APPNOTE

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Determination of Phthalates in Plastic Bottles and Beverages using Thermal Desorption and Gas Chromatography with a Triple Quadrupole Mass Spectrometer

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Keywords

Consumer products, food safety, phthalates, thermal desorption, GC-MS/MS

Abstract

Phthalates are commonly used as plasticizers. These compounds help make plastics more flexible and durable. They are commonly found in medical devices, food packaging, household and personal care items. Migration or leaching from these products can lead to exposure for the consumer. Health concerns regarding phthalates have been raised about their potential adverse health effects, especially regarding endocrine disruption.

Introduction

The GERSTEL Twister is an extraction device used for Stir Bar Sorptive Extraction (SBSE). The Twister enables ultra-trace determination of organic compounds in aqueous and gaseous matrices. It consists of a glass-coated magnetic stir bar coated with an absorbent layer. After sampling, the Twister is placed in an empty TD tube and heated in a thermal desorption system to release the analytes of interest. The advantages of Twister are highly efficient extractions due to the large stationary phase volume, extraction efficiencies are predictable based on octanol/water partition coefficient, solventless extraction and reusable (green technique), more stationary phase than similar devices, and multiple samples can be extracted in parallel. Detection limits in the ppq to ppt range are obtainable using this technique.

Direct thermal extraction (DTE) is a technique in which a solid or liquid sample (in a suitable holder) is heated with inert gas flow, and the analytes evolved are trapped. In an online system, the thermal desorber is used to heat and provide inert gas flow, and the analytes are trapped in the GERSTEL CIS 4 inlet liner. The analytes can be trapped cryogenically or on a sorbent. After analyte trapping is complete, the trap is rapidly heated to transfer the analytes onto the head of the GC column as a narrow band to provide optimum chromatographic performance. A sample size of 10-50 mg is typically used for this technique. The experimental variables that need to be optimized are extraction temperature, extraction time, and flow rate across the sample. Since there is minimal dilution (split) of the analytes before entering the GC column, this technique can provide very low detection limits, even with the relatively small sample size.

The GERSTEL MultiPurpose robotic sampler (MPS) with a TD 3.5^{+} thermal desorber, in combination with the GERSTEL Cooled Injection System (CIS 4), fully automates thermal desorption for the determination of phthalates in plastic and beverages. An Agilent 8890 gas chromatograph with 7000E TQ was used for the separation and detection of the phthalates.

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Experimental

Instrumentation

GERSTEL MPS robotic^{pro} sampler, TD 3.5+ thermal desorber, GERSTEL CIS 4 Cooled Injection System (CIS), and Agilent 8890 GC/7000E TQ MS (Figure 1).

Figure 1: Instrument used for this study.

Analysis Conditions

TD 3.5^{+}	splitless: 40 °C (0.0 min); 12 °C/sec, 280 °C (3 min) Twister splitless: 40 °C (0.0 min); 12 °C/sec, 200 °C (10 min) DTE
CIS	solvent vent: 10:1 split transfer 10 °C (0.0 min); 12 °C/sec, 280 °C (5 min) glass with Tenax-TA®
Pneumatics	He; P_i = 7.1 psi constant flow = 1.0 mL/min
Oven	100 °C (1.0 min), 15 °C/min, 280 °C (9.0 min)
Column	30 m DB-1701 (Agilent #122-0732) d_i = 0.25 mm, d_f = 0.25 µm

MS Parameters

Dwell	50 ms
Collision energy	15 V
Gain factor	10

Table 1: Transitions used in this study.

