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Determination of Four Certain Phthalates in the Electronic and Electrical Product by High Performance Liquid Chromatography

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Abstract: *Precise detection of phthalates in the electronic and electrical product is essential. The method of the determination of four certain phthalates in the electronic and electrical product by high performance liquid chromatography (HPLC) was investigated in this study. The sample was extracted with n-hexane by Soxhlet extraction, then the extract was concentrated to dryness by rotary evaporation and diluted with methanol. The analytes were separated on a ADME (4.6×150 mm, 5 μm) chromatographic column with the column temperature 35 ℃. Methanol and water was used as mobile phase for gradient elution with the flow rate of 1.0 mL•min-1. The four certain phthalates were detected with DAD at the wavelength of 228 nm. Quantification analysis was performed by the external standard method. Linear relationships were found between the peak areas and the mass concentrations of the four certain phthalates in definite ranges, with detection limits (3S/N) of 5 mg kg-1 and the low limits of determination (10S/N) of 10 mg kg-1. Recovery rates obtained by standard addition method were in the range of 100.8~106.8% and RSDs (n=6) were less than 4%. The positive samples were further verified by LC-MS/MS.*

Keywords: *Electronic and electrical product; High performance liquid chromatography; Phthalates; RoSH*

1. Introduction

Restriction of Hazardous Substances (RoHS) is a mandatory standard formulated by EU legislation. This standard is widely used to standardize the material and process standards of electronic and electrical products, making it more conducive to human health and environmental protection. In June 2015, the European Union (EU) 2015/863 [1] revised the Annex II of the EU Directive 2011/65/EU, and officially listed the four phthalates of bis (2-ethylhexyl) phthalate (DEHP), butyl benzyl phthalate (BBP), dibutyl phthalate (DBP) and dibutyl phthalate (DIBP) in the Annex II of RoHS 2.0. At the same time, the content limit of the four new PAEs was 0.1% (w/w). At present, the main detection method used at home and abroad is gas chromatography-mass spectrometry (GC-MS), which is expensive to purchase and expensive to use and maintain. Based on this, taking into account the high boiling point of phthalates and the properties suitable for liquid chromatography, it is urgent to study the low cost and high accuracy liquid chromatography.

Because DBP and DIBP are isomers. The peaks overlap under common chromatographic conditions and have the same mass spectrum. The detection of liquid chromatography is limited [2]. The Capcell Pak ADME liquid chromatographic column, which was launched in October 2014, is different from the traditional column with C18 functional group as the main group. The introduction of three-dimensional cage adamantine group (ADME) has a good effect on the analysis of structural analogues .

For the accurate detection of four specific phthalates in electronic and electrical products, this study selected ADME liquid chromatography column, optimized the chromatographic conditions, and established a method for the determination of four phthalates (PAEs) in electronic and electrical products by liquid chromatography.

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2. Experimental Part

2.1 Equipment and Reagents

Agilent 1200 high performance liquid chromatograph, equipped with diode array detector (DAD) and 6410B triple quadrupole mass spectrometer (Agilent Technologies, USA), Shimadzu UV1800 UV-visible spectrophotometer, N9548R liquid nitrogen freeze grinder (Beijing Herde Company), SCT-06 Soxhlet extractor (Hangzhou Hr Instrument Company), rotary evaporator (RE-52AA, Shanghai Yarong Instrument Company), and Milli-Q ultra-pure water machine.

Methanol (chromatographically pure, Merck, Germany), n-hexane (chromatographically pure, Merck, Germany), DBP, DIBP, BBP and DEHP (purity ≥ 99.5%) are all purchased from Shanghai Ample Technology Co., Ltd.

Single standard stock solution: 1000 μ G • mL-1, respectively weigh 10 mg of phthalate standard material, dissolve it with methanol and dilute to 10 mL.

Single standard solution: 10 μ G • mL-1, respectively transfer 10 μL of single standard stock solution into a 10 mL volumetric flask, and dilute to volume with methanol (only for qualitative analysis).

Mixed standard stock solution: 100 μ G • mL-1, with the concentration of 1000 μ G • mL - 1 mixed standard solution of four phthalate esters in methanol, 1 mL to 10 mL volumetric flask, and dilute to volume with methanol.

2.2 Chromatographic conditions

ADME liquid chromatographic column (4.6 * 150 mm, 5 μ m); Column temperature 35 ℃; Flow 1.0 mL • min-1; Injection volume 10 μ L; Detection wavelength: 228 nm; Mobile phase A is water and B is methanol. Gradient elution: B is 80% at 0-6 min; At 6~8 min, B rises from 80% to 95% and remains for 4 min; B dropped from 95% to 80% at 12~13 min and remained for 2 min.

