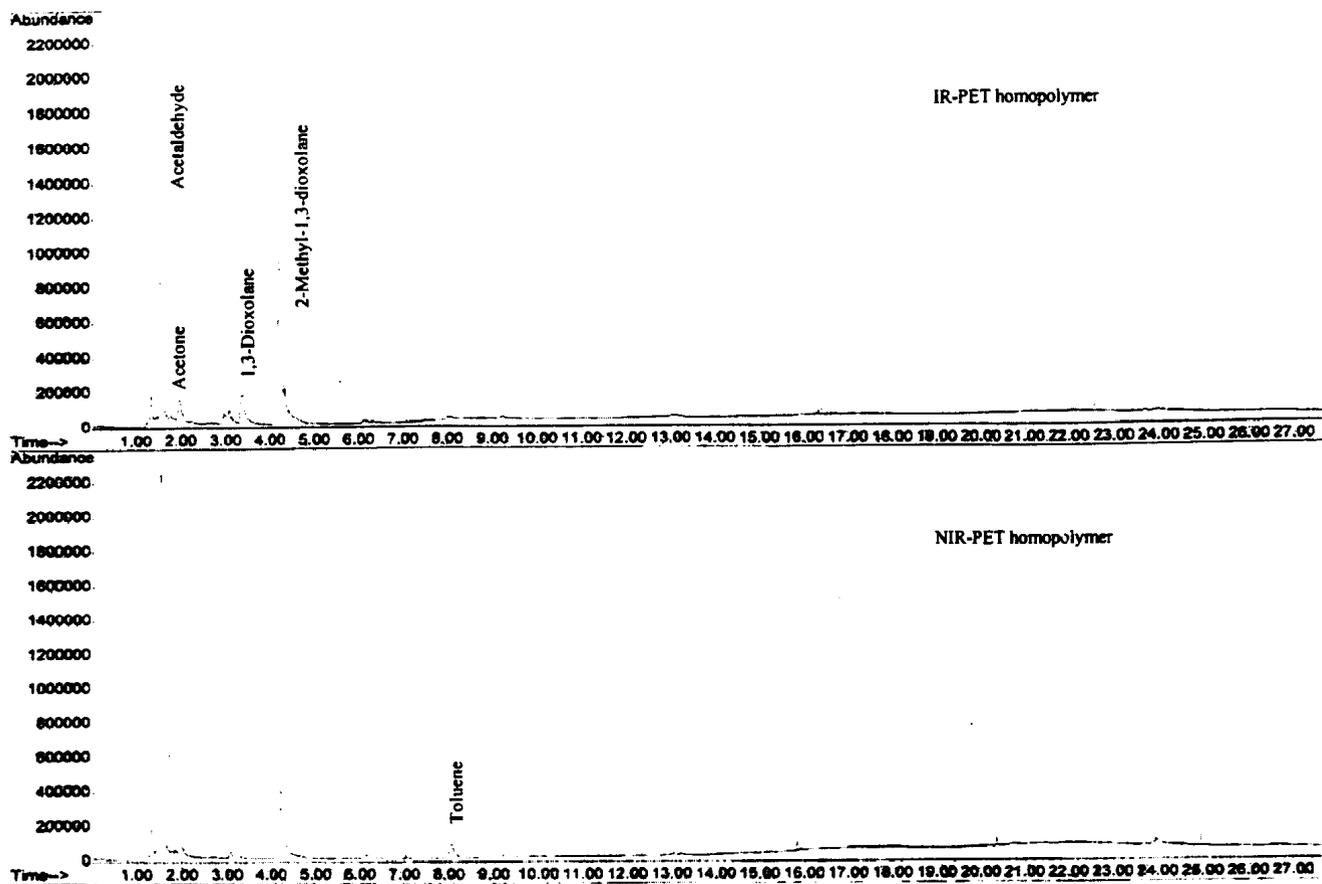


Figure 5. Total ion chromatographs of volatiles in the irradiated (IR) (top) and non-irradiated (NIR) (bottom) PET homopolymer specimens analyzed by thermal desorption.

### Non-volatile compounds

**Soluble solids.** The percent of methylene chloride (MC) soluble solids extracted from the non-irradiated and irradiated PET test materials was determined and is shown in table 4. Statistically, the irradiation did not significantly change soluble extracts in any PET specimens.

