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Simultaneous screening and determination eight phthalates in plastic products for food use by sonication-assisted extraction/GC–MS methods

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Abstract

Studies on determination of eight kinds of phthalates, e.g. di-ethyl phthalate (DEP), di-propyl phthalate (DPP), di-isobutyl phthalate (DIBP), di-butyl phthalate (DBP), benzyl butyl phthalate (BBP), di-cyclohexyl phthalate (DCHP), di-(2-ethylhexyl) phthalate (DEHP), di-octyl phthalate (DOP), in 25 kinds of plastic products for food use, including packaging bags, packaging film, containers, boxes for microwave oven use, sucking tubes, spoons, cups, plates, etc. by gas chromatography in combination with mass spectrometry detector (GC–MS) in electronic ionisation mode (EI) with selected-ion monitoring (SIM) acquisition method (GC–MS (EI–SIM)) have been carried out. Methods have been developed for both qualitative and quantitative analysis of phthalates. Extraction, clean-up and analysis procedure have been optimized. Determination of samples were performed after frozen in liquid nitrogen and sonication-assisted extraction with hexane, clean-up with LC-C18 SPE and analyzed by GC–MS methods. The base peak ($m/z = 149$) of all the phthalates was selected for the screening studies. The characteristic ions, 121, 177, 222 for DEP; 191, 209 for DPP; 57, 223 for DIBP; 104 for DBP; 91, 132, 206 for BBP; 55, 167 for DCHP; 113, 167, 279 for DEHP; 279 for DOP were chosen for quantitative studies. These techniques are possible to detect phthalates at the level of 10.0 μg/kg. Overall recoveries were 82–106% with R.S.D. values at 3.8–10.2%. Only one of the 25 examined samples was free from phthalates. The rest 24 samples were found to contain at least three or more of these phthalates. The predominant phthalate detected in the studied samples was DEHP.
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Keywords: Phthalates; Plastic products for food use; Sonication-assisted extraction; GC–MS (EI–SIM)

1. Introduction

In the recent years, phthalates (phthalic acid esters, PAEs) have attracted great public attention because of the suspicion of their carcinogenic and estrogenic properties [1,2]. Phthalates are widely used as plasticizers and additives in many daily used products such as plastics, pesticides, paints and cosmetics, etc. Due to their widespread use, relatively large amounts of these compounds are released into the environment [3,4]. Some phthalates are included in the priority lists of pollutants in several countries [5]. For instance, the US Environmental Protection Agency (EPA) has established a maximum admissible concentration (MAC) in water of 6 mg/L for the di(2-ethylhexyl) phthalate (DEPH) [6]. The determination of these compounds in various samples is demanded urgently for environmental risk assessment.

During the last few years, several methods were proposed for the determination of PAEs by gas chromatography (GC) [7,8] and high performance liquid chromatography (HPLC) [9,10] preceded by different preconcentration liquid–liquid extraction (LLE) [11], solid-phase extraction (SPE) [12–15], and solid-phase microextraction (SPME) [16–20]. Among these reports, sample matrices, such as polyvinyl chloride (PVC) plastic products were the most common ones, since phthalates were most commonly used plasticizers in PVC-based products due to their compatibility and softening capability [21]. Other matrices were environmental samples, including water, soils [1,5], and some tissue, plasma samples

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[12]. So far, studies on plastic products for food use were quite limited [22].

In this paper, the studies of gas chromatography in combination with mass spectrometry detector (MSD) for the determination of eight kinds of phthalates, e.g. di-ethyl phthalate (DEP), di-propyl phthalate (DPP), di-isobutyl phthalate (DIBP), di-butyl phthalate (DBP), benzyl butyl phthalate (BBP), di-cyclohexyl phthalate (DCHP), di-(2-ethylhexyl) phthalate (DEHP), di-octyl phthalate (DOP), in plastic products for food use have been reported. Analytical methods for determination of phthalates in various matrices were developed. Twenty-five kinds of samples, including packaging bags, packaging film, containers, boxes for microwave oven use, sucking tubes, spoons, cups, plates, etc. were tested. It was tried to use both screening and determination techniques by elaborate selection of ions, in order to have a fast and reliable method to meet unequivocally the quality criteria of EU, US, etc. The ion of base peak ($m/z = 149$) of all the phthalates was selected for the screening studies. At least two characteristic ions of individual phthalate were selected for quantitative studies. The methods were evaluated by investigating the accuracy and precision with spiked samples and applied for the determination of phthalates in 25 kinds of real samples.

2. Experimental

2.1. Materials

Acetone, hexane, acetonitrile, methanol, sodium sulfate of HPLC grade were purchased from TEDIA Company (Fairfield, OH, USA) and used as received. DEP, DPP, DIBP, DBP, BBP, DCHP, DEHP, DOP standards were purchased from Dr. Ehrenstorfer company (Augsburg, Germany) with purity higher than 99%. SPE columns (LC-C18, 3 mL cartridge) were purchased from Supelco (Supeclco Park Bellefonte, PA, USA). The water used was and purified using a Milli-Q gradient A10 system (Billerica, MA, USA).

