Phthalates

Easy extraction of plasticizers from toys

The US Consumer Product Safety Commission's (CPSC) Test Method CPSC-CH-C1001-09.3 [1] is used by testing laboratories for the determination of phthalate content in children's toys and child care articles covered by the standard set forth in the Consumer Product Safety Improvement Act Section 108. The general manual approach is to dissolve the sample completely in tetrahydrofuran, precipitate any PVC polymer with hexane, filter and dilute with cyclohexane, and then analyze by Gas Chromatography/Mass Spectrometry (GC/MS). A combined autosampler and sample preparation robot can be used to automate these sample preparation steps.

Chemical additives are widely used to impart desirable properties to many products. For some compounds, however, due to toxicity issues, the amounts used need to be closely monitored.. Phthalic acid esters, also known as phthalates, are among these. They are widely used as plasticizers in polymers, making the material more pliable. Phthalates influence the physical properties of the polymer material significantly making it softer and more flexible. PVC, for example, is a highly durable material. Plasticizers give PVC the flexibility and elasticity that have made it so widely used and appreciated. Applications where PVC is used range from flooring, artificial leather, shower curtains, baby care articles, toys, packaging, shoes, sport and leisure materials, and medical products such as IV bags used for medical infusions and blood storage. Some further uses are: Cable coating, roofing materials, truck tarpaulins and undercoating of vehicles. However, there is a flipside to these benefits: Some phthalates, such as Di(2-ethylhexyl)phthalate [DEHP] as well as dibutylphthalate [DBP] and Benzylbutylphthalate [BBP] are considered harmful to human health and are banned by the European Union (EU) for a wide range of uses [3]. According to EU guidelines, DEHP is harmful to reproduction. Within the EU, restrictions apply to items used by children who are less than 3 years of age. Toys for this age group as well as baby care articles that contain the aforementioned phthalates at individual concentrations higher than 0.1 % w/w are not allowed into the market place.

The US Congress has permanently restricted the use of three phthalates (DEHP, DBP and BBP) as well as (on an interim basis) three additional phthalates (DINP, DIDP and DnOP) in any amount greater than 0.1 percent (computed for each phthalate, individually) in children's toys and certain child care articles. The risk of a negative health impact due to the transfer of the additives from PVC based products is deemed particularly great in small children.

In order to ensure compliance with governmental health and safety regulations, products that fall under the regulation must be monitored for these compounds.

Sample preparation is key

Sample preparation of polymers being monitored for additives is the most time consuming part of the overall analysis. When phthalates are determined in polymer matrices following manual extraction procedures described in CPSC-CHC1001-09.3, these procedures are often the rate-limiting step in terms of overall productivity and throughput, and they involve the use of hazardous chemicals and solvents. Typically, liquid dissolution of the polymer is first performed in order to quantitatively release additives and other compounds of interest from the material. A solvent, in which the polymer is not soluble, is then added to precipitate the polymer while leaving the analytes of interest in solution. Filtration of the final extract is performed prior to analysis by either GC or HPLC. This general procedure can be applied to a wide variety of polymers and plastics. In this work, we show that the manual procedure established for the extraction of phthalates from consumer products produced from PVC is easily automated using the GERSTEL MultiPurpose Sampler (MPS). The entire process is conveniently controlled using MAESTRO software.

Weigh a 50 mg sample of polyvinylchloride (PVC) in a sealable glass vial.

Add 5 mL of THF to the sample

Mix the sample for at least 30 minutes, to ensure complete dissolution. Ultrasound and/or mild heating can be used to accelerate the dissolution process. If the sample hasn't been completely dissolved, the mixing period should be extended by another 2 hours before continuing.

Precipitate the PVC polymer using 10 mL of hexane for each 5 mL of THF used during the dissolution step.

Shake and wait at least 5 minutes for the polymer material to precipitate and settle.

Filter the THF/Hexane solution through a 0.45 mm PTFE filter and collect a few mL of the filtrate in a separate glass vial.

Combine a 0.3 mL aliquot taken from the THF-hexane mixture with 0.2 mL of the internal standard, in case this is used, and top up to 1.5 mL with cyclohexane.

Inject 1 µL of the solution into the GC/MS.

