Elucidation of the off-odor of a PE masterbatch using off-line HPLC-GC-ODP/MS

N. **Wolf**[1,2,*], S. **Säger**[2], M. **Lommatzsch**[2], T. J. **Simat**[1]

*E-Mail: nancy.wolf@chemie.tu-dresden.de

[1]TU Dresden, Chair of Food Science and Food Contact Materials, Bergstr. 66, D-01062 Dresden, [2]Laboratory Lommatzsch & Säger, Gottfried-Hagen-Str. 60-62, D-51105 Cologne

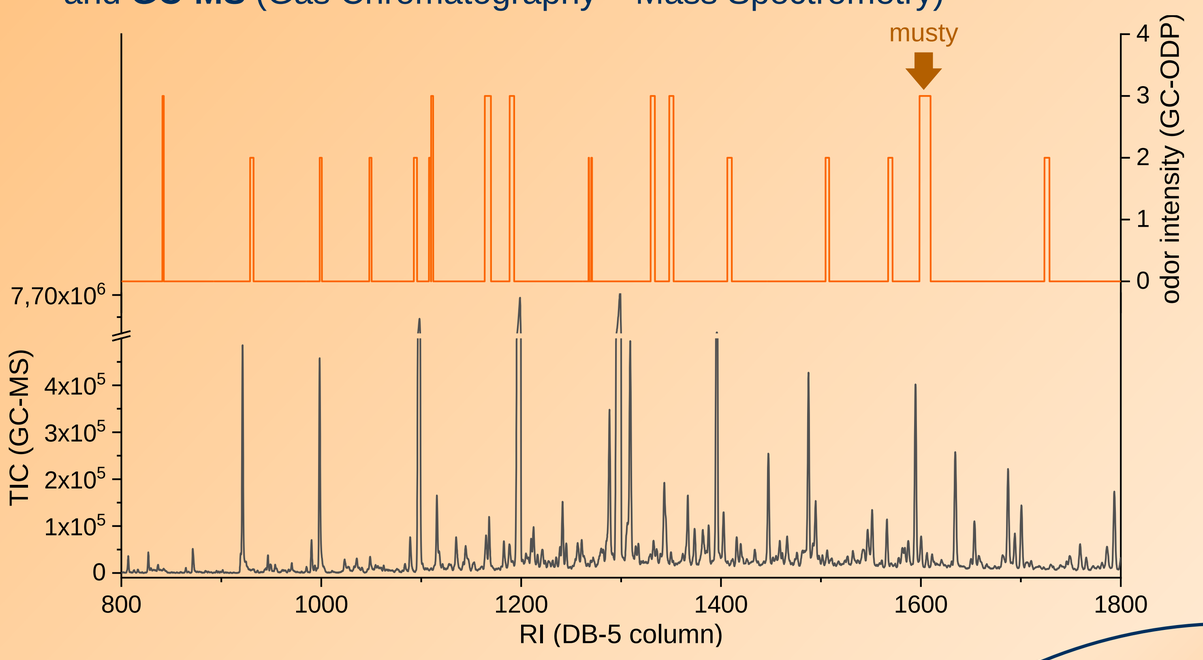
Introduction

A polyethylene (PE) masterbatch granulate with a noticeable off-odor was rejected by food packaging producer. In general, a masterbatch contains higher amounts of dyes and additives and is mixed with nearly non-additivated granulates of the same polymer in the processing of plastic products. In terms of quality assurance, it was evaluated as sensory unacceptable as its musty odor was recognizable in the granulate as well as in the final packaging product. The aim of this work was to find the source of this off-odor by means of identifying the volatile organic substances (VOC) responsible for the smell.

