Application Note no. 121

Phthalates in Polymers

Key words: Phthalates, Thermal desorption, Solid sample, LINEX, OPTIC, GC/MS, PAL3

Introduction

Phthalates are a group of plasticizers with softening and elastic effects. They are widely used in hundreds of types of products. The EU Directive 2005/84/EC[1] sets the limits for the use of 6 phthalates in toys and childcare articles. The usage is limited to 0.1% by mass of the plasticized material. All the following 6 substances are also added into REACH Restriction List: bis (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), di-"isononyl" phthalate (DINP), di-"isodecyl" phthalate (DIDP), di-n-octyl phthalate (DNOP).

This application note describes a simple and quick thermal desorption (TD) based approach for the sampling and analysis of target compounds (phthalates) in plastic toys and childcare articles . The approach exploits Difficult Matrix Introduction (DMI) technique widely used for controlled TD-GS/MS analysis of different kind of samples[2,3].

Sample Preparation

Two solid samples of polymer with concentrations 100 mg/kg and 1000 mg/kg of the target compounds have been prepared using a simple manual hole punching device. The weight of each sample was limited to 0.50 mg. Further, the sample is placed in a 60 µl DMI sample insert (fig. 1), which in turn is placed in an OPTIC DMI liner.

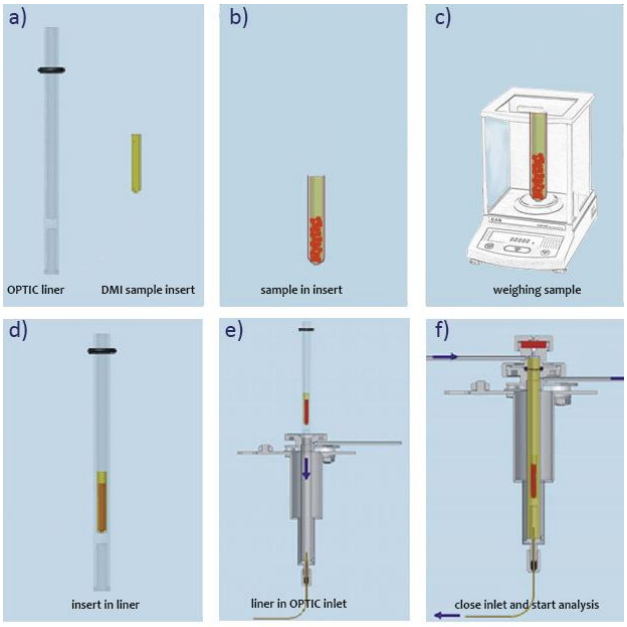

Figure 1: Sample preparation procedure

To reduce environmental effects on the just-prepared samples, the liners are capped with the PTFE caps and placed in an auto-sampler rack for automated analyses using an analytical system comprising of a GC/MS, a PAL3 auto-sampler, a LINEX-2 liner exchanger, a Capping-De-Capping (CDC) Station and an OPTIC-4 inlet.

Equipment

GC/MS system:	QP2010 (Shimadzu Inc.)
Auto-sampler:	PAL3 - PAL RTC (CTC Analytics AG) equipped with LINEX-2 and CDC Station (GL Sciences B.V.)
GC inlet:	OPTIC-4S (GL Sciences B.V.)
Liner:	2414-1013, OPTIC DMI liner with taper (GL Sciences B.V.)
Sample insert:	2406-1020, DMI sample insert, 60 µl (GL Sciences B.V.)
GC column:	InertCap 5MS/Sil, 0.25 m x 15 m, 0.05 µm (GL Sciences Inc.)

LINEX-2 is an automated liner exchanger based on PAL3 system. It is equipped with a pneumatic inlet head allowing the robot to exchange the inlet liner. Capped liners are stored in the PAL3 rack and are automatically de-capped by the CDC station before placing it in the OPTIC-4 inlet. OPTIC-4 has a possibility to flush the liner with carrier gas before heating it up.

OPTIC-4 Method

Details of the OPTIC-4 method used with this application are described below. The initial parts of the method's profiles are shown in Figure 2.

Method Type	Expert
Equilibration Time	00:05 min:sec
End Time	23:00 min:sec
Initial Temperature	50 °C
Ramp Rate 1	40.0 °C/sec
Hold Temperature 1	350 °C
Hold Time 1	04:00 min:sec
Hold Temperature 2	50 °C
Septum Purge Flow	3 mL/min
Vent Mode	Fixed Time
Vent Time	01:00 min:sec
Carrier Control Mode	Flow Control
Zero LINEX Head Pressure	Yes
Column Flow	1.5 mL/min
Split Flow	75.0 mL/min

