AppBrief

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Determination of Off-Odors Emitted from Recycled HDPE

Highlights

- Thermal desorption/extraction GC-MS allows sensitive determination of off-odors from plastic material
- No sample preparation other than shredding necessary
- High throughput VOC determination due to lack of solvent use

Introduction

To ensure a sustainable material cycle, used plastic materials undergo a recycling process. These recyclate pellets are often made of used containers, and odor emissions occur repeatedly during the recycling process, making the re-use of the plastic difficult, if not impossible.

Two solvent-free analysis techniques are used to determine the composition of such odors and thus to trace the source. These are thermal desorption with prior air sampling and direct thermal extraction of the plastic.

Experimental

Samples

Three containers with HDPE recyclate pellets were analyzed for off-odors.

Sample Introduction

Thermal desorption and thermal extraction were selected as sample introduction techniques. In thermal desorption, analytes previously collected from air samples on sorbent-filled tubes are made available for GC analysis. For active sampling of the air from the sample containers, an Accuro hand pump from Drägerwerk AG & Co. KGaA was used to draw 500 mL of container air onto an AirToxic tube, which subsequentially was heated under carrier gas flow to release volatile and semi-volatile compounds.

Thermal extraction is a variant of thermal desorption in which volatile and semi-volatile analytes are thermally released from a small amount of sample instead of being trapped on a sorbent. The pellet sample size was reduced using clean scissors, and approximately 30 mg was weighed into an empty TD tube.

The sample was then heated under carrier gas flow to release volatile and semi-volatile compounds. Non-volatile matrix residues are removed and discarded in the process, keeping the GC-MS system clean and stable.

Both techniques avoid time-consuming, manual, solvent-based sample preparation steps. The analytes were re-focused in a cold injection system for subsequent temperature-programmed transfer to the GC-MS system. There are no valves or active sites in the sample path, ensuring the best possible recovery of all analytes.

LabWorks Platform on Agilent 8890 GC / 5977C MSD

Analysis

The sorbent-filled tubes were thermally desorbed at 290 °C and the analytes were then focused in the cooled injection system (CIS 4) with a Tenax®-filled liner at a trap temperature of -40 °C. The parameters for collecting the analytes in the CIS were maintained for all analyses. Detection was performed with a mass selective detector from Agilent Technologies in scan mode. The verification of the detected components was carried out using a NIST database.

90 °C was selected as the extraction temperature for the thermal extraction, based on the VDA 278 method (emissions from materials in vehicle interiors). The desorption time was set to 15 minutes.

Instrumentation

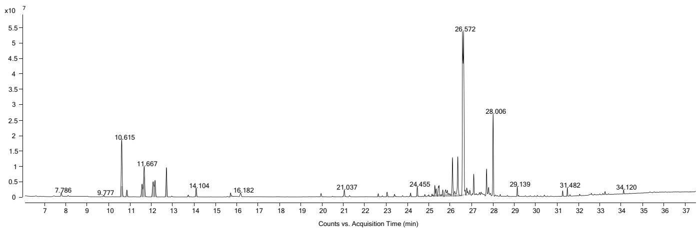
A GERSTEL LabWorks Platform, supplemented with an Agilent GC-MS, was used for this application. The GERSTEL LabWorks Platform is a universal system for sample introduction and offers unrivaled capabilities and flexibility to solve your critical challenges. The platform's basic version already offers 10 automated sample introduction techniques, all controlled by GERSTEL Maestro software and seamlessly integrated with Agilent ChemStation, MassHunter, and Open Lab software.

As a result, it is no longer necessary to use a separate device for each technique. Liquid, headspace and thermal desorption are all included without the need for additional bench space.

Results and Discussion

Thermal Desorption - Active Sampling on a Sorbent

All three air samples taken from the containers with HDPE show a significant VOC content. Identified compounds included C9 and C10 aromatics, α-pinene, limonene, and other terpenes.



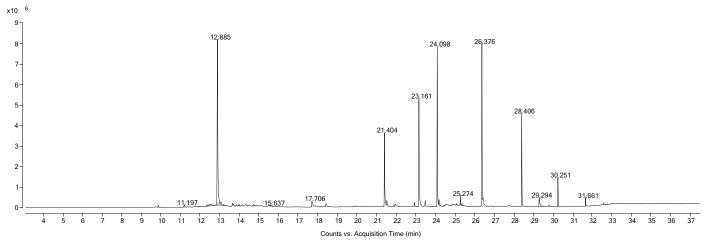
Chromatogram of air above sample 1

Main components of active air sampling from samples 1-3

sample 1	sample 2	sample 3
acetic acid	acetic acid	acetic acid
propylene glycol	propylene glycol	
α-pinene	α-pinene	
o-ethyl toluene	o-ethyl toluene	
m,p-ethyl toluene	C9-aromatics	C9-aromatics
limonene	limonene	limonene
cymene	cymene	cymene
terpenes	terpenes	
C10-aromatics	C10-aromatics	C10-aromatics
1-dodecene	1-dodecene	
β-myrcene	indane	ethyl benzene
γ-terpinene		xylenes

Thermal Extraction

Thermal extraction makes it possible to determine the VOCs and SVOCs in the material.



Chromatogram of sample 1, thermal extraction at 90 °C

Thermal extraction shows the compounds still in the material and have not yet been emitted to the air. The largest response was that for limonene, which could be found in all three samples.

Main components of the thermal extraction experiment for samples 1-3

sample 1	sample 2	sample 3
limonene	limonene	limonene
cymene	cymene	cymene
other terpenes		
alkanes	alkanes	alkanes
alcohols	alcohols	aAlcohols

Other terpenes in sample 1 could not be positively identified due to similar fragmentation patterns.

Conclusions

- Using active air sampling and thermal extraction, compounds and compound groups suspected of causing the odor emission were detected.
- Aromatics and terpenes are possible odor causing compounds. Limonene was detected as a major component in all three samples using both techniques.
- Apart from a sample size reduction step, no sample preparation was necessary.
- No solvents were used.