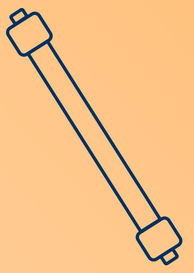
Conclusion

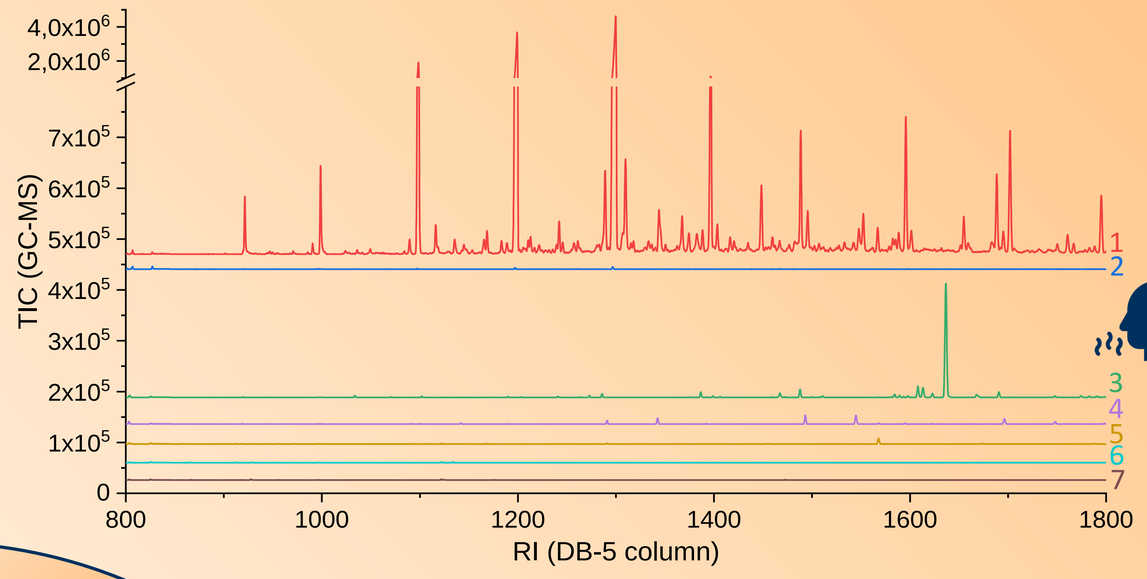
The off-odor of a PE masterbatch was elucidated. After extracting, enriching and screening the odor-active VOC by GC-ODP, one substance peak with a musty odor could be detected. The extract had to be fractionated by NP-HPLC to separate coeluting substances (mainly polyolefin oligomers) in GC-MS. By interpreting the mass spectrum, the sum formula of $C_8H_4Cl_3NO$ could be ascertained. The substance tentatively identified as 5,6,7-trichloro-1-isoindolinone is assumed to be a degradation product or an impurity related to the dyestuff Pigment Yellow 110, which was an ingredient of the granulate.

- **Extraction** of 30 g granulate by simultaneous distillation-extraction with dichloromethane, enrichment to 0.5 mL
- **GC-ODP** (Gas Chromatography – Olfactory Detection Port) and **GC-MS** (Gas Chromatography – Mass Spectrometry)



- **NP-HPLC**: fractionation of the extract into 7 fractions
  column: LiChrospher Si60, 5 µm, 250 x 2 mm; mobile phase: n-hexane, dichloromethane and methyl tert-butyl ether; flow rate: 300 µL/min [1]
- **Sensory evaluation** by at least three skilled assessors and **GC-MS of the fractions**





➢ **GC-ODP**: detection of odorous substance peak described with a **musty odor** at a retention index of **RI ~ 1600**

➢ **GC-MS**: identification not possible due to coelutions with other substances

➢ **Sensory evaluation**: **fraction 3 smelled musty**

➢ **GC-MS**:
- separation of the substances in all 7 fractions
- mainly odorless polyolefin oligomers in fraction 1
- in fraction 3 one peak could be assigned to the unknown odorous substance with RI ~ 1600
  → also detected by GC-ODP

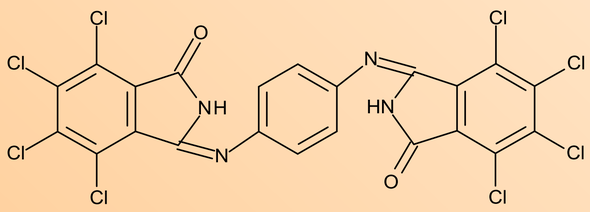
Screening for odor-active VOC by GC-ODP

Sensory evaluation and GC-MS of HPLC fractions

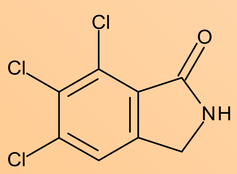
Elucidation of the off-odor source

Efforts for Identification

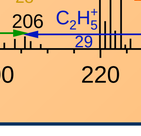
- limited list of additives containing chlorine atoms
- Screening for chlorinated dyes typically used to color polyolefins
- Assumption of **Pigment Yellow 110:** isoindolinone pigment with reddish-yellow color



- Confirmation of the producer that this pigment was included in the granulate
- Tentative structure of the odor-active substance, which is assumed to be an degradation product or impurity of Pigment Yellow 110: **5,6,7-trichloro-1-isoindolinone**



- no sufficient match of the mass spectrum could be found in the NIST database
- **Isotope ratios**: substance contains 3 chlorine atoms



- **Nitrogen rule**: odd number of N atoms due to odd nominal molecular mass (235 u)
- **High resolution MS**: exact mass 234,931177 u
- **Calculation of the sum formula**: molecular mass should be as close as possible to determined exact mass, 3x Cl, 1x N → **$C_8H_4Cl_3NO$** (234,935847 u)

[1]: Wolf et al. (2021). Analysis of volatile oxidized oligomers from polyolefins by off-line normal phase high performance liquid chromatography and one-dimensional and comprehensive two-dimensional gas chromatography. *Polymer Degradation and Stability* 185, 109490.

Labor Lommatzsch & Säger