

Gas Chromatography

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Determination of Benzene, Acetaldehyde and Limonene in Polyethylene Terephthalate by Headspace GC

Introduction

Polymers play an ever-expanding role in our everyday lives. Some are easy to identify, such as food packaging, but many others

are hidden in the everyday things all around us, from automotive parts to electronic circuit boards, and the insulation of houses and buildings. The road to our current polymer-infused world began taking shape in the mid-1900s. In 1950, global polymer production was about two million tons¹. In the early 1970s, a trend of increasing polymer production began to emerge². By the year 2018, global polymer production was at about 360 million tons, with revenue of more than 700 billion USD, and packaging was long established as the front runner in polymer use³.

Polymers are inexpensive, easy to mold, and lightweight. These and various other attributes make polymers a popular choice for a multitude of commercial applications. Polymer recycling reduces environmental problems caused by polymeric waste accumulation generated from daily usage of polymer materials in packaging and construction. Increased recycling will lead to a decrease in oil consumption and green-house gas emissions, as well as a reduction in the use of other valuable natural resources. Polymer recycling is a rapidly growing industry, fueled by the increasing consumption of goods and the associated increase in landfill waste. The increasing quantity of recyclable materials is creating challenges for the recycling industry, as it is crucial that materials used both in the production of products and in the recycling process be consistent and free of impurities and contaminants. Regulatory pressure regarding recycled material has brought to light the challenges associated with the sorting and recycling processes of these materials. Global (or multinational) companies struggle to realize recycling commitments as they are faced with the dilemma of sorting materials and meeting quality control requirements⁴.

Plastic bottles made of polyethylene terephthalate (PET) have achieved a very high market share over the past decade, replacing glass bottles, cans, and beverage cartons, and are mainly used as one-way bottles. PET is made from terephthalic acid and ethylene glycol, with both substances combining to form long polymer chains. The reaction product is water, and the polymerization reaction is a multi-level process. PET is a colorless, transparent polymer that is almost unbreakable, yet easy to recycle. These desirable properties led to the widespread use of PET as a packaging material for beverages⁵.

PET is widely used in the beverage industry as it is easy to recycle, and the number of bottles being created from recycled material is increasing. To ensure safety and uniformity, the quality of recycled bottles need to be monitored and maintained. There are several steps in the quality control process, and within this work, the determination of benzene, acetaldehyde, and limonene are highlighted.

Benzene is a degradation product of polymer impurities in post-consumer PET recyclates. Most probably, polyvinyl chloride (PVC) leads to traces of benzene under thermal conditions during re-extrusion to PET recyclates or preforms⁶. The concentrations determined are in most cases below 0.2 mg/kg. However, at times slightly higher concentrations of benzene are detectable. Owing to the toxicological properties of benzene, it is important to control the concentrations in post-consumer PET recyclates.

Acetaldehyde is a thermal degradation product of the PET polymer by the reaction of the vinyl end groups. Typically, acetaldehyde is determined in PET in concentrations between 1 mg/kg and 10 mg/kg. If acetaldehyde migrates or leaches into the bottled water, it might influence the organoleptic properties of the bottled water⁷. The organoleptic threshold concentration of acetaldehyde in mineral water is in the range of 10 to 20 µg/L. Owing to this low threshold limit, the concentration of acetaldehyde in the bottle wall, as well as in the raw materials (pellets, preforms), needs to be controlled⁸. In addition, 2-methyl-1,3-dioxolane is the reaction product between acetaldehyde and the monomer ethylene glycol, which can be found in nearly every PET sample.

The flavor substance limonene is one of the key substances used to recognize or identify soft drink post-consumer recyclates, as most soft drinks contain limonene. When soft drinks are filled in polyethylene terephthalate (PET) bottles, the flavor compounds are absorbed into the bottle wall. As such, the recyclates of

PET soft drink bottles typically contain detectable amounts of flavor compounds, especially limonene⁹. Recyclates of mineral water bottles can also contain limonene, as during recollection, the mineral water bottles are in contact with soft drink bottles. However, recyclates from mineral water bottles show significantly lower limonene concentrations than recyclates from soft drink bottles¹⁰.

In addition to the above-mentioned target substances that should be monitored, the method can also be utilized to identify a broader range of compounds. Additionally, the screening method is suitable for a non-target monitoring of PET recyclates. Detection of sporadic impurities in post-consumer PET recycle samples up to a molecular weight of approximately 250 g/mol is possible. In the same context, the method is suitable to detect non-intentional added substances (NIAS) in PET preforms and bottle production.

Experimental

Instrumentation

For the determination of volatile components in solid materials, headspace gas chromatography is the most convenient analytical setup, because the headspace sampling minimizes sample preparation.