As explained by Ed Pfannkoch, Technical Director, GERSTEL, Inc., Baltimore, MD: "It was our aim to transfer the manual steps one by one and automate the entire process while using the PrepAhead function in MAESTRO to perform sample preparation simultaneously with the GC/MS run and increase productivity". To this end, Ed Pfannkoch and his team used the Dual Head version of the GERSTEL MPS. One head was fitted with a 2.5 mL syringe for liquid transfer used for sample preparation, the other with a 10 µL syringe used for liquid injection into the GC/MS system (Agilent 7890GC/5975MSD); the PTV inlet used was a GERSTEL Cooled Injection System (CIS 4). The MPS was further equipped with a heated agitator, GERSTEL Automated Liner Exchange (ALEX) as well as a Filtration Option. Method and sequence table setup including all sample preparation steps were performed using the GERSTEL MAESTRO Software, completely integrated with the Agilent ChemStation.

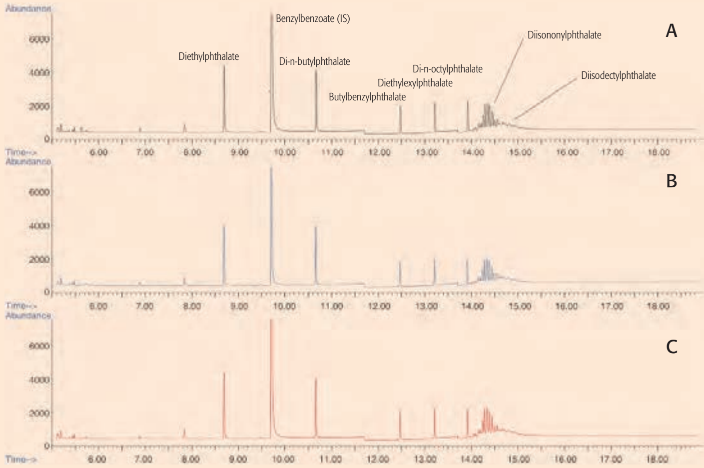
For this method, the PVC sample is dissolved in tetrahydrofuran (THF) and the PVC precipitated using hexane followed by filtration, dilution with cyclohexane and finally analysis using GC/MS. The test procedure is listed in the box to the left on this page.

Greetings from the rubber duck

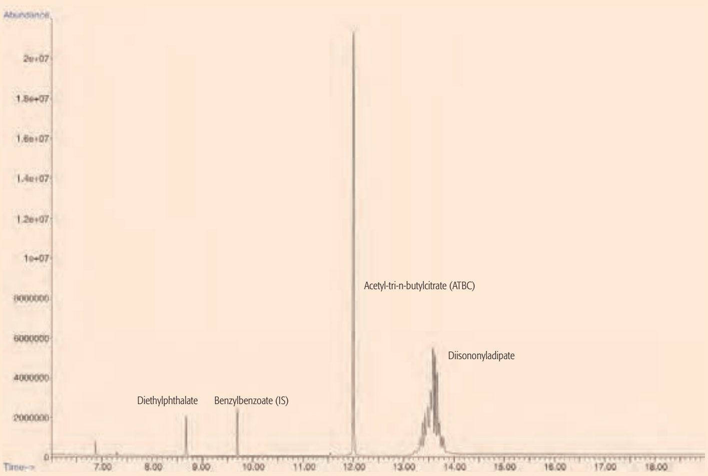
As research objects, Ed Pfannkoch and his team chose ordinary rubber ducks as well as other toys made of PVC. Three other samples were obtained from a local CPSC testing station (CPSC-1, CPSC-2, and CPSC-3). All PVC samples to be extracted were initially cut into small pieces of no more than 2 mm particle size. These were weighed in 10 mL glass vials fitted with screw caps and placed in the MPS sample tray. Analysis method parameters were established as shown in the box on the right. The method was calibrated using standard solutions covering two concentration ranges: Lower range (50-1000 ng/mL) and upper range (5-100 µg/mL). "Initially, we tested whether the solvents used for the extraction were free of phthalates", Edward Pfannkoch explained: "We went through an entire blank extraction procedure, without any sample present, and no phthalates were detected in the final extract." Following the initial experiment, the certified reference samples were extracted – first using the manual sample preparation method and then using the automated extraction procedure. The results obtained using the two methods were found to be in good agreement. The automated sample preparation method combined with GC/MS analysis of the sample extracts worked reliably and pro-

