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One-Minute Method for the Screening of Phthalates in Toys at Regulatory Limits Using UPLC/MS and Empower Software

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APPLICATION BENEFITS

- One-minute screening method for phthalates in toys at legislative limits
- Benefits of MS, such as selectivity and sensitivity, can be brought to existing Empower users, without the need for additional training
- Users can define specific limits and quickly identify samples that exceed permitted levels with Empower™ Software's system suitability functionality.

WATERS SOLUTIONS

ACQUITY® SQD
Empower 2 Software

KEY WORDS

Phthalates, DEHP, BBP, DINP, DIDP, DnOP, phthalic acid, plastics

INTRODUCTION

Phthalates, esters of phthalic acid, are widely used to modify the physical properties of plastics. They are added to products to increase flexibility, transparency, softness, durability, and longevity. Owing to their unique properties, phthalates are widely used in toys, childcare items, food packages, raincoats, shower curtains, paints, lubricants, detergents, and personal care products.

Since there is no chemical bond between phthalates and the plastics, phthalates can migrate into the environment. Upon use by children or adults, they have the potential to cause serious side effects such as hormone malfunctioning, reproductive defects, and cancer.[1]

According to the Consumer Product Safety Improvement Act (CPSIA, August 2008),[2] some phthalates are restricted in particular products. Since February 2009, children's toys and childcare articles cannot contain concentrations of more than 0.1% of Bis (2-ethylhexyl) phthalate (DEHP), Di-n-butyl phthalate (DBP), and Benzyl butyl phthalate (BBP). Temporary restrictions were also placed on children's toys and childcare articles that contain more than 0.1% Diisononyl phthalate (DINP), Di-isodecyl phthalate (DIDP), or Di-n-octyl phthalate (DnOP). The European Union and Japanese toy safety standards also enforce the same legislative limits for all six phthalates listed above.[3,4]

This application note describes a screening method for 14 phthalates (six of which are legislated) in one minute, using the Waters® ACQUITY UPLC® with SQ Detector and Empower 2 Software. A typical quantitative phthalate analysis using GC/MS takes approximately 30 minutes per sample.[5] Using this one-minute screening method dramatically increases the sample throughput. Those samples that show positive results can then be submitted for confirmatory analysis.

SAMPLE PREPARATION

The sample was prepared as described previously.[6] Briefly, a child's teething toy was finely chopped. Two grams of the sample was sonicated with 200 mL of methanol for 10 min. The supernatant was collected and filtered through a 0.2 µm nylon filter. The filtrate was diluted 10-fold in methanol and placed into a Waters certified vial for analysis.

EXPERIMENTAL

LC conditions

LC system:	ACQUITY UPLC
Runtime:	1.0 min
Column:	ACQUITY UPLC BEH C_{18} 1.7 µm, 2.1 x 50 mm
Mobile phase A:	Methanol + 0.1% formic acid
Isocratic flow rate:	0.6 mL/min
Injection volume:	2 µL
Weak needle wash:	98:2 Water: Methanol + 0.1% formic acid
Strong needle wash:	Methanol + 0.1% formic acid

MS conditions

MS system:	ACQUITY SQ Detector
Ionisation mode:	ESI+
Capillary voltage:	3.5 kV
Source temp.:	150 °C
Desolvation temp.:	450 °C
Desolvation gas:	800 L/H
Acquisition:	Selected Ion Recording (SIR)

IntelliStart™ Technology was used to tune all the phthalates in this application note. IntelliStart, a standard feature of Waters MS systems automates system calibration, sample tuning, and daily checks, so that non-expert users can acquire data with confidence that the system is operating optimally. The resulting tuning parameters are shown in Table 1.

Phthalate	Parent ion	Dwell time(s)	Cone voltage (V)	Peak name
Dimethyl phthalate	195	0.02	15	a
Diethyl phthalate	223	0.02	20	b
Dipropyl phthalate	251	0.02	20	c
Di-n-butyl phtahlate	279	0.02	25	d
Diisobutyl phthalate	279	0.02	20	e
Bis (methylglycol) phthalate	283	0.02	20	f
Dipentyl phthalate	307	0.02	20	g
Benzyl butyl phthalate	313	0.02	20	h
Dihexyl phthalae	335	0.02	20	i
Butyl phthylyl phthalate	337	0.02	20	j
Bis (2-Ethylhexyl) phthalate	391	0.02	25	k
Di-n-Octyl phthalate	391	0.02	20	l
Diisononyl phthalate	419	0.02	30	m
Di-isodecyl phthalate	447	0.02	15	n

Table 1. MS tuning parameters for phthalates obtained using IntelliStart.

RESULTS AND DISCUSSION

Using the ACQUITY SQD, 14 phthalates were analyzed within 1 min. The chromatograms of each of the phthalates analyzed at 1000 ng/mL are shown in Figure 1.