**Quantification of PET oligomers.** High performance liquid chromatograms of extracts obtained from non-irradiated and irradiated PET are shown in figure 7. There are several oligomers but the most abundant one is cyclic trimer. Concentrations of the PET cyclic trimer present in the soluble extract obtained from PET specimens before and after irradiation were determined and they are shown in table 5. The results suggest that irradiation had no significant effect on the PET cyclic trimer in the PET specimens. A lower molecular weight oligomer than

the cyclic trimer eluted at 14 min may be dimer or linear oligomer. Changes in concentrations of this linear oligomer were determined in ratios of peak areas of irradiated to those non-irradiated, and they are shown in table 5. The ratios are relatively unity, indicating that irradiation had no significant effect on the linear oligomer concentrations present in these PET specimens.

### Conclusion

There is a significant increase in concentration of these volatile compounds in both PETs after irradiation. The results obtained from this study indicate that volatiles detected in non-irradiated and irradiated PET specimens are relatively the same; no new chemicals were generated. Major volatiles are acetaldehyde, formic acid, acetic acid, 1,3-dioxolane,

Compounds in poly(ethylene terephthalate) polymers

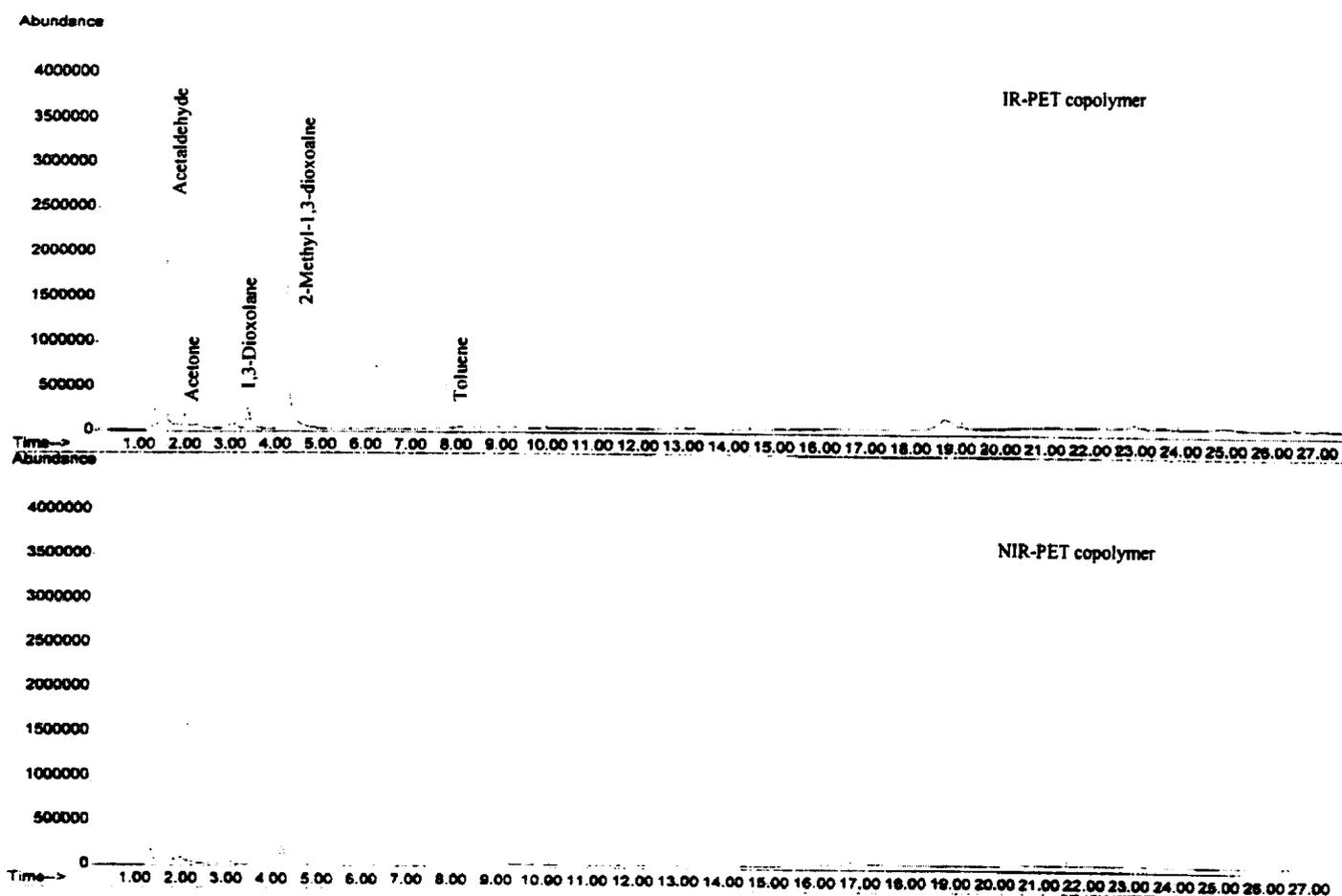


Figure 6. Total ion chromatographs of volatiles in the irradiated (IR) (top) and non-irradiated (NIR) (bottom) PET copolymer specimens analysed by thermal desorption.

Table 3. Concentrations of volatiles desorbed from non-irradiated (NIR) and irradiated (IR) PET specimens heated to 200°C and analyzed by thermal desorption and mass spectrometry.