Multiple headspace extraction (MHE) is used for the determination of benzene, as it facilitates the quantification of compounds in solid or complex matrices without matrix matching the calibration standards¹¹. MHE is an option the user can select in the method which initiates a specific extraction process in the instrument. With this technique, the sample vial is subjected to multiple pressurization, analysis and venting cycles. The resulting data of several cycles is used to determine the total amount of analyte within the sample, as well as the rate of extraction specific to the sample matrix. This data is input into a report template and used to calculate the amount of analyte in each sample of similar matrix¹².

We want to highlight, that according to the experience of the Fraunhofer Institute for Process Engineering and Packaging IVV, it is advantageous not to grind the sample, but only crush the samples to PET granule size. This greatly simplifies sample preparation and reduces the risk of cross-contamination of the samples via the mill, since the mill must be cleaned accordingly after each grinding process, which can lead to cross-contamination.

The instrument conditions are summarized in Tables 1-3.

Headspace Unit	PerkinElmer TurboMatrix™ HS 40
Headspace Mode	Multiple Headspace Extraction (MHE) at least 6 times
Oven Temperature	200 °C
Needle Temperature	210 °C
Transfer Line Temperature	210 °C
Thermostat. Time	60 minutes
Vial Pressurization Time	3 minutes
Withdraw Time	0.5 minutes
Injection Time	0.02 minutes to 0.04 minutes, depending upon HS-needle used
Column Pressure	145 kPa
Vial Vent	On
Transfer Line	Fused Silica uncoated, 0.32 mm

Table 1: Headspace Method for Benzene (MHE).

When using the specific HS-needle for Hydrogen, set the vial venting time to < 18 seconds.

Headspace Unit	PerkinElmer TurboMatrix HS 40
Headspace Mode	Standard Headspace Mode
Oven Temperature	200 °C
Needle Temperature	210 °C
Transfer Line Temperature	210 °C
Thermostat. Time	60 minutes
Vial Pressurization Time	3 minutes
Withdraw Time	0.5 minutes
Injection Time	0.02 to 0.04 depending upon HS-needle used
Column Pressure	145 kPa
Vial Vent	On
Transfer Line	Fused Silica uncoated, 0.32mm

Table 2: Headspace Method for Acetaldehyde and Limonene.

Gas Chromatograph	PerkinElmer Clarus® 590 GC
Injector	Capillary Injector @ 250 °C
Detector	Flame Ionization Detector @ 335 °C
Carrier Gas	Helium @ 100 kPa
Split	10 mL/minute
Column	Elite 1, 30 m x 0.25 mm x 0.25 µm or similar
Temperature Program	50 °C hold for 4 minutes 20 °C/minute to 320 °C 320 °C hold for 5 minutes

Table 3: GC-Setup and Method.

Consumables utilized in this work are outlined in Table 4.

Component	Description	Part Number
Vials and Caps	20 mL PTFE/Sil Crimp Vial w/ Patch Pkg.100	N9303992
Column	Elite 1, 30 m x 0.25 mm x 0.25 µm	N9316010
HS Transfer Line	Fused Silica Tubing, 5 m x 0.32 mm	N9301357
Standard	Restek Custom Mixed Standard CS-28342-1 in Toluene, 1 mL each	RT-CS-28342-1
Standard	Restek Custom Mixed Standard CS-28342-2 in Toluene, 1 mL each	RT-CS-28342-2

Table 4: Consumables utilized.

Sample Preparation

Standards for acetaldehyde and limonene were prepared as matrix-matched standards. 1,00 g of virgin PET material was weighed into a 22 mL HS-vial, and 5 µl standard solutions were added with a suitable microliter syringe.

The benzene standard solution, which was analyzed using MHE, was directly injected using a suitable microliter syringe into an empty 22 mL HS-vial. Additionally a 2nd vial is analyzed, which contains 1,00 g of a PET-masterbatch with a known concentration of benzene. These two data sets allow the calculation of benzene concentration in the samples.

Custom-made standards for this application can be obtained by RESTEK Corporation in whatever concentration is needed. For this application note the following standards were utilized:

- RT-CS-28342-1, Restek Custom Mixed Standard CS-28342-1 in Toluene, 1 mL each of:
 - Acetaldehyde (CAS 75-07-0), 10,000 µg/mL
 - 2-Methyl-1,3-dioxolane (CAS 497-26-7), 8,000 µg/mL
 - d-Limonene (CAS 5989-27-5); 7,500 µg/mL
- RT-CS-28342-2, Restek Custom Mixed Standard CS-28342-2 in Toluene, 1 mL benzene (CAS 71-43-2), 3,500 µg/mL

Sample Preparation

1,00 g of PET sample is weighed into a 22 mL headspace vial and then sealed with respective septa (e.g. P/N N9303992), and analyzed according previous mentioned methods. The septa need to be conditioned for several hours at 207 °C, and can be stored after conditioning in a glass jar with lid that does not contain rubber sealing.

Results and Discussion

Chromatograms from the analysis are displayed in Figures 1-3.