2.2. Equipment

Agilent 6890N-5973N GC–MS (Palo Alto, CA, USA) with electronic ion sources; Organomation N-EVAP analytical evaporator (Organomation, South Berlin, MA, USA); CHA-S Homoiothermic Mechanical Shaker (Jiangsu Huanyu Company, Jiangsu, PR China); FJ-200 Homogenizer (Shanghai Molding Manufactory, Shanghai, PR China); HS 3120T Ultrasonicator (Ningbo Jiangdong Scientific Instrument Company, Zhejiang, PR China).

The GCMSD analysis was performed on a Agilent 6890N gas chromatograph equipped with a Agilent 7683 automatic liquid sample coupled to a Agilent 5973N mass selective detector. Capillary GC analysis was performed on a HP-5MS (30 m × 0.25 mm ID, 0.25 um) capillary column (5% diphenyl, 95% dimethylpolysiloxane, J&W Scientific, Folsom, CA, USA) with helium as carrier gas.

2.3. Standards and spiked samples

Standards were prepared in hexane. Stock solutions of each standard at a concentration of 100 mg/L were prepared and stored at 4 °C. The stock mixture solution of the eight phthalates standards at a concentration of 10 mg/L was prepared and stored at 4 °C. Suitable working solutions with concentration in the range of 0.05–10 mg/L were also prepared as standards before use for the calibration curves. The calibration curves were made by area versus concentration.

Polyethylene packaging bags (1 g), previously shown to be free from the target compounds, were spiked with 100 mg each of the phthalates. The treated materials were then stored under 4 °C for 24 h and used as spiked samples.

2.4. Extraction and precautions

Analysis of phthalates in samples may pose a serious problem because high blanks are often encountered. This is due to presence of phthalates in many laboratory products, including chemicals and glassware. To avoid phthalates contamination, all glassware used in the study was soaked in acetone for at least 30 min, then washed with acetone, rinsed with hexane, and dried at 120 °C for at least 4 h. All the solvents, blanks, standards, spiked samples and real samples were undergone similar extraction and analysis procedure. To ensure efficient extraction of the phthalates, samples were treated by liquid nitrogen before being grated or cut for sampling. Each sample was put in a glass beaker and the beaker was frozen in liquid nitrogen for several seconds. The frozen sample was then grated with an agate mortar to produce a finely ground material (with a typical particle size of less than 2 mm). Grating was not applicable to the packaging film and bags, since they were very thin. Instead, they were cut with scissors into pieces of less than 2 mm^2.

Approximately 1 g of each grated sample (weighed accurately) was transferred to a glass bottle and soaked in 10 mL hexane for 30 min, followed by sonication for 10 min to improve contact between solvent and sample. The solvent fraction was decanted off, fresh solvent added and the process repeated. The two solvent fractions were combined. The extract was reduced to dryness with a stream of nitrogen in a water bath at 45–50 °C.

2.5. Clean-up

Further clean-up procedure was performed by solid phase extraction (SPE) technique with LC-C18 cartridge.

LC-C18 column was conditioned sequentially with 5 mL methanol, 5 mL water. All washes were discarded. The dry residue was re-dissolved in 500 uL of 5% acetonitrile aqueous solution and loaded onto the LC-C18 column. The sample tube was washed by another 500 μL of 5% acetonitrile

Table 1
Gas chromatographic and mass spectrometric parameters used for analysis of phthalates in selected plastic products used in food packing, storage and in utensil

Parameter	
Injector (splitless mode): temperature (°C)	250
Injection volume (μL)	1.0
GC temperature program	150 °C (hold 0.5 min) 220 °C (5.0 °C/min) 275 °C (3.0 °C/min, hold 13 min)
GC carrier gas: He (mL/min)	1.0
Aux (°C)	280
EI	
Ion source (°C)	230
Quadrupole (°C)	150
Electron energy (eV)	70
Ionisation current (mA)	34.6
Electronic multiplier potential (V)	1200

aqueous solution and the rinses were added onto LC-C18 column. The eluates were discarded. The LC-18 column was washed by 5 mL water. All washes were discarded. The phthalates to be determined was eluted from the LC-C18 column with 5 mL acetonitrile.

The final eluting solution was dried under nitrogen stream. The rest residue was re-dissolved in 1.00 mL of hexane, vortexed, and transferred into an auto-sampler vial. The solution was then ready for analysis.

2.6. Data acquisition and analysis conditions

An overview of the GC–MS parameters was given in Table 1. The transfer line, ion source and quadrupole analyser temperatures were maintained at 280, 230, 150 °C. A solvent delay of 3.8 min was selected. In the full-scan mode, electron ionization (EI) mass spectra in the range of 35–550 (*m*/*z*) were recorded at 70 eV electron energy with an ionisation current of 34.6 mA and a multiplier potential of 1200 V. In the selected-ion monitoring (SIM) mode, target ions under study were monitored, maintaining a dwell time of 100 ms for each ion. The detailed selected target ions for each phthalate were listed in Table 2.

