Determination of phthalates in PVC by thermal desorption-GC/MS

Part 1: Determination of the thermal desorption temperature zone by EGA

[Background] Phthalates are widely used in the plastic industry; the six phthalates listed in Table 1 are regulated by the EU and the US when used in toys and other childcare products. In Japan, the Health, Labor and Welfare Ministry guideline No.336 issued on September 6, 2010 regulates the six phthalates listed in Table 1; consequently, the analysis of phthalates is becoming commonplace and there is a near universal interest in a simple, accurate method for analyzing phthalates in polyvinyl chloride (PVC). Traditional (e.g. solvent extraction, filtration, etc.) sample preparation techniques are cumbersome, time consuming and suffer from analyst-to-analyst variability.

Thermal desorption (TD)-GC/MS.[1)] is a simple, one-step technique which appears to be ideally suited to the analysis of phthalates in PVC. PVC often contains a large amount of other plasticizers (several tens of percent) which co-elute with the phthalates of interest. This so-called matrix interference many lead to either false positives or false negatives. In addition, matrix interference makes an accurate determination of the co-eluting phthalates problematic, at best. This report describes how Evolved Gas Analysis (EGA) – GC/MS is used to define the optimal thermal desorption temperature zone for the phthalates of interest.

[Experimental] A sheet of PVC containing DINCH at 40% (Fig. 1) and six restricted phthalates at 0.1% each was analyzed. Small pieces (≈ 20mg) sampled from several different locations were dissolved in 1 mL of THF (20 mg/mL). 10 µL of the solution was placed in a sample cup and the solvent evaporated leaving a thin film of the sample on the surface of the cup. EGA-MS analysis was performed on this sample using a Multi-shot pyrolyzer: EGA/PY-3030D.

[Results] The EGA thermogram of the PVC sheet is shown in Fig. 2. It contains peaks originating from the plasticizers, HCl (thermal decomposition of PVC), and aromatic compounds (which are attributed to the thermal decomposition of polyenes upon the dehydro-chlorination of PVC). Characteristic ions for DINCH, HCl, and the phthalates of interest are used to define the optimal thermal desorption temperature zone: 100-320ºC. S*ee Technical note PYA1-059E which describes the determination of phthalates in PVC using TD-GC/MS.*

Table 1. Restricted phthalates
(0.1 % upper limit by Directive 2005/84/EC)

Di(2-ethylhexyl)phthalate (DEHP)
Dibutylphthalate (DBP)
Butylbenzylphthalate (BBP)
Diisononylphthalate (DINP)
Diisodecylphthalate (DIDP)
Di(n-octyl)phthalate (DNOP)

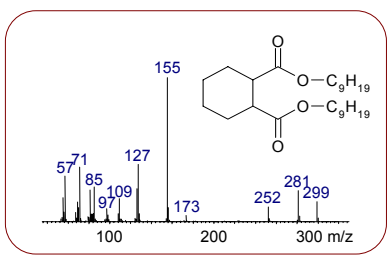

Fig. 1 Structure and mass spectrum of DINCH
DINCH: 1,2-Cyclohexane dicarboxylic acid di-isononyl ester

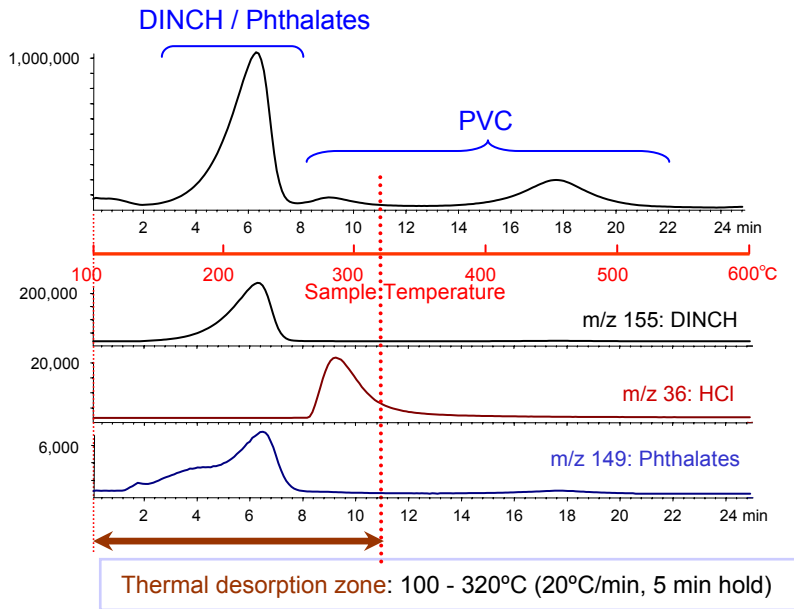

Fig. 2 EGA thermogram and mass fragmentgrams of PVC sample
Pyrolyzer: 100 – 600ºC (20ºC/min), GC oven: 300ºC
EGA tube: UADTM-2.5N (L=2.5 m, i.d.=0.15 mm)
Column flow rate: 1 mL/min He, split ratio: 1/20, injection port temp.: 320ºC

Ref. 1) Yuzawa, *et al., Anal. Sci.*, **25** (2009) 1057

Keyword : Use restricted phthalate, infant plastic toy, thermal desorption temperature, EGA, thermogram, PVC

Applications : Restricted phthalate, plasticizer

Related technical notes : PYA1-063E, PYA1-064E, PYA1-069E

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R&D and manufactured by :
Frontier Laboratories Ltd.
1-8-14 Saikon, Koriyama,
Fukushima 963-8862 JAPAN
Phone: (81)24-935-5100 Fax: (81)24-935-5102
http://www.frontier-lab.com/