Determination of the Banned Phthalates in PVC Plastic of Toys by the Soxhlet Extraction-Gas Chromatography/Mass Spectrometry Method

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Abstract

A Gas Chromatography/ Mass Spectrometry method for the determination of six phthalates which are banned by European Union Regulation and USA CPSIA, in polyvinyl chloride (PVC) toys is studied in this article. The samples were extracted in six hours by Soxhlet extractor when using dichloromethane as the extracting agent, researched by orthogonal experiment. Using TIC (total ion chromatogram) and SIM (select ion monitor) of GC-MS to achieve phthalate's qualitative and quantitative determination, of which detection limit, accuracy and operating procedure are better than the standards in EN 14372:2004 clause 6.3.2 and ASTM D7083-04.

Keywords: Phthalate, Plasticizers, Toys, Orthogonal test, Soxhlet extraction, Gas chromatography/Mass spectrometry

1. Introduction

Phthalates have much toxicity such as carcinogenesis, teratogenesis, immunization failure, and reproduction failure, harming human liver and kidney, and the toys with this substance will seriously harm children's health.

Europe and USA begun to established strict standards and laws for the use of phthalates. For example, in ASTM F963-03, the using quantity of DEHP was strictly limited. In the Regulation (EU) No 1907/2006 (REACH) and USA CPSIA, DBP, BBP, DEHP, DNOP, DINP, and DIDP were limited in toys.

To strengthen the control of the quality of toy products and protect children's health, it is very important and meaningful to study the determination methods of plasticizers in PVC plastics.

The pretreatment method of plasticizers in PVC plastics generally used the ASTM D3421-75 (this method had been canceled in 1987) (ASTM D3421-75, 1975) for reference, but the time of using this method is too long, and this method is not environmental. In 2004, EN 14372:2004 (EN 14372:2004, 2004) and ASTM D7083-04 (ASTM D7083-2004, 2004) were issued, but only the GC-FID method was adopted in some literatures (Song, 2004, P. 286 & S. C. Rastogi, 1998, P. 724-726) after that, and it only suits to analyze the phthalates without isomerides, and the LOD (limit of detection) is high. ST2002 of Japan (ST2002, 2002) is only used to test the migratory plasticizers. China also established corresponding recommended standards, such as GB/T 20388-2006 (Wang, 2004), but the test range only includes textiles, not the PVC plastics in toys, and this standard and some literatures (Tan, 2007, P. 133-135) adopted the ultrasonic extraction, and some methods used the high performance liquid chromatography (HPLC) (Chen, 2004, P. 61-64) or the microwave extraction method (Wang, 2008, P. 30-33), which all are largely different with the international standard methods such as Soxhlet extraction method and the gas chromatography/mass spectrometry.

2. Experiment

2.1 Key instruments

(1) Gas chromatography/mass spectrometer. USA Thermo Finnigan TraceMS Plus, with AS2000 Automatic Sample injector.

(2) Soxhlet extractor.

2.2 Key reagents

(1) Dichloromethane. Pure-class chromatography, product of Germany Meker Company.

(2) DBP, CAS No. 84-74-2. Standard product of USA ChemService Company.

(3) BBP, CAS No. 85-68-7. Standard product of USA ChemService Company.

(4) DEHP, CAS No. 117-81-7. Standard product of USA ChemService Company.

(5) DNOP, CAS No. 117-84-0. Standard product of USA ChemService Company.

(6) DINP, CAS No. 28553-12-0. Isomeride mixture, standard product of Germany Dr.Ehrenstorfer Company.

(7) DIDP, CAS No. 26761-40-0. Isomeride mixture, standard product of Germany Dr.Ehrenstorfer Company.

2.3 Experiment conditions

(1) Chromatograph conditions. Chromatographic column: J&W DB-5 capillary column (15 m×0.25 mm×0.25 μm); Heating procedure: keep 1 min in 150°C, and heat to 230°C by the speed of 30°C /min and keep 0 min, and heat to 260°C by the speed of 5°C /min and keep 1 min, and heat to 300°C by the speed of 20°C /min and keep 5 min; Gas (He) carrier flow rate: 1.2mL/min, and the sample injection volume: 1.0μL; the split ratio: 30:1.

(2) Mass spectrum conditions. Electron impaction (EI) ion source; electron energy 70eV; the temperature of transmission line 280°C, the temperature of ion source 230°C; selected ions m/z 149, 293, 297, 307; quality scanning range m/z 50-500, collection time 3-12.5min, scanning time: 0.1s.