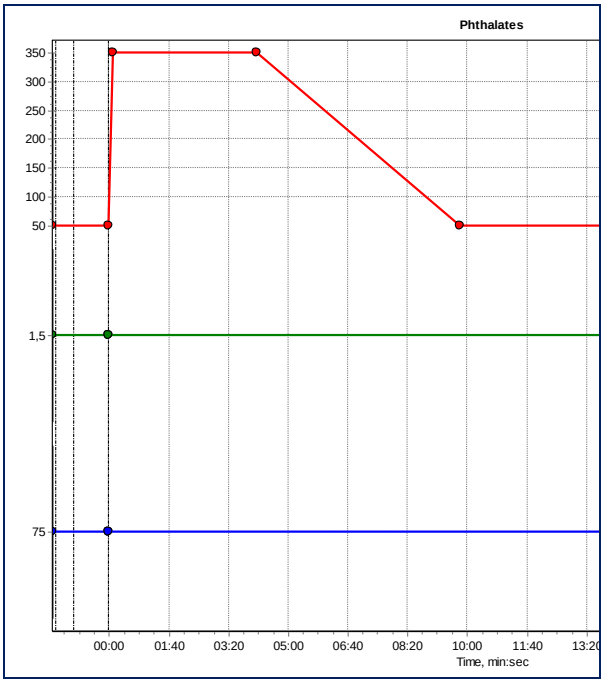

Figure 2: OPTIC-4 method profiles - initial part

Analysis

A liner with sample is automatically placed into the OPTIC-4 inlet by the PAL3/LINEX-2/CDC Station system. The OPTIC method starts with flushing the inlet with clean carrier gas to get rid of air, which may enter the inlet while liners are exchanged. After the inlet is flushed, it is heated up to 350°C with 40°C/sec. The compounds of interest are desorbed and transferred onto the GC column while non-volatile sample residue is retained in the sample insert and is disposed after analysis. After four minutes of the method run, the inlet temperature control is set to floating mode. Floating mode and also careful optimization of the maximum inlet temperature (Hold Temperature 1) are needed in order to minimize transfer of the matrix components into the column. This , so-called, temperature selective exclusion principle allows to avoid any possible contamination of the GC column and the detector. Both, the column and the split flows are not changed during the entire run. After the completion of the GC/MS run, the liner with the analyzed sample is returned to the sample rack and the next sample is processed.

Results

The results (Figure 3 – Figure 5) show that the target compounds are very well separated from the polymer matrix, the difference in concentrations is clearly visible and quantifiable.

This work has demonstrated that very simple and easy polymer sample preparation in combination with the automated TD (DMI) - GS/MS analysis is a powerful approach that is suitable for assisting compliance with phthalates regulations. It can also be used for production quality control and R&D purposes.

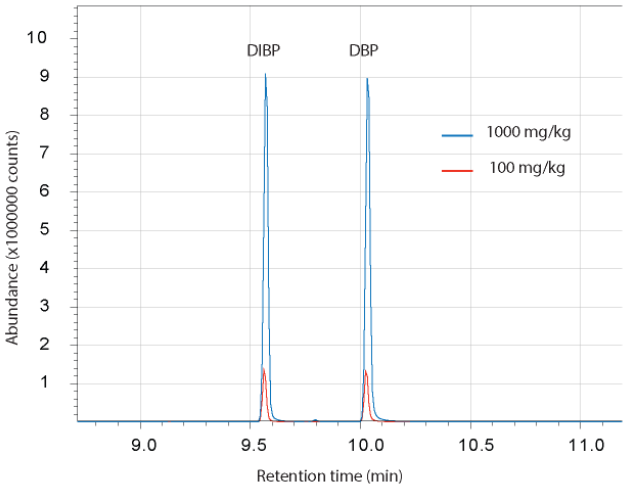

Figure 3: GC/MS chromatogram showing DIBP and DBP phthalates in polymer sample

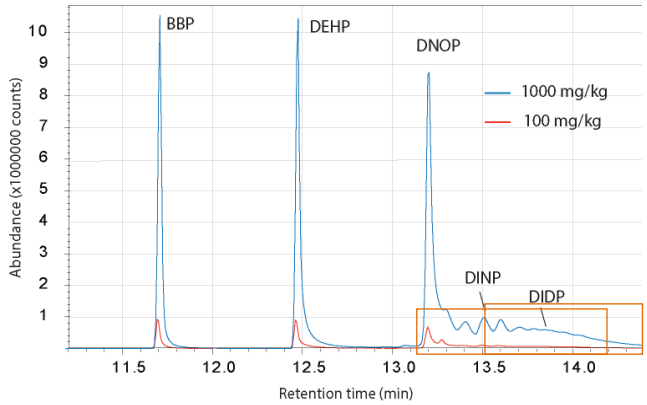

Figure 4: GC/MS chromatogram showing remaining target components in polymer sample

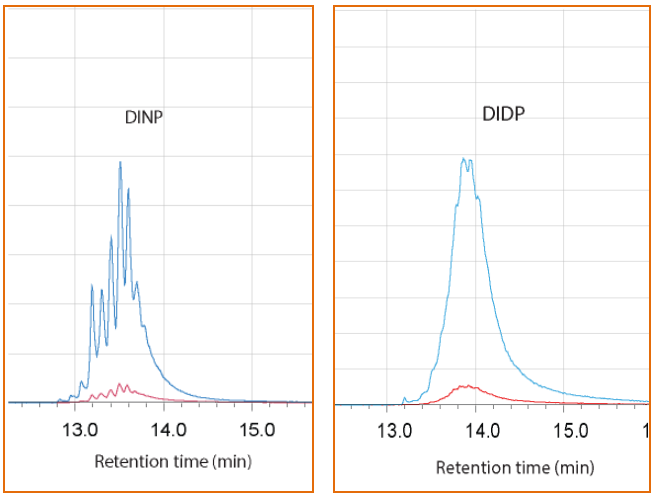

Figure 5: Single-ion-chromatograms showing DINP and DIDP phthalates in polymer sample

References

1. EU Phthalates Directive 2005/84/EC, http://eur-lex.europa.eu/eli/dir/2005/84/oj
2. Patel K., Fussell R.J., Goodall D.M., Keely B.J., Evaluation of large volume-difficult matrix introduction-gas chromatography-time of flight-mass spectrometry (LV-DMI-GC-TOF-MS) for the determination of pesticides in fruit-based baby foods, *Food Addit. Contam. 2004, Jul, 21(7), p. 658-69.*
3. Akoto L., Vreuls R.J., Irth H., et al., Fatty acid profiling of raw human plasma and whole blood using direct thermal desorption combined with gas chromatography-mass spectrometry, *J. Chromatogr. A, 2007, Sep, 11.*