Phthalates Analysis in Toys Using Agilent 5977E GC/MS

Application Note

Environmental

Author

Suli Zhao Ming Yan
Agilent Technologies (Shanghai) Co., Ltd.
412 Yinglun Road
Shanghai 200131
China

Abstract

This application note demonstrates that the Agilent 5977E GC/MSD System provides good performance and a cost-efficient solution to help test the six regulated phthalates in children's toys. All six phthalates have been clearly spiked and the results show good repeatability and relative standard deviations (RSD%).

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Introduction

Phthalates are the most commonly used plasticizers, often used as softeners in PVC plastic and as solvents in cosmetics and other consumer products. According to animal studies, phthalates can damage the liver, kidneys, lungs, the hormone system, and the reproductive system, particularly developing testes. Children exposed to toys and other baby products that involve phthalates are under a higher risk to be harmed. To limit the use of phthalates, many regions have enforced regulation with specific guidance for phthalates' application range. The European Union (EU) [1] and the US Consumer Product Safety Improvement Act (CPSIA) introduced regulations for children toys and childcare products [2]. China also published the GB/T22048-2008 regulation for six phthalates [3].

Six phthalates were regulated: dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), diethylhexyl phthalate (DEHP), di-*n*-octyl phthalate (DNOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP). This application note uses GB/T 22048-2008 as reference. GB/T 22048-2008 describes a phthalates analysis method using a GC/MS for these six compounds.

Experiment

Reagents and chemicals

All reagents were analytical or HPLC grade. The phthalate standards were purchased from J&K. Dichloromethane (DCM) was purchased from ANPEL, Shanghai.

Equipment and Materials

This experiment was performed on an Agilent 5977E GC/MSD System equipped with an Agilent 7650A Automatic Liquid Sampler (G4567A). Separation of the compounds was achieved on an Agilent HP-5ms UI column (30 m × 0.25 mm, 0.25 µm, p/n 19091S-433UI). Table1 lists the instrumental conditions.

Instrument conditions

Table 1. Instrumentation and Conditions of Analysis

Instrumentation	
ALS	Agilent 7650A Automatic Liquid Sampler, 50 vials
GC/MS system	Agilent 5977E GC/MSD System
Inlet	split/splitless
Liner	ultra inert, (p/n 5190-2295)
Column	Agilent HP-5ms UI LTM 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI)
Experimental conditions	
ALS	
Injection mode	fast
Inlet temperature	290 °C
Injection volume	1 µL
Injection mode	split, 5:1
Carrier gas	helium
Constant flow	1.2mL/min
Oven temperature	180 °C (0.5 minutes), 20/min, 280 °C (7 minutes)
MSD interface	290 °C
Ion source	300 °C
Quad. temperature	150 °C
Ionization mode	EI
Scan mode	full scan, 50–550 u
EMV mode	gain factor
Gain factor	5.00
Resulting EM voltage	1,760 V
Solvent delay	3 minutes

Sample preparation

PVC samples were ground or cut into pieces smaller than 3 × 3 mm. One gram of the cut pieces was Soxhlet extracted in 120 mL of dichloromethane for 6 hours at 60–80 °C. The extract was concentrated to approximately 10 mL using a rotary evaporator and then diluted with DCM to 25 mL. For samples having very large amounts of phthalates, further dilution may be needed to reduce concentration levels into the calibration range [3].

Calibration levels

Five calibration solutions were made by dilution in DCM in accordance with China GB/T 22048-2008 analytical methods. The concentration range of DBP, BBP, DEHP, and DNOP ranged from 0.5 mg/L to 10.0 mg/L. The concentration range of DINP and DIDP ranged from 5.0 mg/L to 100 mg/L in calibration solutions.

Results and Discussion

Qualitative and quantitative results

A typical total ion chromatogram (TIC) of the regulated six phthalates is shown in Figure 1 with 5.0 mg/L calibration levels. As indicated in the TIC, DINP and DIDP were extracted from Figure 1 and the EIC of them are shown in Figure 2. Table 2 lists the retention time and quantitation ions information of the six phthalates.