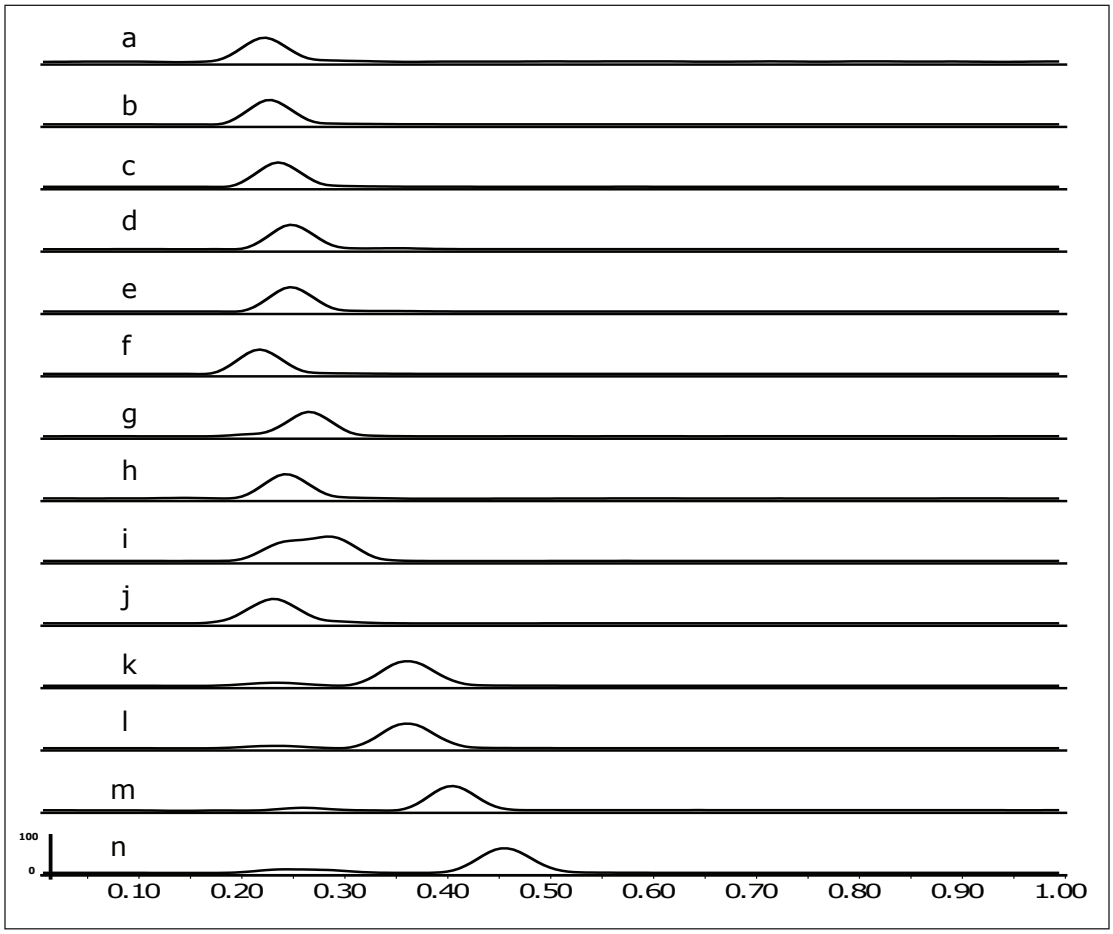

Figure 1. Chromatograms showing separation of 14 phthalates.

The results for each of the phthalates showed good injection-to-injection reproducibility. Table 2 shows the % RSD on the area count from six injections of a toy extract that was spiked at 1000 ng/mL with each of the phthalates.

Compound name	% RSD
Dimethyl phthalate	10.6
Diethyl phthalate	13.4
Dipropyl phthalate	4.1
Di-n-butyl phtahlate	3.7
Diisobutyl phthalate	8.9
Bis methylglycol phthalate	6.1
Dipentyl phthalate	8.5
Benzyl butyl phthalate	7.1
Dihexyl phthalae	4.7
Butyl phthaylyl phthalate	10.0
bis 2 Ethylhexyl phthalate	7.5
Di-n- Octyl phthalate	8.4
Di-isononyl phthalate	6.4
Di-isodecyl phthalate	3.9

Table 2. Relative standard deviation from 6 injections of a spiked toy extract at 1000 ng/mL.

According to the CPSIA legislation,[1] the concentration of phthalates should not exceed more than 0.1% of the total mass. Due to the sample preparation and dilution in the sample extraction, the legislative limit is equivalent to 1000 ng/mL. Figure 2 shows an example 5-point calibration curve of one of the phthalate standards (diisononyl phthalate) around the concentration that corresponds to the legislated level. The calibration curve showed an r^2 value of 0.9951.

