Detection of Plasticizers in Sporting Goods and Toys by Means of TGA-FT-IR

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Introduction

Sporting goods and toys for kids or pets are often made of flexible plastics. Some examples are sensory chewing toys, action figurines, soft grip features as well as balls of any kind. A common polymer used is PVC (polyvinylchloride), which can be made softer and more flexible by adding plasticizers. These compounds are not covalently bonded to the polymer chain, and this is why they can evaporate or be rinsed out by saliva or sweat. Outgassing of plasticizers like phthalates can be harmful. In some cases, this can be even recognized by a bad smell.

The family of phthalates is known to cause a number of health risks. They act like hormones, and have been shown to cause liver damage, infertility, diabetes, cancer and more. Therefore, the European Union has banned a number of phthalates in products, which are in contact with food, in toys, in baby articles and medical supplies since 2007.

Decomposition Behavior and Identification of Plasticizers

Thermal analysis can help detect plasticizers in polymers. By means of TGA-FT-IR analysis, it is possible to analyze products regarding their plasticizer content and to identify the kind of plasticizer used.

In the following use case, the surface layer of different toy balls was cut in small pieces and measured with the PERSEUS® TG 209 ***F1*** *Libra*® according to the measurement conditions in table 1.

Ball no. 1 exhibits several mass-loss steps during pyrolysis, see figure 1. These mass-loss steps result from the evaporation of plasticizer or other organic additives and the pyrolysis of the polymer in the temperature range between 200°C and 500°C. Decomposition of inorganic fillers was detected between 500°C and 700°C. The peaks in the DTG curve (mass-loss rate) represent the temperatures of the maximal mass-loss rates. The Gram Schmidt curve displays the overall IR intensities and behaves as a mirror image of the DTG curve and shows also maximum intensities during mass-loss steps. This proves the interaction of the evolved compounds with the IR beam.

Tab 1. Measurement conditions

Sample	Ball no. 1	Ball no. 2
Sample mass	9.08 mg	10.38 mg
Temperature program	RT to 850°C	
Heating rate	10 K/min	
Gas atmosphere	Nitrogen	
Gas flow rate	40 ml/min	

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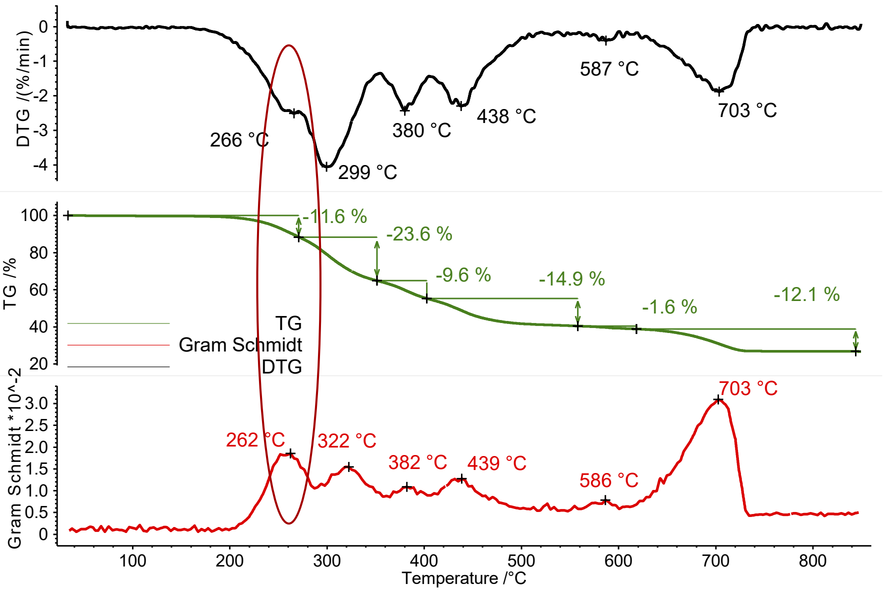
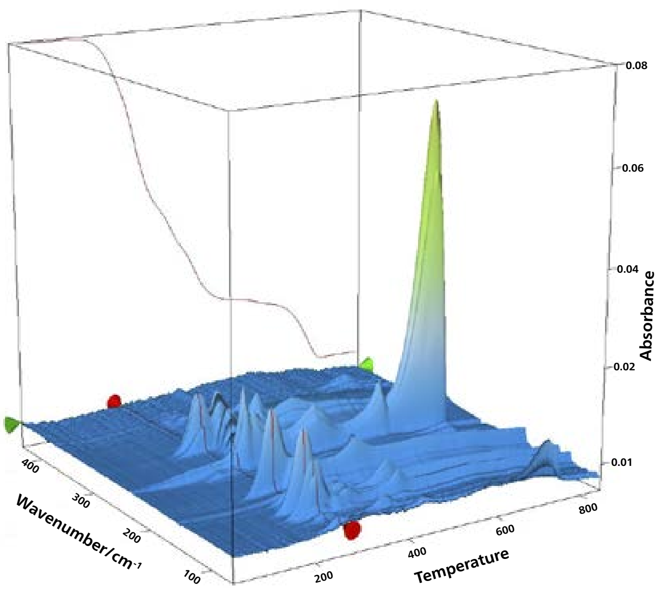


