PHAZIR™

Rapid, quantitative analysis of phthalates in PVC plastics.

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Abstract

Phthalate additives for polyvinyl chloride (PVC) have recently become restricted for use in children's toys both in the European Union and in the United States. The United States restrictions are scheduled to take effect in September 2009. Phthalates have been implicated as reproductive toxins.

Because plastic toys are often made of several parts, each of which may be made of a different type of plastic, a rapid, nonpreparative screening method is desirable. To achieve the desired properties in toys, 10-40% by weight of phthalate plasticizers are added to the PVC. Detection using non-preparative NIR is shown to be accurate to about ±0.1%.

Introduction

PVC is one of the most common plastics in use, in part because of the versatility provided by additives. Children's toys are now required to contain less than 0.1% phthalate esters because of concerns about reproductive toxicity. [1,2] Phthalate-containing PVC remains one of the most common forms of plastic in children's toys. In one study, 60 of 72 toys (>80%) contained phthalate-plasticized PVC components.[3] A more recent study confirms that PVC toy components contain 10-40% phthalates.[4]

Phthalates can be detected in plastics down to the part per billion level using HPLC and GC methods. Accurate determination of plasticizer content requires grinding and extraction of the plasticizer and the plastic. The extraction process can take from 30 minutes[3] to several hours.[4,5] Mid-infrared methods are available that do not require extraction, but only the surface of the prepared plastic piece is measured.

Near infrared (NIR) offers a rapid, non-preparative method for phthalate determination. NIR can provide results within seconds, without grinding the sample. NIR is sensitive to the quantity and environment of CH, NH, OH and other functional groups. As seen in Figure 1, phthalates have a distinct structure from PVC. The unique absorbance band of aromatic ring of the phthalate is easily distinguished from the polymer.

To determine manufacturing compliance for PVC and phthalate-free flexible components, a 0.1% accuracy is not needed. At less than 10% phthalate concentration, PVC is rigid.[6] For regulatory compliance, detection limits can be achieved.

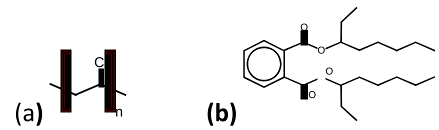

Figure 1. (a) The structure of the PVC polymer. (b) The structure of dioctyl phthalate, a common phthalate ester.

Experimental

Materials

- PHAZIR™ 1624 and 1018
- PhazirMG™ v. 1.63
- PVC powder (Sigma)
- Dioctyl phthalate (Sigma)
- Glass vials
- Temperature-controlled oven
- ±0.1 mg analytical balance

Procedure

Dioctyl phthalate was added to PVC powder in glass vials at 11 levels ranging from 0 to 60% by weight. The PVC powder was allowed to absorb the phthalate at 140°C for 6 minutes. The coarse powder was ground to further distribute the phthalate.

Spectra were recorded through the glass vial using a PHAZIR 1624 and 1018 in multiple locations around the vial. The spectra were analyzed using PHAZIR Method Generator.

Results & Discussion

Increasing phthalate concentration has two effects on the spectrum of PVC. The most dramatic effect is non-specific, the plasticizer acts to make the PVC powder more transparent. Both plasticizers and thermoplastic extrusion processes can have this effect. Mathematical pretreatments of the spectra, like Savitzky-Golay derivatives and normalization remove this non-specific effect from the spectrum.

The specific effect of phthalates is the appearance of aromatic CH bands. This feature is not shared by other classes of PVC plasticizers.[6] As can be seen in Figure 2, the intensity of the band is directly related to the phthalate concentration. A quantitative model can be readily built using just a few calibration samples.

Using a portion of the spectral range and mathematical removal of some of the non-specific effects on the spectrum allow a linear model to be created. The accuracy and lower detection limit for phthalates is estimated to be ±1% by weight. The conditions for the calibration shown in Figure 2 are described in Table 1. Results for the 1624 are similar to the 1018.

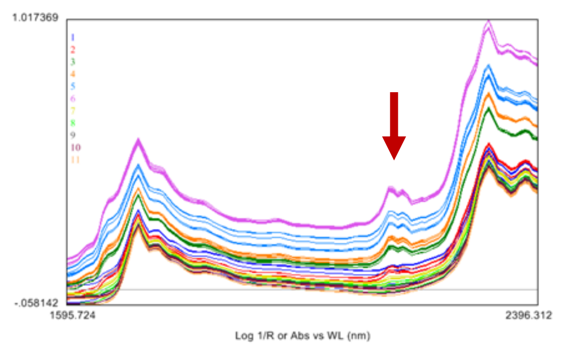

Figure 1. Spectra from the PHAZIR 1624 for the entire set of vials. The signature of phthalate esters is easy to identify visually.

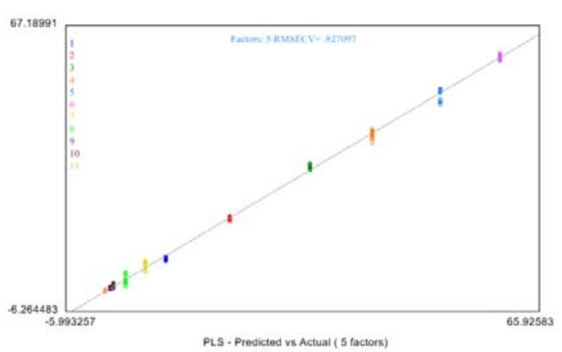

Figure 2. Calibration for dioctyl phthalate in PVC powder.

Additional results with this dataset indicate that 0.5% detection limits can be achieved if the data is limited to low concentrations of DOP and more homogenous samples were used. This would result in underestimates at higher phthalate levels.

Compressing the powders in a heated press allows for further improvement. Detection limits of 0.6% by weight can be achieved for the full concentration range. If the transparent, high DOP samples are omitted, detection limits improve to 0.06%.

Table 1. Results from optimization on the 1018 data.

Preprocessing	**Parameters**
Wavelength range	1039-1789 nm
Savitzky Golay (SG)	1st der., 3-point, 2nd degree
Range Normalization	1039-1789 nm
PLS1 Regression	
3 factors	
Rotation by concentration	
SEP cross-validated = 0.75% w/w	

Conclusions

NIR analysis of PVC plastics for phthalate ester concentration is easy to calibrate and straightforward to implement. The sample needs no preparation and can be analyzed *in situ.* Because the PHAZIR has a small sampling area, it is ideal for the rapid inspection of large and small plastics parts. The accuracy is sufficient for verifying materials provided by suppliers. The analysis is specific to phthalate esters.

In a larger context the PHAZIR can be used for both material identification, such as flexible silicones, urethanes and polyesters, as well as quantitative analyses of plasticizers and other modifiers.

[1] EU Directive 2005/84/EC.

[2] *Consumer Product Safety Improvement Act of 2008*. United States Public Law 110–314—Aug. 14, 2008.

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