(3) Orthogonal test: use the three-factor-two-level L_4 (2^3) orthogonal array to test the samples four times. Factor A: extraction solvent: tetrachloromethane + carbinol, dichloromethane; Factor B: extraction quality, 1g, 2g; Factor C: extraction time: 16 hours, 6 hours. Find out the influencing efficiencies of various factors on the phthalates in same positive PVC plastic samples, and confirm the optimal pretreatment condition by the Soxhlet extraction method.

(4) Final decided experiment method. Exactly weigh 1g (precision: 1mg), and put the test portions (below 5 mm×5 mm) in the paper tube of 150mL Soxhlet extractor, and add 120mL dichloromethane in the 150mL Florence flask, and extract the substances in 60°C -80°C for 6 hours, and the reflux times in one hour should exceed 4. The remained substance about 120mL is metered to 25mL by dichloromethane, and is tested according to the conditions in GC-MS.

3. Experiment results

3.1 Data analysis

Perform the orthogonal test to the blue PVC plastic samples with DEHP and DINP in certain one toy according to the approaches in former chapter, and get the data (seen in Table 1).

(1) In 8 pieces of data, the best result is the experiment No. 3, i.e. weigh 1.0g and use dichloromethane to extract phthalates for 6 hours.

(2) Compute the contribution coefficient K of various factors and levels, i.e. the average value of each level in the experiments. The contribution coefficient is bigger, and the level is better. From 12 values of K, the optimal level is A2B1C2, i.e. weigh 1.0g and use dichloromethane to extract phthalates for 6 hours.

(3) Compute the range R of the contribution coefficients K of various factors, i.e. the difference between the maximum value and the minimum value of K. The range is bigger, the factor is more important. From 6 values of R, the factor influencing the extraction efficiency most is the extraction quality.

3.2 Comparable test with standard method

Compare the blue PVC plastic samples according to the optimal experiment conditions, ASTM D3421-75 and EN 14372:2004. The experiment result is in Table 2, and through tests, there is no significant difference among three methods.

3.3 Precision of Soxhlet extraction method and labeling recovery test

From different toy samples, take out various PVC materials to perform the precision and labeling recovery test. The accuracy is in 2%-7%, and the labeling recovery rate is in 86%-103%.

3.4 LOD and linearity

Perform the LOD test and the linear regression test for instruments. The chromatograms are seen in Figure 1-Figure 5, and the test result is in Table 3. The qualitative LOD of 6 kinds of plasticizer is in 0.05-.056mg/L, and the quantitative LOD of instruments is in 0.17-1.86mg/L, and the LOD of method is in 5-15mg/kg (DBP, BBP, DEHP, DNOP) and 50mg/kg (DINP, DIDP), which all satisfy the limitation requirement of 0.1% (i.e. 1000mg/kg).

3.5 Comparison and demonstration test among laboratories

Organize 13 laboratories in 6 provinces in China (including the subordinate professional laboratories of various provincial and municipal entry-exit inspection and quarantine bureaus, the subordinate professional laboratories of Bureau of Quality and Technical Supervision, the professional laboratories with foreign capital backgrounds, and the subordinate laboratories of toy manufacturers) to perform the comparison and demonstration test among laboratories according to this method, and when the concentration range is in 100mg/kg-150 000mg/kg, the repeatable variation coefficient is in 3.1%-7.1%.

4. Conclusions

This method has following technical characteristics. (1) The qualitative accuracy of this method is better than ASTM D7083-2004. (2) By comparing with the diethyl ether in the extraction of EN 14372:2004, this method needs not to replace solvent when metering volume.

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Table 1. Orthogonal test results and computation analysis by the Soxhlet extraction method

Test No.	Factors				
	Extracted solvent	Extracted mass	Extracted time	Result (mg/kg)	
	Levels				
	1	2	3	DEHP	DINP
1	Tetrachloromethane + carbinol	1g	16 hours	124 329	9 623
2	Tetrachloromethane + carbinol	2g	6 hours	115 260	9 486
3	Dichloromethane	1g	6 hours	125 144	9 902
4	Dichloromethane	2g	16 hours	119 252	9 396
K1(DEHP)	119 794	124 736	121 790	/	/
K2(DEHP)	122 198	117 256	120 202	/	/
R(DEHP)	2 403	7 480	1 588	/	/
K1(DINP)	9 554	9 762	9 509	/	/
K2(DINP)	9 649	9 441	9 694	/	/
R(DINP)	95	321	185	/	/