PET	Rep	Average concentrations ± SD				
		Acetaldehyde <sup>a</sup> (mg/kg)	Acetone <sup>a</sup> (µg/kg)	1,3-Dioxolane (µg/kg)	2-Methyl-1,3-dioxolane (mg/kg)	Toluene <sup>a</sup> (µg/kg)
<i>Homopolymer</i>						
NIR	10	11.6 ± 1.0	138 ± 83	12.7 ± 2.7	3.0 ± 0.3	21.0 ± 4.2
IR	10	(10.0 ± 0.5) <sup>S</sup>	322 ± 67	(479 ± 181) <sup>S</sup>	(6.6 ± 0.5) <sup>S</sup>	21.5 ± 9.0
<i>Copolymer</i>						
NIR	10	24.1 ± 1.5	99 ± 30	15.6 ± 5.0	2.0 ± 0.1	16.9 ± 5.0
IR	10	(12.3 ± 1.1) <sup>S</sup>	314 ± 34	(975 ± 72) <sup>S</sup>	(11.2 ± 1.2) <sup>S</sup>	14.6 ± 1.4

<sup>a</sup> Inadvertent contaminants.

SD = Standard deviation.

<sup>S</sup> Significant at  $P < 0.05$ .

Table 4. Percent of soluble solid extracted from non-irradiated (NIR) and irradiated (IR) PET test materials.

PET	Rep	% Soluble solid	
		NIR	IR
Homopolymer	5	0.776 ± 0.066	(0.784 ± 0.062) <sup>IS</sup>
Copolymer	5	0.672 ± 0.045	(0.681 ± 0.049) <sup>IS</sup>

<sup>IS</sup> Insignificant at P < 0.05.

and 2-methyl-1, 3 -dioxolane. Irradiation decreased concentrations of acetaldehyde, but increased concentrations of formic acid, acetic acid, 1,3-dioxolane, and 2-methyl-1, 3 -dioxolane. The non-volatiles detected in non-irradiated and irradiated PET specimens are a mixture of oligomers, mainly PET cyclic trimer. The results indicate that irradiation did not have a sig-

nificant effect on total extractable soluble solid, concentrations of PET cyclic trimer and linear oligomers in PET specimens. The overall results suggest that the 25-kGy irradiation had significant effects on volatiles but no effect on non-volatiles. These findings are consistent with those reported by Demertzis and coworkers (Demertzis *et al.* 1999).