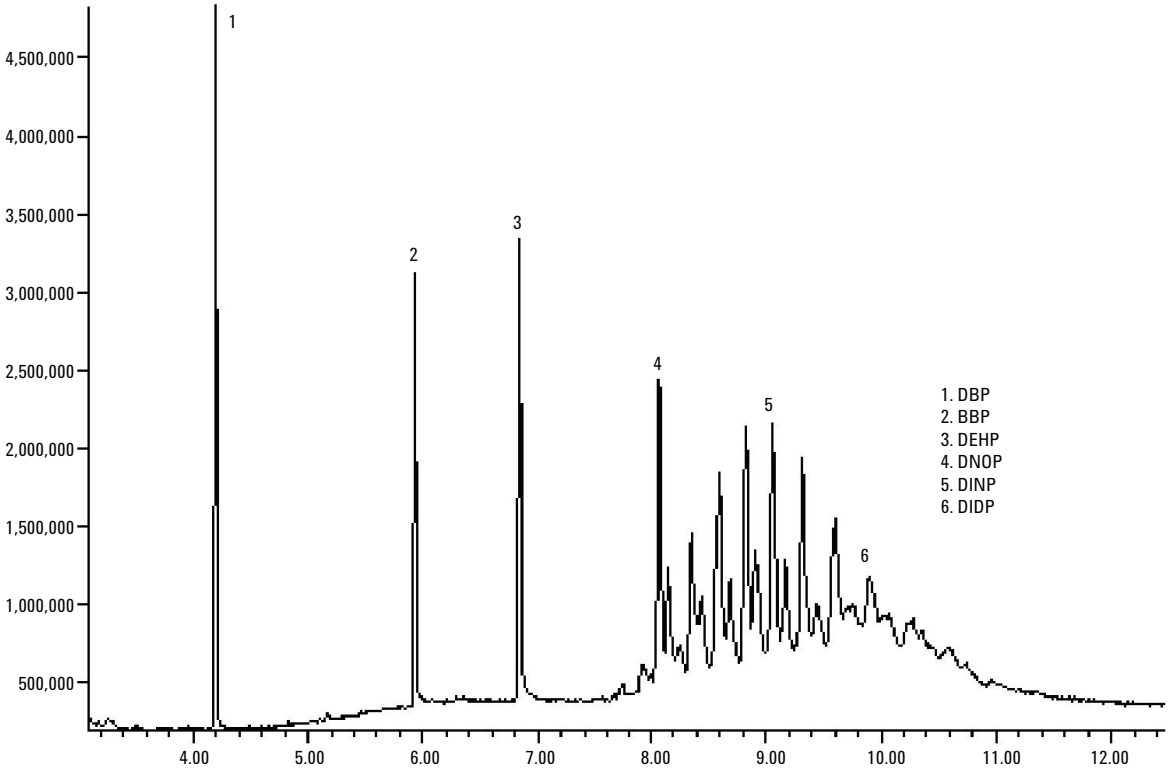

Figure 1. TIC of six regulated phthalates of 5.0 mg/L concentration, DINP and DIDP is at 50.0 mg/L.

Table 2. Calibration of Phthalates

Name	CAS	R.T. (min)	Quantitation ion
Dibutyl phthalate (DBP)	84-74-2	4.198	149
Benzyl butyl phthalate (BBP)	85-68-7	5.931	149
Di-(2-ethylhexyl) phthalate (DEHP)	117-82-8	6.842	279
Di-*n*-octyl phthalate (DNOP)	117-84-0	8.064	279
Diisononyl phthalate (DINP)	28553-12-0	From 7.10 to 10.36	293
Diisodecyl phthalate (DIDP)	26761-40-0	From 7.93 to 12.0	307