Compound	RT	Transition	Transition
Dimethylphthalate	7.99	**194-163**	194-77
Diethylphthalate	8.99	**177-149**	177-93
Diallylphthalate	10.10	**149 SIM**	
Diisobutylphthalate	10.76	**223-149**	205-149
Dibutylphthalate	11.41	**223-149**	205-149
Di(4-methyl-2-pentyl)phthalate	11.93	**251-167**	251-149
Di(2-methoxyethyl)phthalate	12.05	**176-149**	104-76
Dipentylphthalate	12.53	**237-149**	219-149
Di(2-ethoxyethyl)phthalate	12.59	**176-149**	241-112
Dihexylphthalate	13.62	**251-149**	233-149
Benzylbutylphthalate	14.09	**206-149**	149-121
Di(2-butoxyethyl)phthalate	14.76	**176-249**	193-149
Diethylhexylphthalate	14.86	**279-149**	279-93
Dicyclohexylphthalate	15.32	**249-149**	249-93
Diphenylphthalate	16.26	**225-77**	225-104
Di-n-octylphthalate	16.73	**279-149**	279-93
Diisononylphthalate	19.29	**293-149**	293-71

Quantitative transition in **Bold**

Standards

A phthalate mix, 1000 µg/mL, containing 18 phthalates was purchased from AccuStandard (GBS-005S). Working standards were prepared in methanol.

Sample Preparation

Beverage samples (vitamin water, lemon juice, fruit juice, power drink, and freezer pops) were purchased locally.

Direct Thermal Extraction – The liquids were removed from the plastic bottles. The bottles were rinsed three times with DI water and allowed to dry. A portion of the plastic bottle was cut from the side. Approximately 20-30 mg of sample was weighed into a TDU microvial. The microvial was placed in an empty TD 3.5^{+} tube and analyzed by direct thermal extraction.

Twister – Ten milliliters of sample were pipetted into a 10 mL screw cap vial. A Twister was added. The sample was extracted for 90 minutes at 1100 rpm. The Twister was removed from the sample, dipped in DI water, and dried on a lab wipe. The dried Twister was placed in an empty TD 3.5^{+} tube and analyzed by thermal desorption.

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Standard Preparation

Direct Thermal Extraction – A known amount of phthalate standard was spiked onto the fritted end of a thermal desorption tube containing Tenax-TA®. Dry nitrogen was passed through the tube at 50 mL/min for three minutes. The Tenax-TA® tube was then analyzed by thermal desorption.

Twister – Ten milliliters of DI water were pipetted into a 10 mL screw cap vial. A known amount of phthalate standard was added to the vial. A Twister was added. The sample was extracted for 90 minutes at 1100 rpm. The Twister was removed from the sample, dipped in DI water, and dried on a lab wipe. The dried Twister was placed in an empty TD 3.5+ tube and analyzed by thermal desorption.

Results and Discussion

Figure 2 shows a total ion chromatogram of a standard.