Analysis conditions

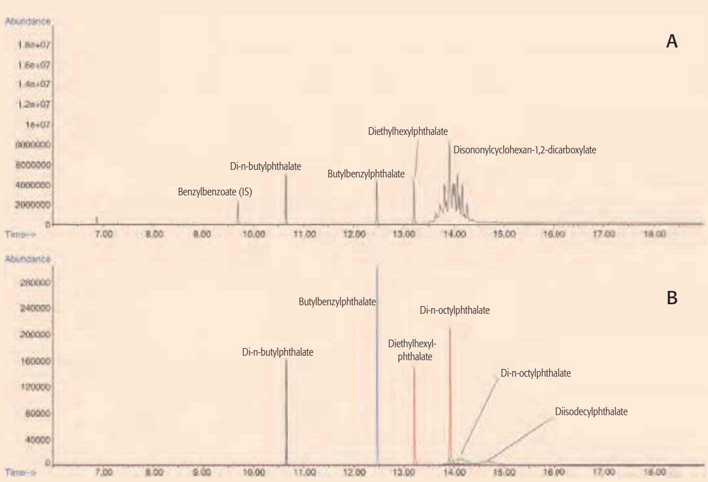
PTV (CIS 4):	Baffled liner, split (20:1) or splitless, 50 °C; 12 °C/s; 280 °C (3 min)
Column:	30 m HP-5MS (Agilent) di = 0.25 mm df = 0.25 µm
Pneumatics:	He, constant flow = 1.0 mL
Oven:	50 °C (1 min); 20 °C/min; 310 °C (5 min)
MSD:	Full scan, 40-350 amu
SIM Parameters (Mass [m/z], Dwell time [ms])	
Group 1:	5 min (91, 10), (105, 10), (149, 10), (167, 10), (194, 10), (194, 10), (205, 10), (212, 10), (223, 10)
Group 2:	11.7 min (91, 10), (149, 10), (167, 10), (206, 10), (279, 10)
Group 3:	13.7 min (149, 10), (167, 10), (261, 10), (279, 10), (293, 10), (307, 10)



Chromatogram resulting from automated preparation of a 50 mg sample (A); automated preparation of a 25 mg sample (B); and manual preparation of a 25 mg sample (C). Conclusion: The chromatograms are equivalent.



Full Scan chromatogram of a rubber duck sample. The chromatogram illustrates the benefits of using SIM/Scan mode: Even plasticizers, which are not selected as target analytes appear in the chromatogram. These include: Diethylphthalate, acetyl-tri-n-butylcitrate and diisononyladipate.



Full scan chromatogram for sample CPSC-2. Figure B shows extracted ion chromatograms of SIM data. Target analytes are identified in the SIM chromatogram. The full scan chromatogram shows the presence of another compound: Diisononylcyclohexane-1,2-dicarboxylate.

duced accurate results. To increase the overall throughput, and to reduce the use of toxic solvents, Pfannkoch and his team reduced the amount of sample and solvent used by 50 % without any measurable impact on the analytical results. Finally, the rubber duck and the CPSC samples were taken through the complete automated procedure.

Extracts were analyzed by GC/MS in split and splitless mode. The MSD was operated in SIM/Scan mode. For the lower concentration range, the instrument was operated in splitless mode. For the higher concentration range, the split was set to 20:1. Analytes were identified based on their mass spectrum and retention times. Quantification was performed based on the calibration curve.

No need to "duck" hard questions

At the end of every method development, the user has to face up to the critical question: Was I successful? Edward Pfannkoch is happy with the results. "Our main aim, to transfer the extraction to the MPS and to automate it completely was achieved", he states. The automated analysis of the certified reference materials gave accurate results. The automated GC/MS method for the determination of DEHP, DBP, BBP, DINP, DIDP and DnOP delivered accurate results with a relative standard deviation (RSD) of 1.9-5.5 percent for all determined phthalates, which is highly precise. In short, the automated GC/MS analysis following test method CPSC-CH-C1001-09.3 performed flawlessly. The results we achieved were highly satisfactory – also for real samples. In the samples CPSC-1 and CPSC-2, we found all six target analytes. Sample CPSC-3 on the other hand contained DEHP at a high concentrations level.[4]

Literature

[1] United States Consumer Product Safety Commission, Test Method: CPSC-CH-C1001-09.3 Standard Operating Procedure for Determination of Phthalates, April 1st, 2010.
[2] German Federal Environmental Protection Agency (Umweltbundesamt): Phthalates: Useful plasticizers with undesired properties, 02/2007; www.umweltbundesamt.de/sites/default/files/medien/publikation/long/3541.pdf
[3] Directive 2005/90/EC of the European Parliament
[4] Fredrick D. Foster, John R. Stuff, Jacqueline A. Whitecavage, Edward A. Pfannkoch: Automated Extraction and GC/MS Determination of Phthalates in Consumer Products, GERSTEL AppNote 4/2013, www.umweltbundesamt.de/sites/default/files/medien/publikation/long/3541.pdf