2.3 Test method

Take about 2g of typical sample, freeze and grind it into powder, and pass 500 μm Standard sieved and stored in glass bottles for testing. Weigh 500 mg ± 10 mg of sample (accurate to 0.1 mg) and put it into the extraction tube of Soxhlet extractor. Add 120 mL of n-hexane into the extraction bottle. After 6 hours of Soxhlet extraction, transfer the extraction solution to the rotary evaporator and concentrate it to nearly dry. Dissolve and transfer the extract in three times with appropriate amount of methanol to a 50 mL volumetric flask, and finally use methanol to volume to the scale. After passing the PTFE membrane, it will be tested on the machine [2].

3. Results and Discussion

3.1 Optimization of chromatographic detection conditions

3.1.1 Selection of detection wavelength

On the UV-visible spectrophotometer, four phthalate standard solutions were scanned in the wavelength range of 200~340 nm, and the results are shown in Figure 1.

It can be seen from Figure 1 that the four phthalates have large absorption wavelength at 226~230 nm, and the detection wavelength selected for the test is 228 nm.

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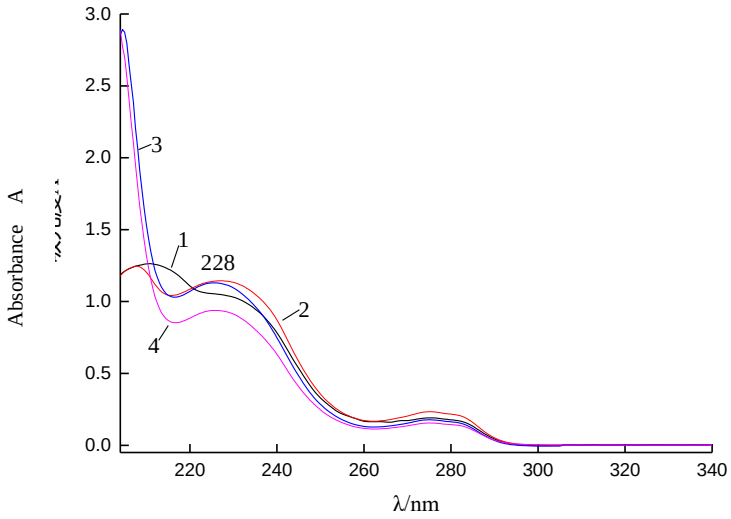


1—DBP; 2—DIBP; 3—BBP; 4—DEHP

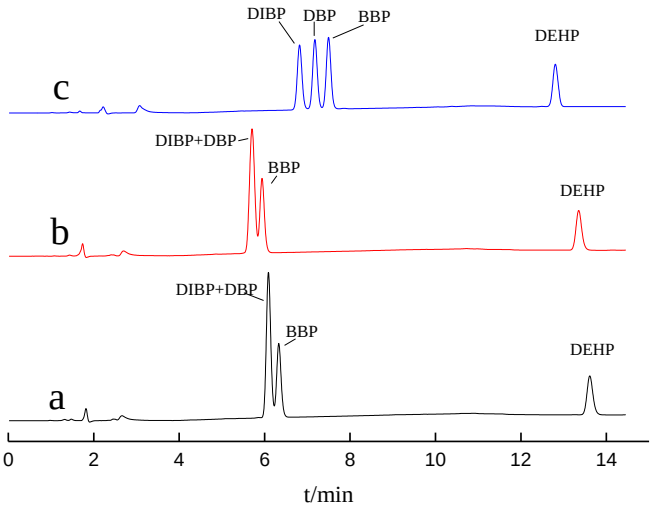
Figure 1: UV absorption spectra of 4 PAEs

3.1.2 Selection of mobile phase

In IEC 62321-8:2017 [2], acetonitrile-sodium formate system is used as the mobile phase in the LC-MS method. This study found that the methanol-water system can be used as the mobile phase and has a good elution effect. At the same time, methanol is used to replace acetonitrile because of its lower toxicity and lower cost.

3.1.3 Selection of chromatographic column

Under the optimized chromatographic conditions, three chromatographic columns, Zorbax SB C18, Eclipse XDB C18 and Capcell Pak ADME, were tested (the specifications of chromatographic columns were 4.6 × 150 mm, 5 μm). The separation effect of the four phthalates (DIBP, DBP, BBP and DEHP) obtained by selecting 1.2 chromatographic conditions is shown in Figure 2, and the resolution is shown in Table 1.



a—Zorbax SB C18;b—Eclipse XDB C18;c—Capcell Pak ADME

Figure 2: Chromatograms of 4 PAEs on different 3 chromatographic columns under the same conditions

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Table 1: Chromatographic resolution of 4 PAEs on different 3 chromatographic columns under the same conditions

PAEs	Separation efficiency		
	Zorbax SB C18	Eclipse XDB-C18	Capcell Pak ADME
DIBP	-	-	-
DBP	0	0	2
BBP	1.11	1.37	1.83
DEHP	32.25	32.95	24.53

It can be seen from Figure 2 and Table 1 that Capcell Pak ADME chromatographic column can achieve good separation of four phthalates, so as to ensure accurate quantitative determination of phthalates under liquid chromatography conditions.