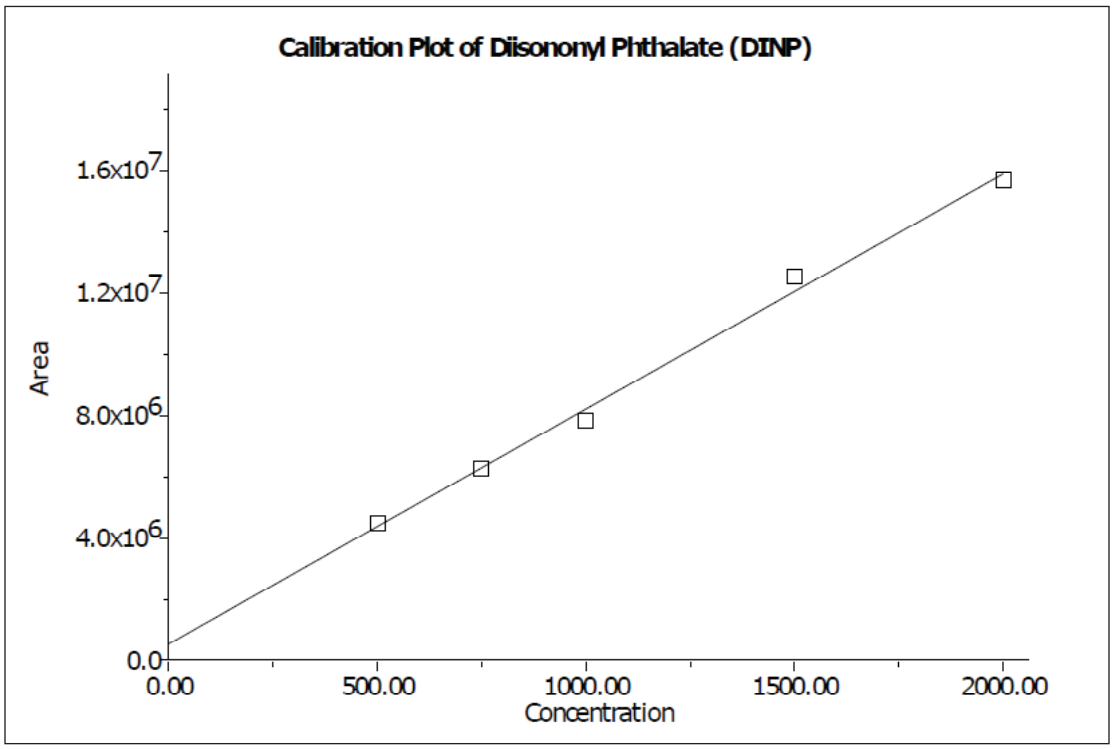

Figure 2. Five-point calibration curve for Diisononyl phthalate from 500 ng/mL to 2000 ng/mL.

The data were acquired using Empower 2 Software and processed using the system suitability function. Empower system suitability software monitors the chromatographic system automatically and provides a summary based on parameters and limits set by the user. This feature was used to set minimum and maximum values in summary charts and to flag out-of-range values.

The target limit for the phthalates is 1000 ng/mL (taking into account the sample preparation), so any sample that exceeded this limit was flagged and reported in a different color and font. A typical system suitability report is shown in Table 3. The table shows the results for diisononyl phthalate from the extracted toy sample as well as two spiked extracts from the toy sample at 500 and 1000 ng/mL. As shown in Table 3, the 1000 ng/mL spiked toy extract had a calculated concentration of 1042 ng/mL, which was flagged as being over the maximum concentration of 1000 ng/mL. The first sample (the toy extract that was not spiked) does not show a reported amount, as the detected peak for this compound was below the minimum reporting level (which was set at the lowest concentration standard, 500 ng/mL).

Component summary table
Name Diisonoyl phthalate

Sample name	Name	RT	Concentration	Units
1 TOY extracted blank	13	0.400		ng/mL
2 TOY spiked 500 ng/mL	13	0.405	542.5	ng/mL
3 TOY spiked 1000 ng/mL	13	0.405	1042.1	ng/mL

Table 3. Report table generated for the unspiked and spiked toy extracts using the system suitability function of Empower 2 Software.

CONCLUSIONS

The results presented in this application note show how the ACQUITY SQD can be used to rapidly screen for the presence of phthalates in toy samples at the regulated limits. The ACQUITY SQD can easily be added to existing laboratories using Empower Software, circumventing the requirement of dedicated MS software. The benefits of MS, such as selectivity and sensitivity, can be brought to existing Empower users without the need for additional training. IntelliStart Technology ensures ease-of-use and consistent performance. The Empower 2 system suitability functionality enables users to define specific limits and quickly identify samples that exceed the permitted levels.

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