Table 2. Validation test results (mg/kg)

Method	Qualification	DEHP	DINP
ASTM D3421-75	Weigh up 1.0g sample, add Tetrachloromethane + carbinol (2:1), and Soxhlet extract for 16 hours	124 329	9 623
EN 14372: 2004	Weigh up 2.0g sample, add ethyl ether, and Soxhlet extract for 6 hours	121 420	9129
Soxhlet extraction	Weigh up 2.0g sample, add dichloromethane, and Soxhlet extract for 6 hours	125 144	9 902

Table 3. Detection limit and linear correlation

Test substance	DBP	BBP	DEHP	DNOP	DINP	DIDP
Limit of Detection (mg/L)	0.11	0.05	0.12	0.16	0.53	0.56
Limit of Quantitation (mg/L)	0.36	0.17	0.40	0.53	1.76	1.86
Correlation	0.9993	0.9997	0.9994	0.9996	0.9995	0.9994
Detection Limit of Method (mg/kg)	10	5	10	15	50	50

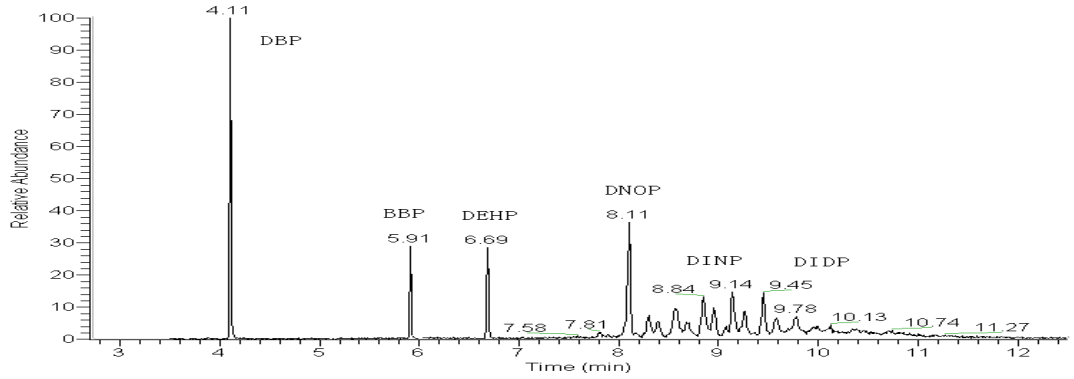

Figure 1. TIC of the six phthalates standard (DBP, BBP, DEHP, DNOP: 5mg/L, DINP, DIDP: 50mg/L)

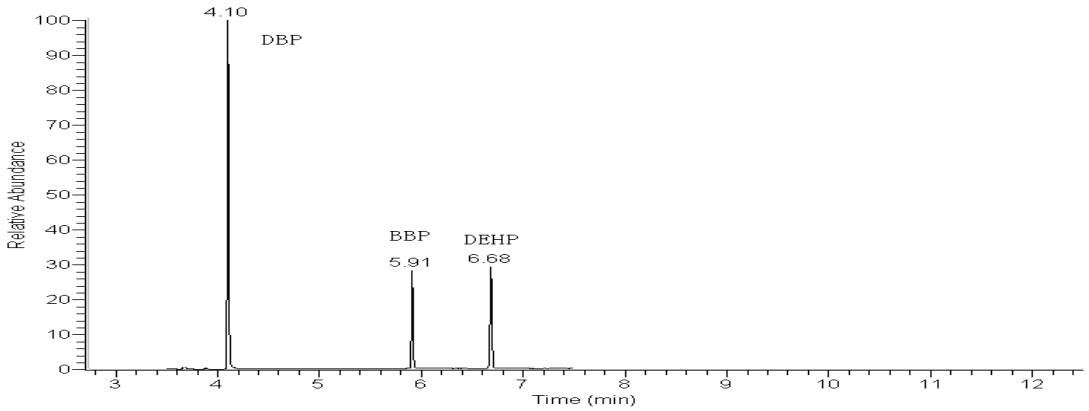

Figure 2. SIM of the DBP, BBP, DEHP Standard (m/Z=149)