3.2 Standard curve and detection limit

Dilute the mixed standard stock solution of four phthalates with methanol to prepare 0.25, 0.5, 1, 2, 5 and 10 μg • mL-1 mixed standard solution. Test the standard solution of this sequence according to the chromatographic conditions in Section 1.2. Take the mass concentration of the detected target as the abscissa and the corresponding response peak area as the ordinate, carry out linear fitting and draw the standard working curve. See Table 2 for the linear range, linear regression equation and correlation coefficient of the four phthalates.

Prepare the mixed standard solution with low concentration. Inject the sample for analysis, calculate the detection limit of the method with 3 times the signal-to-noise ratio (3S/N), and calculate the lower limit of the method with 10 times the signal-to-noise ratio (10S/N). See Table 2 for the results.

Table 2: Linearity parameters, detection limits and lower limits of determination

PAEs	Linear range(μg•mL-1)	Linear equation	Related coefficient	Detection limit(mg•kg-1)	Determination limit(mg•kg-1)
DIBP	0.05~20	y=19.39015x-0.153911	0.9999	5	10
DBP	0.05~20	y=19.30035x-0.337004	0.9999	5	10
BBP	0.05~20	y=18.88449x-0.271419	0.9999	5	10
DEHP	0.05~20	y=13.97567x-0.121904	1.0000	5	10

3.3 Precision and recovery test

Weigh 500 mg ± 10 mg of blank sample (accurate to 0.1 mg), respectively add 25, 100 and 500μg•kg-1 the mixed standard solution with three concentration levels, such as g • kg-1. According to the method in Section 1.3, the precision and recovery results are shown in Table 3.

Table 3: Results of tests for precision and recovery (n=6)

PAEs	the adding standard matter amount		the adding standard matter amount		the adding standard matter amount	
	25 μg•kg-1		100 μg•kg-1		500 μg•kg-1	
	Spike-and-recovery experience/%	RSD/ %	Spike-and-recovery experience /%	RSD/ %	Spike-and-recovery experience /%	RSD/ %
DIBP	102.3	3.58	101.9	1.63	101.5	1.35
DBP	106.8	3.46	102.6	1.77	100.8	1.85
BBP	103.8	3.82	102.3	1.40	100.9	1.63
DEHP	106.7	3.03	102.6	1.97	101.6	1.84

It can be seen from the table that the recoveries of the four phthalates in the sample are between 100.8% and 106.8%, and the relative standard deviation (n=6) of the measured value is within 4%, meeting the determination requirements.

3.4 Practical sample analysis

After sampling, the test was carried out according to this method. DEHP and DBP were more detected in typical positive samples. The test results are shown in Figure 3. The final phthalate content of typical samples 1 and 2 is 0.5% and 0.2%, respectively, which are 5 times and 2 times of the limit value (0.1%), and do not meet the standard requirements.

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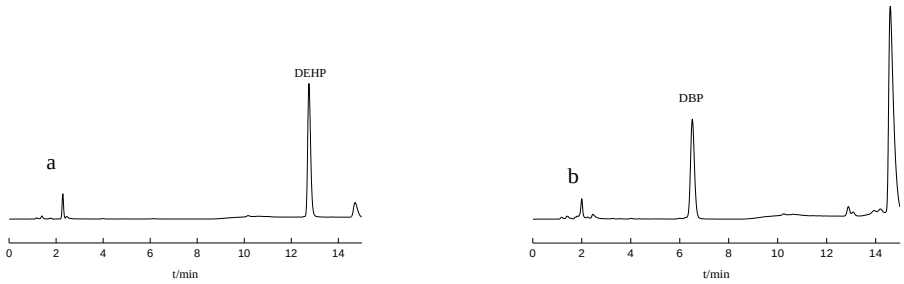

(a) representative sample1;(b) representative sample2

Figure 3: Chromatograms of typical samples

4. Conclusion

A method for the determination of four phthalates (PAEs) in electronic and electrical products by high performance liquid chromatography (HPLC) was established. After comparison and verification, this method has the advantages of good resolution, high precision, low detection limit, simple mobile phase and short analysis time, and can be used for rapid identification and quantitative analysis of four PAEs in electronic and electrical products.

Acknowledgement

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References

[1] European Union (EU) RoSH Directive. Amending Annex II to Directive 2011/65/EU of the European Parliament and of the Council as regards the list of restricted substances. Commission Delegated Directive (EU) 2015/863, 2015.
[2] International Standard. Determination of certain substances in electrotechnical products-Part 8: Phthalates in polymers by gas chromatography-mass spectrometry (GC-MS), gas chromatography-mass spectrometry using a pyrolyzer/thermal desorption accessory (Py/TD-GC-MS), Annex B (informative) Determination of phthalates in polymers by liquid chromatography-mass spectrometry (LC-MS). IEC 62321-8, Edition 1.0 2017-03.