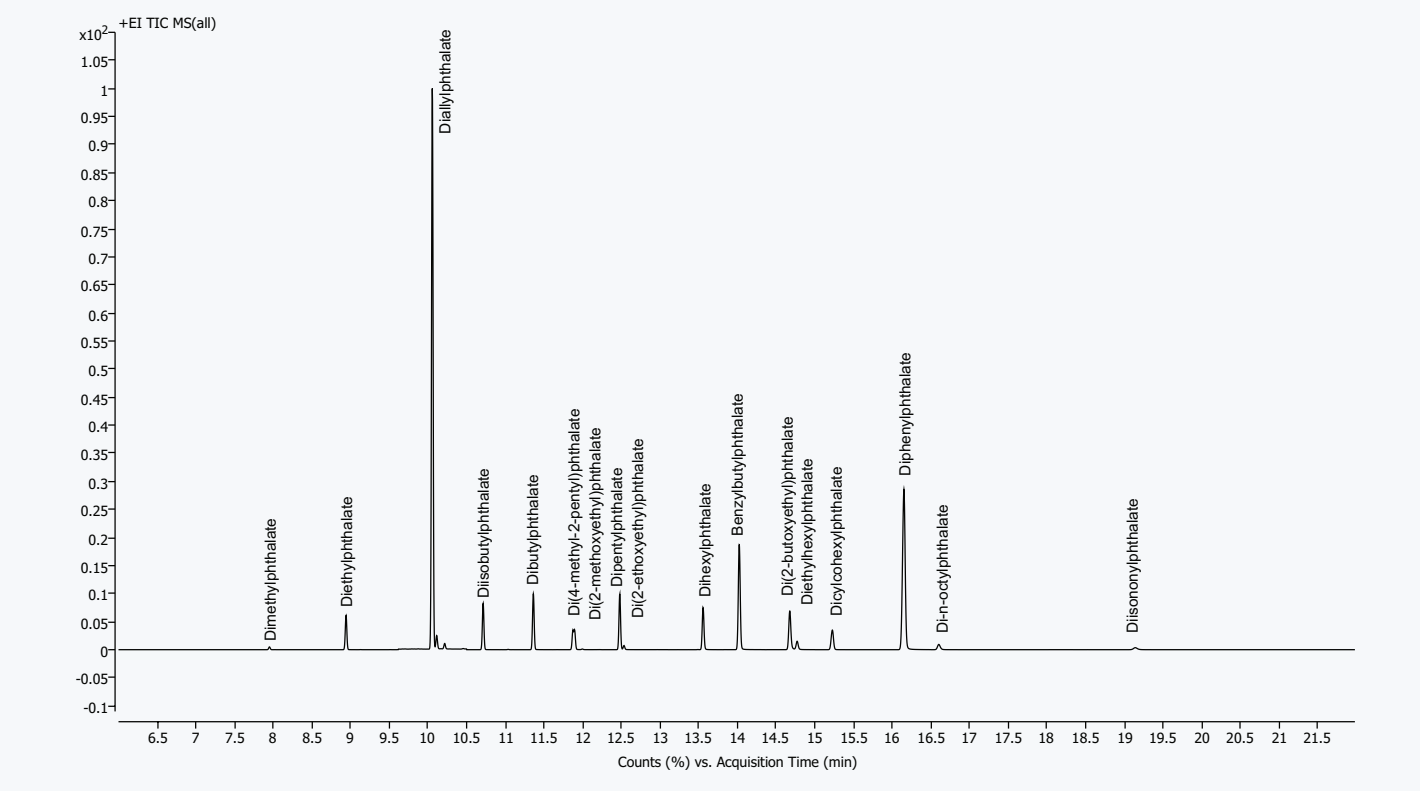

Figure 2: Total ion chromatogram for phthalate standard.

Four-point calibration curves were generated by spiking a known amount of standard onto a Tenax-TA® filled sorbent tube. Figure 3 shows an example curve for diisobutylphthalate. The curves were linear for all analytes with r^2 values greater than 0.99.

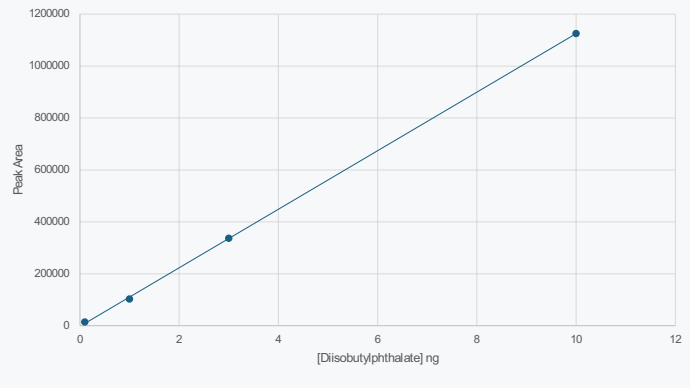

Figure 3: Tenax-TA® calibration curve for diisobutylphthalate.

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The results for the direct thermal extraction of the plastic containers are shown in Table 2. The cap and bottle for the lemon juice container were both analyzed by DTE. Several phthalates were found in the plastic containers. Diethylphthalate, dibutylphthalate and diisobutylphthalate were found in all five samples. The highest amount of phthalates, dibutylphthalate and diethylhexylphthalate, were found in the freezer pop wrapper at 390 and 1720 ng/g, respectively.