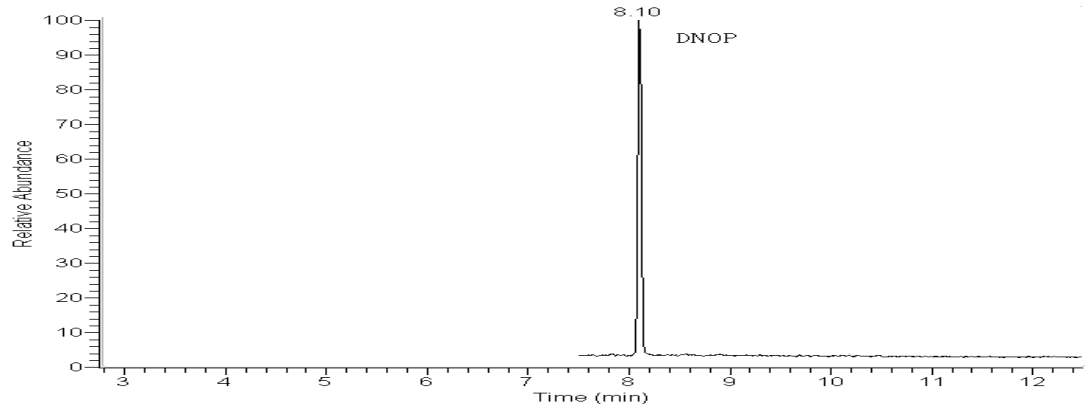

Figure 3. SIM of DNOP standard (m/Z=279)

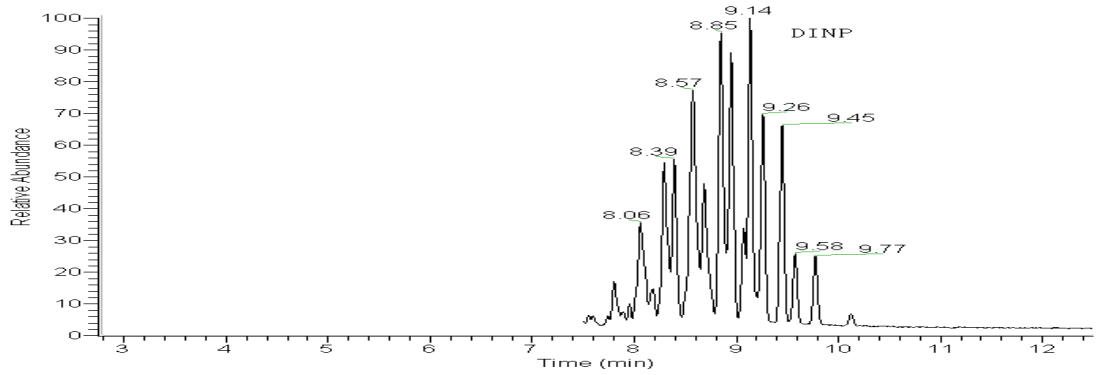

Figure 4. SIM of DINP standard (m/Z=293)

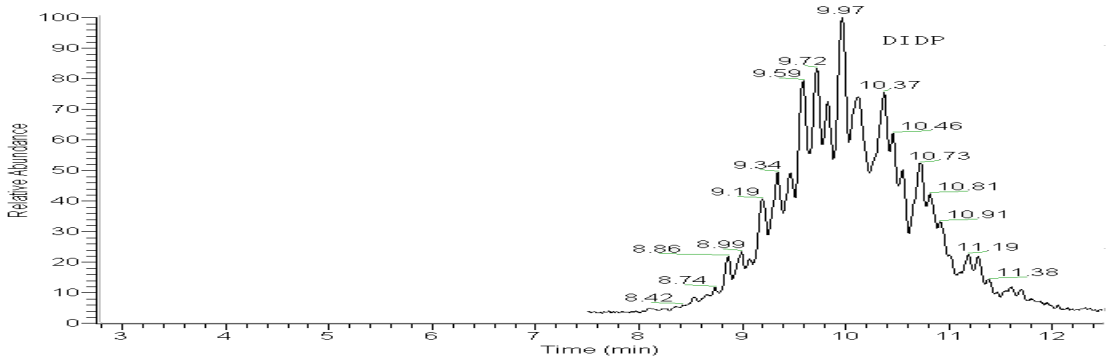

Figure 5. SIM of DIDP standard (m/Z=307)