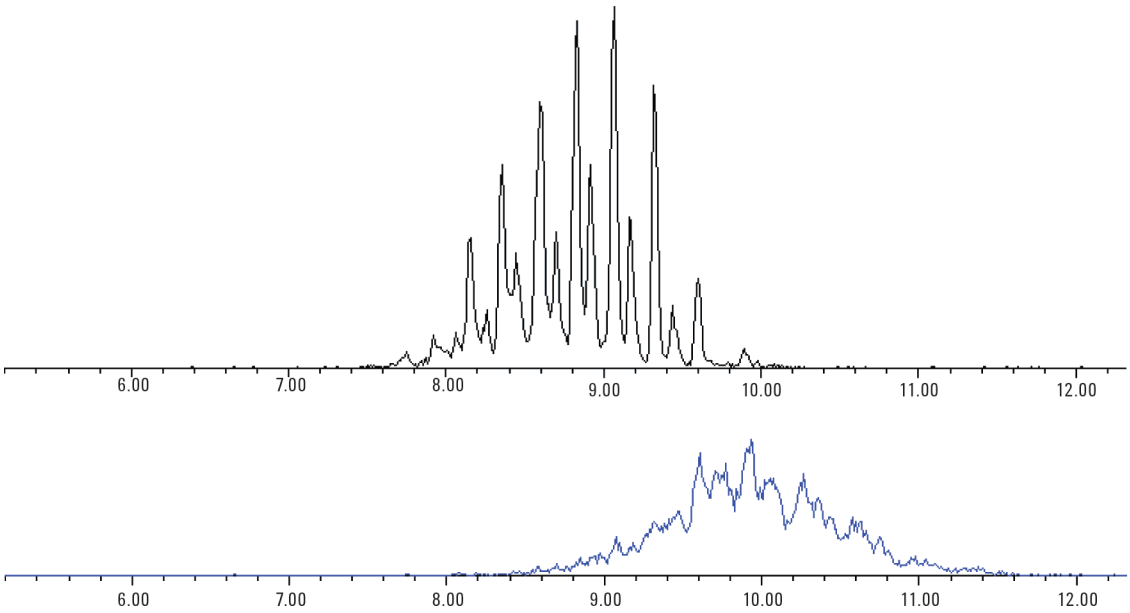

Figure 2. EIC of DINP (top) and DIDP (bottom).

Linearity and repeatability

In this application note, we selected a higher ion source temperature to obtain better linearity and repeatability. A 300 °C ion source temperature was used for the phthalates analysis. Table 3 shows the linearity difference of 230 °C and 300 °C. From Table 3, we can see that higher ion source temperatures can increase the linearity of higher boiling point phthalates such as DNOP, DINP, and DIDP. We used 300 °C as the experiment temperature.

To evaluate the stability of the instrument, five continuous injections were made for calibration solution at 5 mg/L. Table 3 shows the excellent relative standard deviations (RSD%).

Three calibration curves are illustrated in Figures 3, 4, and 5.

Table 3. The Linearity of 230 °C and 300 °C

Name	Ion source (230 °C)	Ion source (300 °C)	RSD% at 5 mg/L
Dibutyl phthalate (DBP)	0.9978	0.9977	3.94
Benzyl butyl phthalate (BBP)	0.9969	0.9995	2.96
Di-(2-ethylhexyl) phthalate (DEHP)	0.9957	0.9986	5.31
Di-*n*-octyl phthalate (DNOP)	0.9946	0.9993	3.53
Diisononyl phthalate (DINP)	0.9891	0.9994	2.71
Diisodecyl phthalate (DIDP)	0.9921	0.9994	3.62

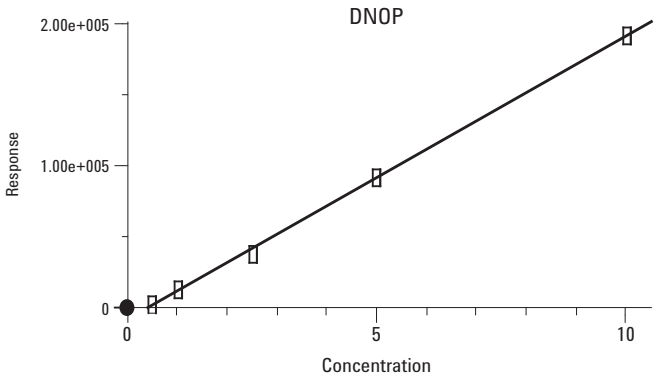

Figure 3. Correlation efficient of DNOP: R^2 = 0.9993.

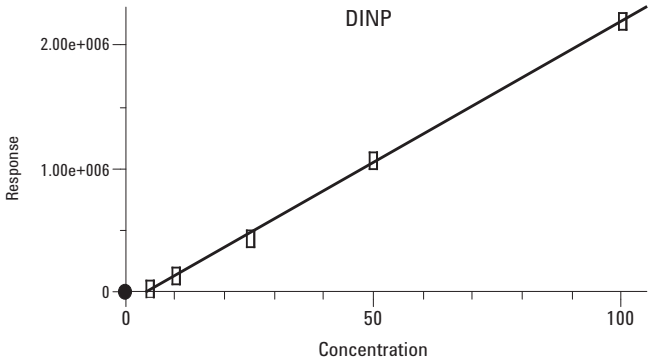

Figure 4. Correlation efficient of DINP: R^2 = 0.9994.

Sample

One PVC toy sample was prepared according to the sample preparation step. Twenty injections of the extraction were made to test the stability of the sample; DEHP was a major phthalate in the sample. The RSD% was less than 5% for all of the phthalate compounds. Figure 6 is an EIC (at *m/z* 149) of the sample chromatogram.

