

Determination of volatile phthalate esters using polymer coated sample cups - Part 1 Effect of PVC coating

[Background] The determination of six regulated phthalate esters in polyvinyl chloride (PVC) by thermal desorption (TD)-GC/MS has been standardized in ASTM D7823-13. However, there is wide spread interest in applying D7823 to the analysis of several non-regulated phthalates such as dimethyl phthalate (DMP). DMP is the most volatile of the phthalate esters and measurements typically exhibit poor precision and accuracy. Even though the ASTM method attempts to compensate for this by using standard addition to calculate the phthalate concentrations, the high vapor pressure of DMP leads to non-linear losses of DMP prior to analysis. In order to reduce losses due to evaporation Frontier has developed a polymer coated glass sample cup in which a thin film of PVC is coated on the inner wall of the sample cup. In this study, the loss of volatile phthalate esters like DMP placed in a PVC coated sample cup was investigated using TD-GC/MS analysis..

[Experimental] The inner wall of glass sample cups (od. 4 mm, id. 3 mm, height 8 mm) was coated by adding a plasticizer-free PVC dichloromethane solution to the cup. The temperature of the cup was increased to 200°C for 60 min. The PVC film thicknesses varied from 0 to 4.8 µm. 10 µL of a dichloromethane solution containing 10 ppm each of 15 phthalate esters were injected in the cup. The sample was placed in the auto-Shot carousel for up to 200 minutes before analysis. The analytical system was a Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Labs) directly interfaced to the split injector of a GC-MS.

[Results] Fig. 1 shows the plots of peak areas of several phthalate esters including DMP and diethyl phthalate (DEP) vs. standing time at room temperature. Losses of the volatile DMP and (DEP) are observed immediately and are significant after 200 min at room temperature. Phthalate esters with molecular weights greater than n-propyl phthalate (DPRP) were mostly retained even after 200 min at room temperature. The chromatograms of 15 different phthalate esters obtained using uncoated and PVC-coated glass sample cups (coating thickness: 2.4 µm) are shown in Fig. 2. When PVC-coated sample cups with coating thickness of 1 µm or greater were used, all the phthalates including DMP and DEP were quantitatively retained. The reproducibility of the phthalate esters peak areas was investigated. The results are shown in Table 1. The peak area precision, expressed as relative standard deviation (RSD) is less than 2.3%. This compares favorably with the values cited in ASTM D7923. Interferences from PVC pyrolyzates were essentially non-existent and do not affect the phthalate determinations (see also PYA1-076E).

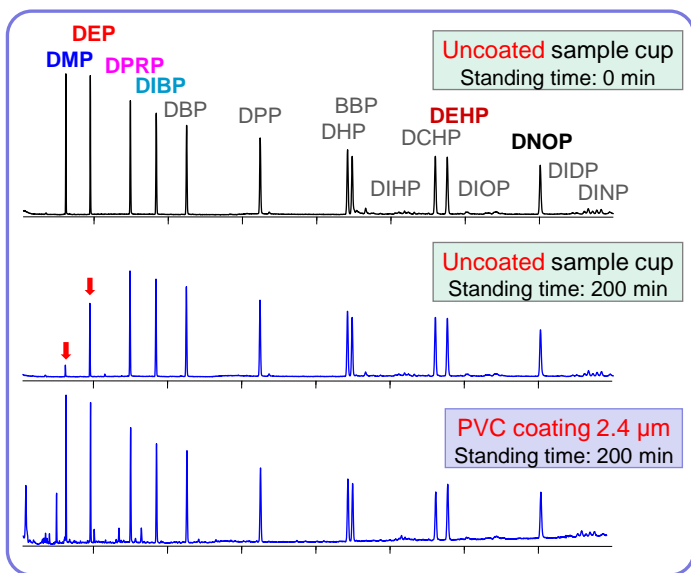


Fig.2 Chromatograms of phthalate esters obtained with uncoated and PVC-coated sample cups

Thermal desorption temp.: 40 - 320°C (20 °C/min, 5 min hold),
 Separation column: Ultra ALLOY+5 (L= 30 m, id.= 0.25 mm, df= 0.25 µm),
 GC oven temp.: 40 - 200 (40 °C/min) - 280°C (5 °C/min), GC inj. Temp.: 300°C,
 Column flow rate: 1.2 ml/min He, Split ratio: 1/20, Detector: quadrupole MS

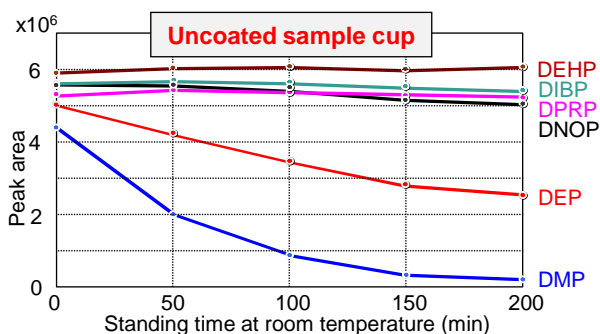


Fig.1 Plots of phthalate peak areas against standing time before analysis

Table1 Reproducibility of phthalate peak area (PVC coating: 2.4 µm, 200 min standing)

Phthalate ester	RSD % (n=5)
DMP: dimethyl phthalate	1.66
DEP: diethyl phthalate	1.80
DPRP: di-n-propyl phthalate	0.65
DIBP: diisobutyl phthalate	0.64
DEHP: di(2-ethylhexyl) phthalate	1.13
DNOP: di-n-octyl phthalate	2.21

Keywords : Phthalate esters determination, DMP, DEP, TD-GC/MS, Polymer coated sample cups, PVC

Products used : Multi-functional pyrolyzer, Auto-Shot Sampler, Vent-free GC/MS adapter, UA+5

Applications : General polymer analysis, Analysis of additives in toys

Related technical notes : PYA1-063E, PYA1-064E, PYA1-068E, PYA1-069E, PYA1-074E, PYA1-076E

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