Extraction of Phthalates from Polyvinyl Chloride

Summary

The EDGE® automated solvent extraction system is the most advanced extraction system available. By combining pressurized fluid extraction and dispersive solid phase extraction, the EDGE is able to drastically reduce the sample preparation time and potential for human error. The result is fast, simple, and efficient extractions. In just 15 minutes phthalates can be extracted from different types of plastics such as polyvinyl chloride (PVC). This includes sample filtration and cooling as well as system washing.

Introduction

Phthalates have been described as dangerous chemical toxins that can damage the liver, kidneys, lungs, and reproductive systems and have been linked to alteration of DNA integrity. They have been used since the 1950s to soften plastics and can be found in products that most people encounter on a daily basis including personal care products, vinyl flooring, children's lunch boxes, backpacks, and toys. Even more alarming is the presence of phthalates in items marketed toward and/or used by young children, who are more prone to put items in their mouths. Since they are not chemically bound to the plastic, phthalates are continuously released into the environment and people are exposed through repeated contact. The extraction of phthalates from plastics must be a quick and simple process so that manufacturers can confidentially release products that meet the safety guidelines of the CPSC.

The extraction of phthalates from plastics is difficult for a number of reasons. First, the low melting point of the plastic makes it difficult to extract. The plastic must be transformed to extract but not melt and reaching that balance is challenging. Second, due to the complexity of samples, the existing extraction methods, including Soxhlet and pressurized fluid extraction both referenced in CPSC-CH-C1001-09.3, often yield extracts that are cloudy and contain multiple co-extracts, making analysis difficult. Third, all extraction methods referenced in CPSC-CH-C1001-09.3 can be time-consuming and require large volumes of solvent. The EDGE is capable of producing a clean, filtered, and cooled extract that is ready for analysis in less than 15 minutes using no more than 50 mL of solvent. Each 15 minute extraction cycle also includes an efficient dual solvent wash which cleans the system and mitigates risk of carryover.

Materials and Methods

Reagents

A polyvinyl chloride CRM-PVC001 was purchased from SPEX CertiPrep. The CRM contained the following phthalates of interest: dimethyl phthalate, diethyl phthalate, bis(2-ethylhexhyl) phthalate, butylbenzyl phthalate, di-*n*-butyl phthalate, and di-*n*-octyl phthalate. A 50/50 mixture of isopropanol/cyclohexane was used for the extraction, rinse and wash solvent. Three standards purchased from SPEX CertiPrep were used to construct a calibration curve for each phthalate of interest, dimethyl phthalate in methanol (S-1590), diethyl phthalate in methanol (S-1515) and phthalate standard in isooctane (C1001-09).

Sample Preparation

All samples were extracted, filtered and cleaned on an EDGE® system from CEM Corporation (Matthews, NC). For each sample a C1 Q-Disc® was placed into the Q-Cup® base and the two parts were screwed together creating a seal between the Q-Cup and Q-Disc. 1 g of polyvinyl chloride was weighed into an assembled Q-Cup. The Q-Cups were placed in the EDGE removable rack, each with a collection vial, and the rack was slid into place on the EDGE and queued for extraction using the CEM approved method parameters outlined below.

EDGE Method

Q-Disc:	C1
Solvent:	50/50 isopropanol/cyclohexane
Top Add:	20 mL
Bottom Add:	10 mL
Rinse:	0 mL
Temperature:	80 °C
Hold Time:	10 min
Wash 1:	10 mL 50/50 isopropanol/cyclohexane
Wash 2:	10 mL 50/50 isopropanol/cyclohexane

Analysis

Extract samples were diluted to 50 mL with 50/50 isopropanol/cyclohexane. An aliquot of each extract was injected into the Agilent 7890A with a 5975C MSD for analysis adhering to EPA 8270. A Phenomenex ZB-5MSplus 30 m, 0.25 mm column was used.

Results and Discussion

Figure 1 is a representative GCMS chromatogram showing clean separation of the phthalates of interest with the retention times of the analytes of interest in **Table 1**. Recovery data was determined via 8 point calibration curves, at 12, 24, 48, 60, 80 and 100 ppm, for all phthalates of interest. All calibration curves had R^2 values greater than 0.99. The final concentration of the extracts for each of the phthalates of interest was 60 ppm.

Figure 1: GCMS chromatogram of phthalates of interest

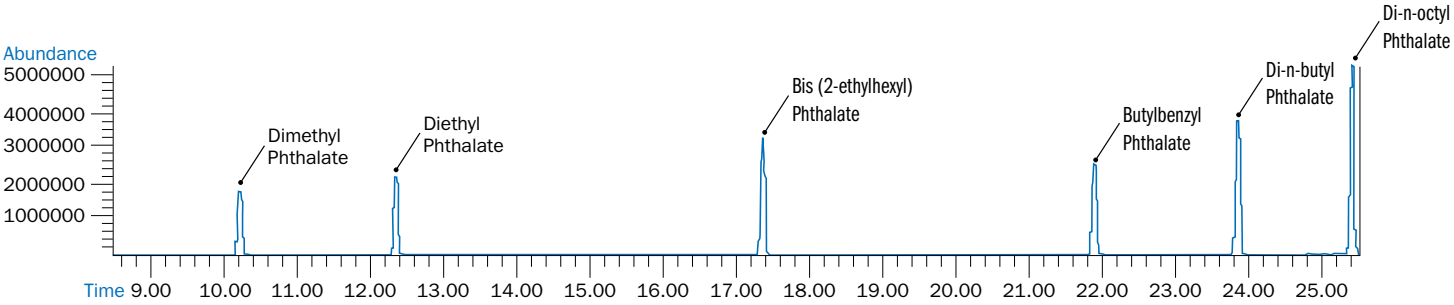

Table 1: Retention times of phthalates of interest

Standard Compound	Retention Time (min)
Dimethyl Phthalate	10.297
Diethyl Phthalate	12.375
Bis (2-ethylhexyl) Phthalate	17.305
Butylbenzyl Phthalate	21.758
Di-*n*-butyl Phthalate	23.223
Di-*n*-octyl Phthalate	25.223

Table 2 shows the % recovery of the extraction of phthalates from polyvinyl chloride. All methods for sample prep, extraction, and analysis were based on CPSC-CH-C1001-09.1. For the extraction process, the total method time, including extraction, filtration, and system washing never exceeded 15 min. The total extraction volume was 30 mL and additional 20 mL of solvent was used to wash the system.

Conclusion

To be in the acceptable recovery range, the percent recovery data for the extraction of phthalates from plastics should be within 80-120%. The EDGE with Q-Cup technology yielded acceptable recoveries for the extraction of phthalates from polyvinyl chloride. Furthermore, the EDGE addressed all the limitations of existing extraction methods. Due to precise temperature control, the low melting point of PVC was not a concern. The fine filtration of the sample enabled by the Q-Disc minimized interference from other contaminates yielding clean and easy to analyze extracts. The EDGE method used less solvent and time than the extraction methods referenced in CPSC-CH-C1001-09.3. Lastly, since the EDGE is an automated system it eliminates human error often existing with other extraction techniques. EDGE was able to economically and accurately extract phthalates from plastics.

Table 2: % recovery data for polyvinyl chloride

Standard Compound	Average Recovery (n=6)	RSD
Dimethyl Phthalate	86	1.9
Diethyl Phthalate	83	1.5
Bis (2-ethylhexyl) Phthalate	88	1.5
Butylbenzyl Phthalate	86	1.7
Di-*n*-butyl Phthalate	84	2.5
Di-*n*-octyl Phthalate	101	1.7

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