We injected 5.0 mg/L calibration standards for two injections before and after 20 sample injections; the RSD% between the two injections was less than 5.0%. This data shows that the 5977E GC/MS System has very good stability and reliability.

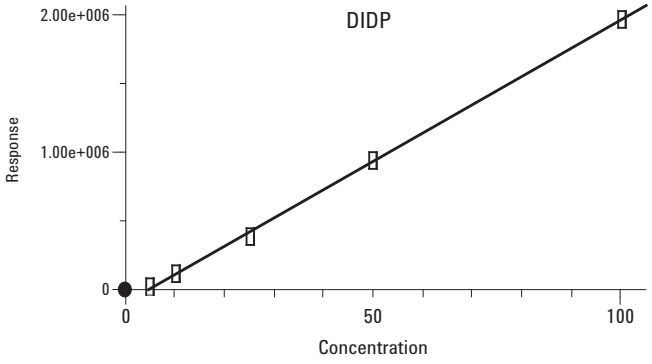

Figure 5. Correlation efficient of DIDP: R^2 = 0.9994.

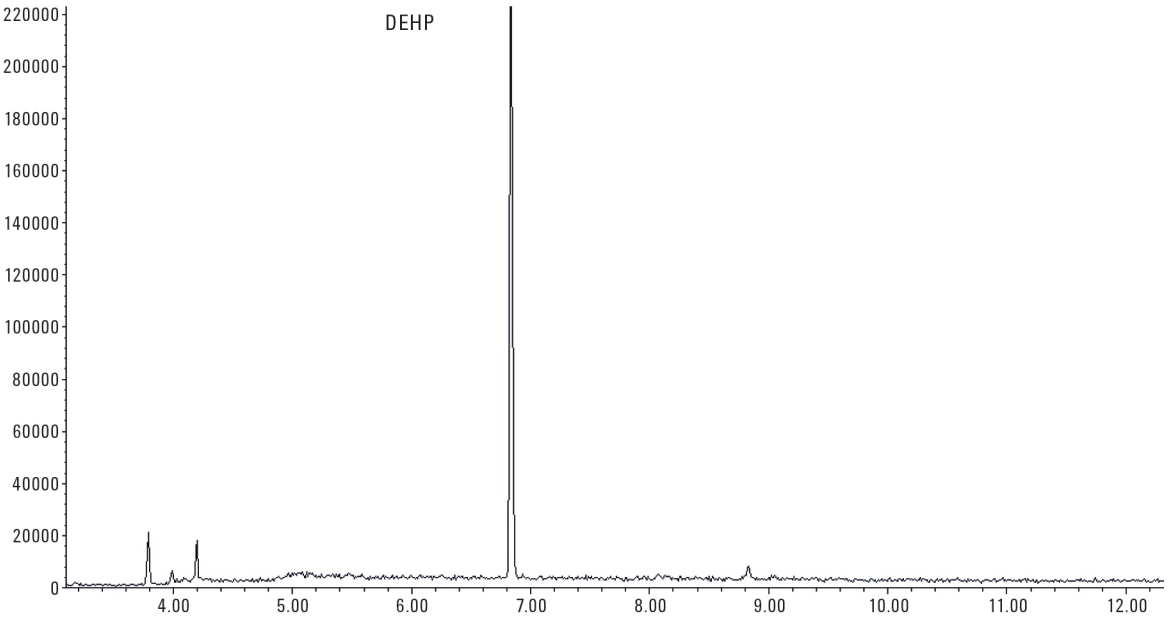

Figure 6. The EIC of DEHP in the PVC toy sample.

Conclusions

The method developed on the Agilent 5977E GC/MS System provides excellent results in the determination of phthalates. According to the approved China standard method, the 5977E GC/MS System with SSL ion source is verified for the determination of phthalate esters in toys and children's products. The method meets the requirements of regulatory methods and has good linearity and repeatability for all the target phthalate esters. The 5977E GC/MS System can be an economical and reliable instrument for the analysis of phthalates.

References

1. Official Journal of the European Communities Decision198/815/EC. 1999, European Commission; European Union Scientific Committee on Toxicology, Ecotoxicology, and the Environment.
2. U.S. Congress enacted the Consumer Product Safety Improvement Act (CPSIA 2008). http://www.cpsc.gov/cpsia.pdf

3 GB/T22048-2008 Toys and children's products – determination of phthalate plasticizers in polyvinyl chloride plastic.

For More Information

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