1 Temperature-dependent mass change (TGA, green), rate of mass change (DTG, black) and Gram Schmidt curve (red) of ball no. 1

The complete IR data is shown in figure 2 in a temperature- and wavenumber-dependent 3D plot. The TGA curve is plotted in red at the back and shows the correlation of the mass loss to the increase in IR intensity. In this example, only the first mass-loss step is investigated more precisely. For detailed analysis of the plasticizer contained, a 2D FT-IR spectrum was extracted and compared to gas phase libraries to identify the evolved compounds. High similarity was found for the spectrum at 266°C to the library spectra of di-n-octylphthalate (DOP, blue) und bis(2-ethylhexyl)phthalate (DEHP, green). It can be assumed that a single compound or a mixture of different phthalates was released. However, this comparison clearly indicates that ball no. 1 contains harmful phthalates. As the following mass-loss step is slightly overlapping with the release of phthalates, some small amount of CO_2 was also found by means of FT-IR at 266°C.



2 3D plot of all detected IR spectra of ball no. 1, TGA curve plotted in red at the back of the cube

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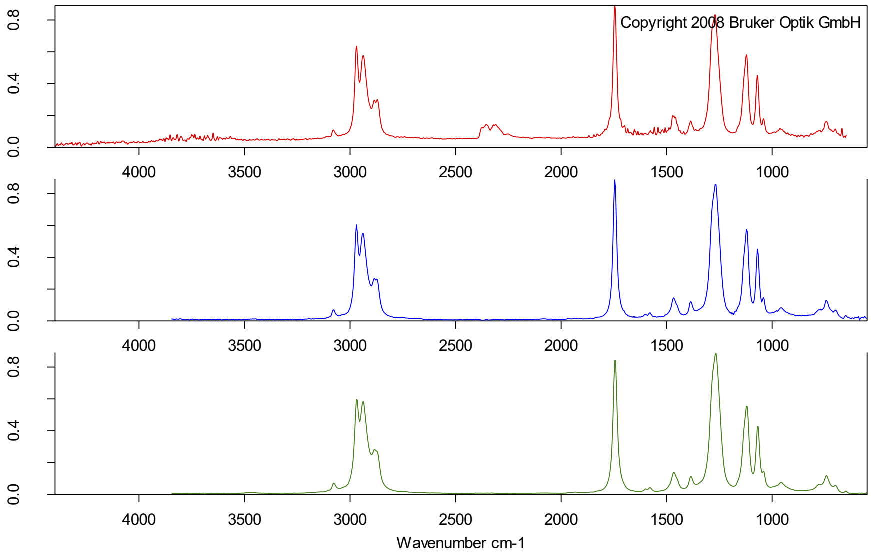
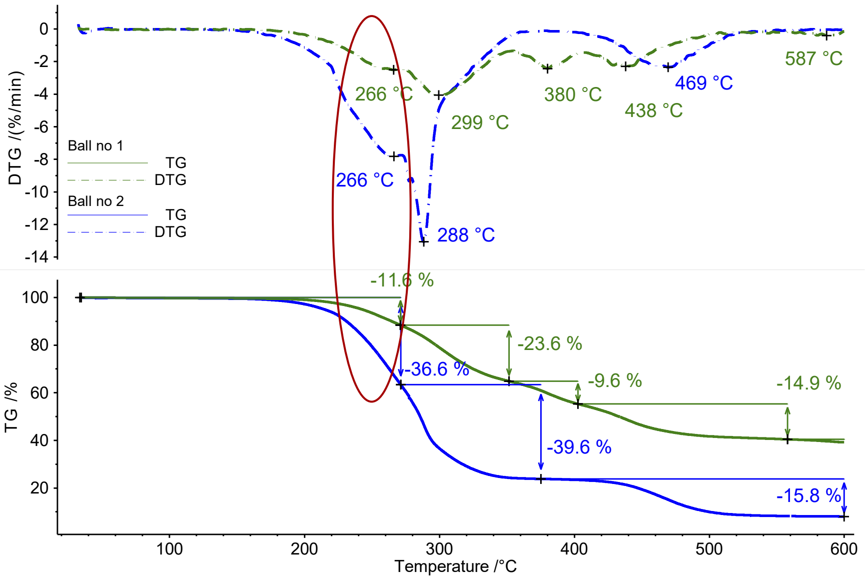