Table 2: Phthalates found in plastic bottles by DTE in ng/g.

Compound	Lemon cap	Lemon bottle	Vitamin water	Fruit juice	Power drink	Freeze pop
Dimethylphthalate						
Diethylphthalate	26.2	16.8	14.5	26.5	14.4	54.7
Diallylphthalate						
Diisobutylphthalate	36.6	10.9	5.14	38.4	5.94	67.1
Dibutylphthalate	103	34.0	6.36	30.9	6.64	390
Di(4-methyl-2-pentyl)phthalate						
Di(2-methoxyethyl)phthalate						
Dipentylphthalate						
Di(2-ethoxyethyl)phthalate						
Dihexylphthalate						
Benzylbutylphthalate			7.09	6.38	7.40	19.3
Di(2-butoxyethyl)phthalate						
Diethylhexylphthalate			89.5	15.3	30.1	1720
Dicyclohexylphthalate						
Diphenylphthalate						
Di-n-octylphthalate						
Diisononylphthalate						

Four point calibration curves were generated by spiking a known amount of standard into DI water and extracting it using a Twister. The calibration range was 0.1-10 ng/g. Figure 4 shows an example curve for benzylbutylphthalate. The curves were linear for all analytes with r^2 values greater than 0.99.

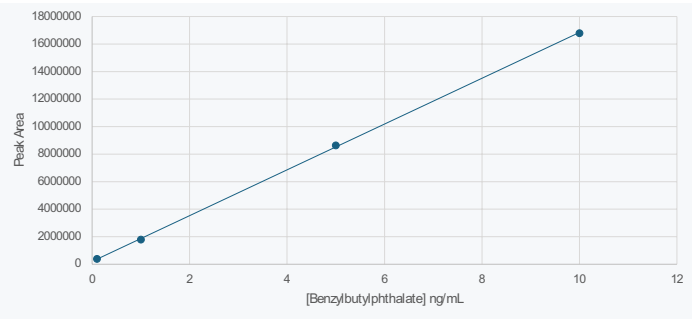

Figure 4: Twister calibration curve for benzylbutylphthalate.

The results for the Twister extraction of the liquid samples are shown in Table 3. Dibutylphthalate was detected in all five samples. It was not quantitated in the vitamin water as the response was below the lowest standard. The levels of phthalates detected in the samples were low. The highest values were for dibutylphthalate in the lemon juice and freezer pop at levels of 1.11 and 1.09 ng/mL, respectively.

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Table 3: Phthalates found in liquid samples by Twister extraction in ng/mL.

Compound	Lemon juice	Vitamin water	Fruit juice	Power drink	Freeze pop
Dimethylphthalate					
Diethylphthalate					
Diallylphthalate					
Diisobutylphthalate	0.585		0.234	0.258	0.443
Dibutylphthalate	1.11	D	0.375	0.634	1.09
Di(4-methyl-2-pentyl)phthalate					
Di(2-methoxyethyl)phthalate					
Dipentylphthalate					
Di(2-ethoxyethyl)phthalate					
Dihexylphthalate					
Benzylbutylphthalate					0.269
Di(2-butoxyethyl)phthalate					
Diethylhexylphthalate					
Dicyclohexylphthalate					
Diphenylphthalate					
Di-n-octylphthalate	0.174				
Diisononylphthalate	0.141				

Conclusions

This study showed the use of thermal desorption techniques for the determination of phthalates in plastic bottles and in beverages. Low levels of phthalates were detected in both sample types.

The GERSTEL MPS robotic^{pro} sampler with TD 3.5^{+}, GERSTEL CIS 4 Cooled Injection System (CIS), and Agilent 8890 GC/7000E TQ MS provide a solvent free, minimal sample prep method for the determination of phthalates in plastic and beverage samples at low levels. This method could be applied to the analysis of plastics used for food contact and for beverages stored in plastic containers to monitor for possible phthalate migration from the container to the beverage.