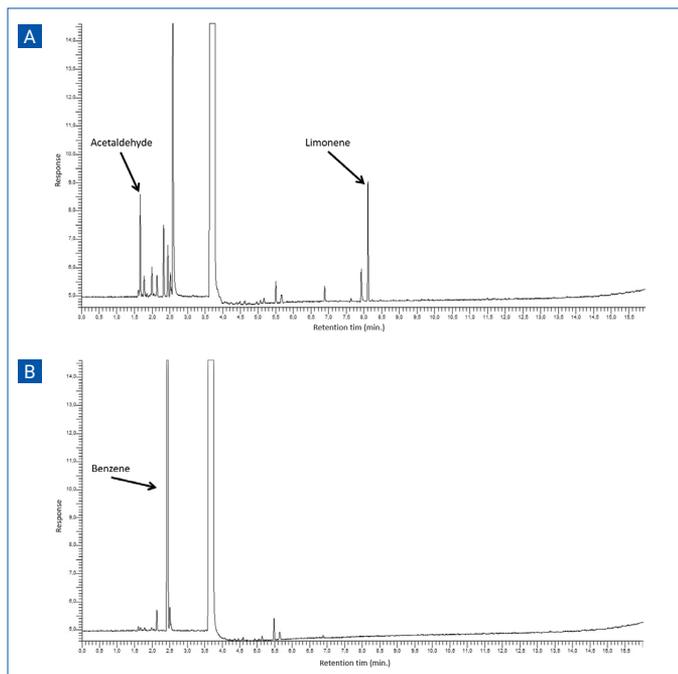


Figure 1: Standards (A: acetaldehyde and limonene, B: benzene).

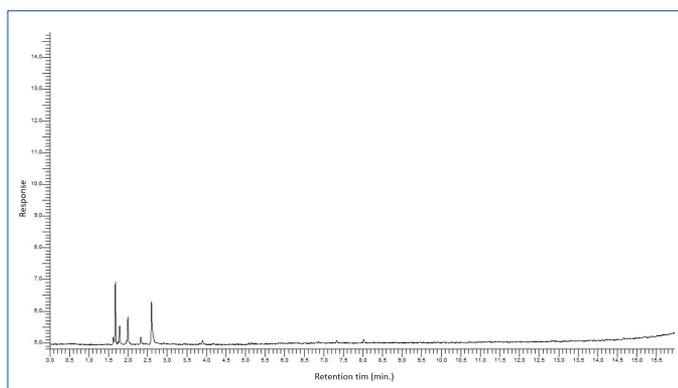


Figure 2: Very good recycled PET, close to virgin material.

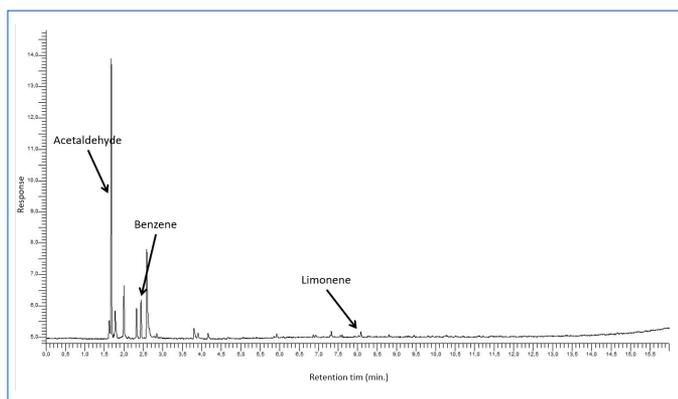


Figure 3: PET recycling product.

Retention times for the shown chromatograms are as follows:

- 1.75 min: Acetaldehyde
- 2.47 min: Benzene
- 8.1 min: Limonene

To calculate the concentration of acetaldehyde and limonene an external calibration is used, whereas the calculation of benzene concentrations was achieved utilizing an Excel-based macro available from PerkinElmer.

Summary

This application note details a method utilizing headspace sampling combined with gas chromatography and FID-detection. The method is robust, and suitable for the determination of volatile compounds (e.g. benzene, acetaldehyde and limonene) in PET granulates and/or flakes resulting from the virgin production process or any other recycling/washing process. The method is also suitable for non-target monitoring of NIAS in PET packaging materials.

Headspace sampling of solid samples without grinding reduces sample preparation to a minimum, therefore allowing for an increase in the number of samples in the QA/QC process to maintain the highest production and recycling quality. Whilst this application note deals only with polyethylene terephthalate (PET), further investigations are underway to expand this methodology to other widely used polymers like polyethylene (PE) or polypropylene (PP).

As an alternative to GC-FID setup described herein, the use of a GC-mass spectrometer (e.g. PerkinElmer SQ8) with headspace sampling will lead to a more detailed insight on unexpected products identification/quantitation, and could help to better identify other hazardous or unwanted volatile components in virgin as well as in recycled plastics.

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