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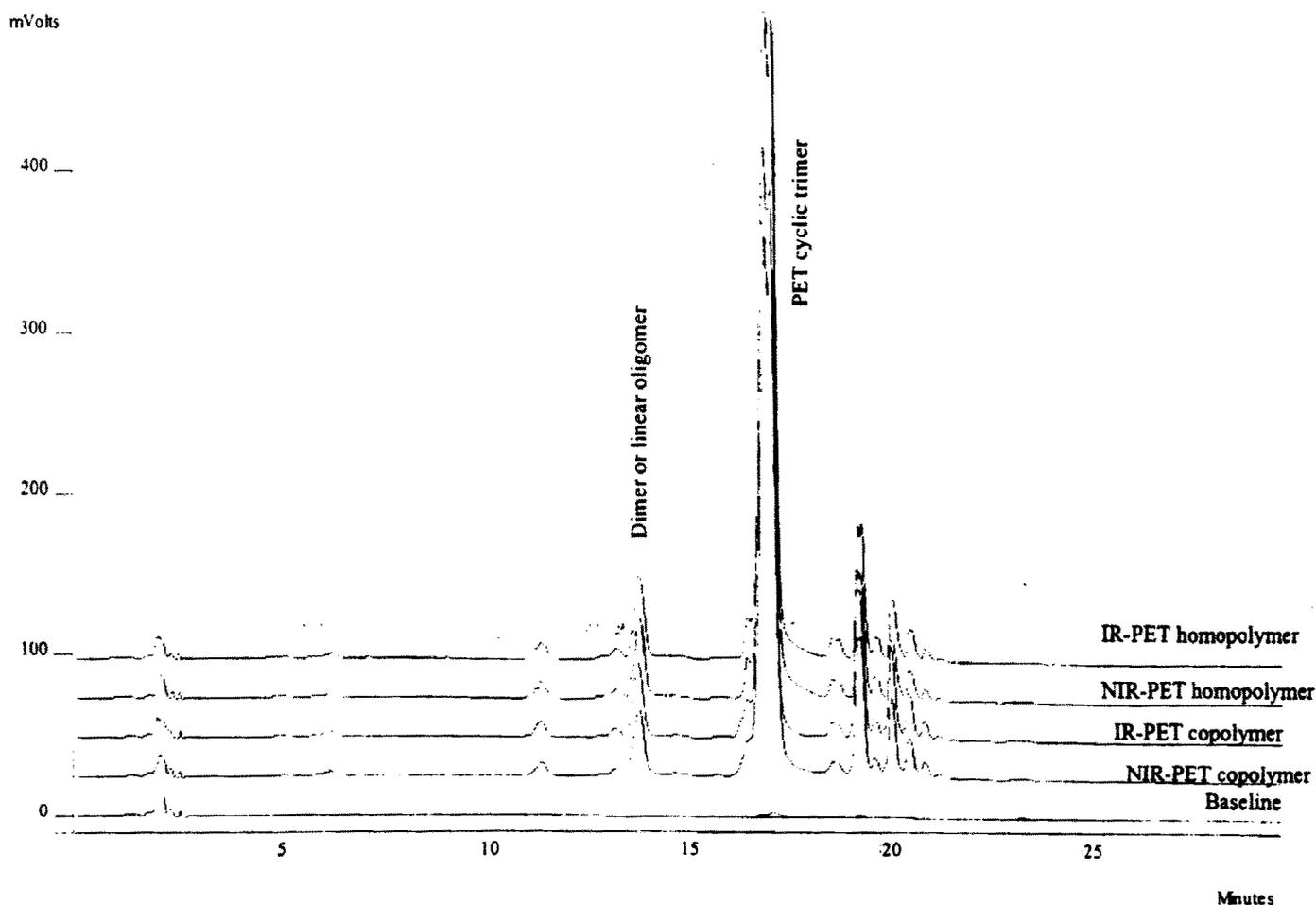


Figure 7. High performance liquid chromatograms of the soluble solid extracted from PET homo- and co-polymer before (NIR) and after (IR) 25-kGy gamma irradiation against baseline, detected by UV at 254 nm.

Table 5. Percent of PET cyclic trimer in soluble solid extracted from non-irradiated (NIR) and irradiated (IR) PET test materials and ratio of peak areas of linear oligomer with irradiation to those without.

PET	Rep	% Cyclic trimer (NIR)	% Cyclic Trimer (IR)	Ratio of peak areas of dimer of linear oligomer
Homopolymer	5	0.498 ± 0.005	(0.499 ± 0.008) <sup>1S</sup>	(1.01 ± 0.02) <sup>1S</sup>
Copolymer	5	0.406 ± 0.014	(0.407 ± 0.017) <sup>1S</sup>	(0.99 ± 0.02) <sup>1S</sup>

<sup>1S</sup> Insignificant at  $P < 0.05$ .

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