Notes on the analysis of volatile additives in polymers by Thermal Desorption Gas Chromatography (TD-GC)

[Background] The quantitative analysis of volatile additives such as BHT in polymers, is adversely effected by additive losses at or near room temperature. Analytical precision decreases due to a multitude of factors (storage temperature, time between prep and analysis, surface area/sample weight, etc), many of which are not easily controlled. This Note illustrates the magnitude of the losses due to evaporation of volatile additives from the polymer surface and suggests a simple way to minimize the losses. The quantitative analysis of BHT in PE by TD-GC is used as a test sample.

[Experimental] Two PE samples, containing *ca*. 500ppm of BHT, were prepared - one by cutting the PE chunk into 20 pieces of *ca*. 0.5^{3}mm (method 1), and the other by cutting a single piece of PE *ca*. 1 x 1 x 3mm (method 2). The two samples were placed in separate sample cups, and quantitatively analyzed by TD-GC. Also, the effect of elapsed time from sample preparation to the start of the analysis is examined.

[Results] A typical chromatogram, obtained by TD-GC, is shown in Fig. 1. The level of BHT determined by five replicate analyses are 456 ppm (RSD=5.3%) - method 1, and 510 ppm (RSD=2.5%) with - method 2. These results indicate that during sample preparation, BHT loss from the sample surface is less if a single chuck of sample (method 2) is analyzed: 510 vs. 456 ppm (% difference = 11).

The influence of elapsed time from cutting the sample to the start of the analysis is shown in Fig. 2. As the elapsed time increases, the BHT level decreases and eventually stabilizes. About an 8% decrease in the BHT level is observed in the first hour, this increases to 13% in the next 2 hours. The BHT level remains fairly constant after 3 hours. This may be best explained by the fact that the BHT distributed inside the PE matrix does not migrate to the polymer surface at room temperature. These results clearly show that when performing quantitative analysis of volatile polymer additives such as BHT by TD-GC, it is particularly important that (1) the surface area to sample weight ratio be as low as possible, and (2) the samples should be analyzed immediately after the polymer is cut and placed in the sample cup.

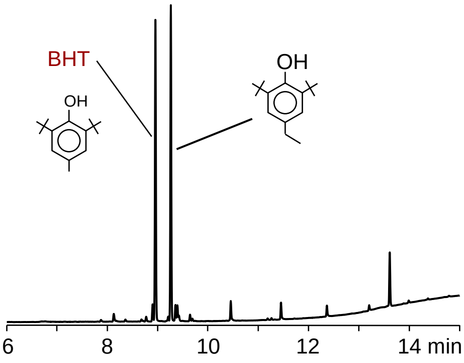

Fig. 1 Chromatogram of thermally desorbed components from the PE sample

Furnace temp.: 100-200ºC, (20ºC/min, 3min hold), gas flow rate : 1 mL/min,
Split ratio : 1/50, GC oven temp.: 40-320ºC (20ºC/min), sample size : *ca*. 3mg,
Sample pretreatment : method 2, detector FID,
Separation column : Ultra ALLOY-5
(5% diphenyl 95% dimethyl polysiloxane, L = 30 m, id = 0.25 mm, d_f = 0.25 µm)

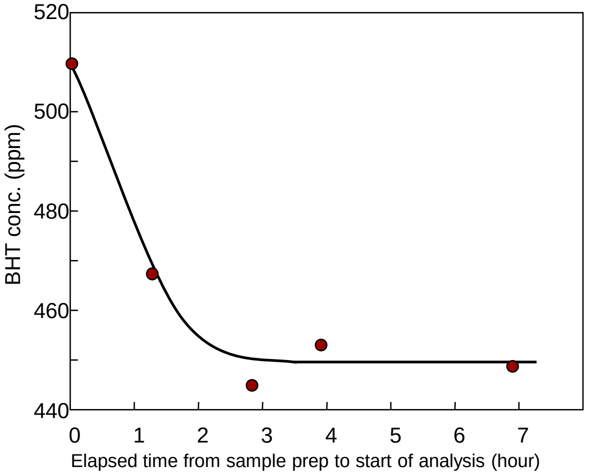

Fig. 2 BHT conc. plotted against Elapsed Time from Sample Preparation

Analytical conditions are identical to those shown in Fig. 1

Keywords : Additives, Thermal desorption, BHT, antioxidant, polyethylene

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

Applications : General polymer analysis

Related technical notes : PYA1-055E

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