3 Measured spectrum at 266°C (red) in comparison to the library spectra of di-n-octylphthalate (DOP, blue) and bis(2-ethylhexyl)phthalate (DEHP, green)

A second ball was investigated under the same measurement conditions. A comparison of both TGA measurements is shown in figure 4. A clear difference can be observed in the pyrolysis behavior. However, also for ball no. 2, the first mass-loss step was detected in the temperature range between 200°C and 280°C, also with a peak in the DTG curve at 266°C. Only FT-IR can yield detailed information about the contained plasticizer.

The comparison of the extracted FT-IR spectra for the two ball samples, both extracted at 266°C, show completely different vibration pattern, see figure 5. The comparison of the spectra at 266°C of ball no 2 (blue) to the gas phase library gives clear accordance with the spectrum of tributyl citrate (green). For ball no. 2, the toxic phthalate plasticizers were replaced by nontoxic citric ester, which also acts as a plasticizer.



4 Temperature-dependent mass change (TGA) and rate of mass change (DTG) of ball no. 1 (green) and ball no. 2 (blue)

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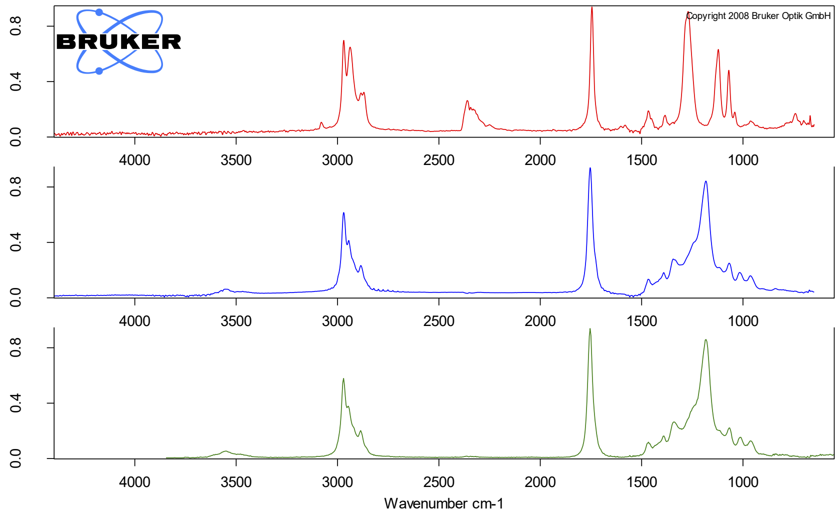

5 Measured spectrum of ball no. 1 at 266 °C (red) and ball no. 2 (blue) in comparison to the library spectra of tributyl citrate (green).

Summary

Outgassing and decomposition processes of polymers can be investigated by thermal analysis. Thermogravimetry indicates the release of gases already below 300°C. Only evolved gas analysis like FT-IR can identify the gases released. In this example, it was possible to identify the different plasticizers used and therefore, to distinguish between toxic and non-toxic additives. The PERSEUS® TG 209 ***F1*** *Libra*® is perfectly suited to solve this task.

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