3. Results and discussion

3.1. Sample preparation

3.1.1. Optimization of sampling treatment procedure

To investigate the effects of different sampling treatment procedure of the phthalates, samples were treated by liquid nitrogen, dry ice, or untreatment before being grated or cut for sampling. After the samples were treated by liquid nitrogen or dry ice, it was found that samples became friable and easy to be grated with an agate mortar. However, samples without treatment were not able to be grated to fine powder.

Table 2
Selected ions for each of the eight phthalates by GC–MS studies *m*/*z* values, repeatability (R.S.D., %), average recovery (*R*, %), squared correlation coefficient (r^2) obtained in this work

	m/*z*[*]	Retention time (min)	R.S.D. (%)	*R* (%)	r^2
DEP	121, 149[a], 177, 222	5.74	8.5	90.5	1.000
DPP	149[a], 191, 209	8.45	4.5	85.6	1.000
DIBP	57, 149[a], 223	10.00	5.2	88.7	0.995
DBP	104, 149[a]	11.61	6.8	95.2	0.998
BBP	91, 132149[a], 206	18.51	7.3	92.3	0.998
DCHP	55, 149[a], 167	21.83	5.9	89.2	0.998
DEHP	113, 149[a], 167, 279	22.45	6.3	87.5	0.997
DOP	149[a], 279	26.32	9.2	86.4	0.997

[*] Ions selected for quantification analysis.
[a] Ions selected for screening.

Samples after treated under low temperature would be easy to be weighted and more representive. It was found that treated by liquid nitrogen for 5–10 s samples became friable enough to be grated to fine powder. It would improve the extraction efficiency and repeatability of the experiments. Spiked polyethylene packaging bags were used to evaluate the optimum procedure. Polyethylene packaging bags (1 g), previously shown to be free from the target compounds, were spiked with 100 mg each of the phthalates. The treated materials were then stored under 4 °C for 24 h, and then treated along with blanks. The results were shown in Fig. 1. When the samples were treated with liquid nitrogen for 5 s, the average recovery would reach to 92.3%, with R.S.D. for five times at 7.2% (Fig. 1a). However, by the treatment with dry ice, more time (at least 30 min) was needed to achieve similar extraction efficiency (average recovery at 85.3%, with R.S.D. for five times at 8%, Fig. 1b). While without any treatments, neither the recovery (only at ∼80%) nor the reproductivity (R.S.D. for five times at 20.8%, Fig. 1c) was satisfied. So, in this study, samples were treated with liquid nitrogen for 5–10 s before extraction.

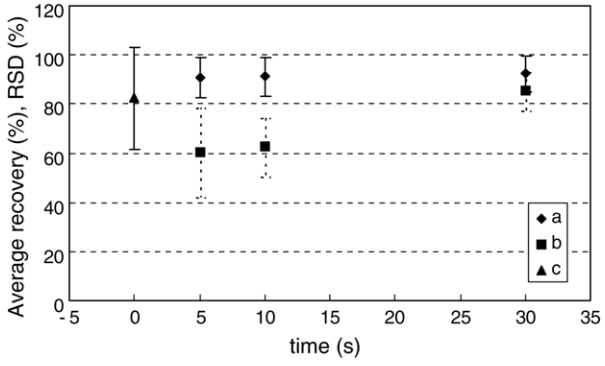

Fig. 1. Effects on samples treated by liquid nitrogen (a), dry ice (b), or untreatment. Average recoveries of phthalates (%) and R.S.D. values (%) of spiked packaging bags (100.0 μg/kg) vs. sample treatment time.

Table 3
Effects of isolation approaches and extractants on extraction of phthalates in selected plastic products used in food packing, storage and in utensil spiked packaging bag of DEP (100.0 ug/kg) determined by GC–MS–SIM

Entry	Isolation[a]	Extractant	DEP (found μg/kg)	Average recovery[b] (%)	R.S.D.[b] (%)
1	Homogenisation	Hexane	86.2	86.2	11.5
2		Acetone	76.8	76.8	15.6
3		Water	68.5	68.5	12.8
4	Ultrasonication	Hexane	90.5	90.5	8.5
5		Acetone	126.2	126.2	12.5
6		Water	78.5	78.5	9.8
7	Shaker	Hexane	83.1	83.1	10.2
8		Acetone	113.2	113.2	15.3
9		Water	75.6	75.6	11.5

[a] Isolation time, 10 min.
[b] $n = 5$.

3.1.2. Optimization of extraction procedures

The optimization of extraction efficiency was performed with varying the extractants: hexane, acetone or water. Homogenization, ultrasonication or shaker was taken as the second factor from optimizing of phthalates isolation from matrices. The results of the experiments of spiked polyethylene packaging bag were shown in Table 3.

Acetone as extractant provided good recoveries, but many interfering compounds were co-isolated that did not allow phthalates to be determined at low levels. However, phthalates can be extracted efficiently by hexane. Analysis of variance evaluation of the data suggested comparing to homogenization, shake, there were a significant effect of ultrasonication on phthalates recovery from the spiked matrices. Considering both isolation technique and extractant, ultrasonication was selected for our present work as it was fast, easy to handle and to be controlled with significant recoveries of phthalates. Comparing to extraction for 6 h by Soxhlet technique

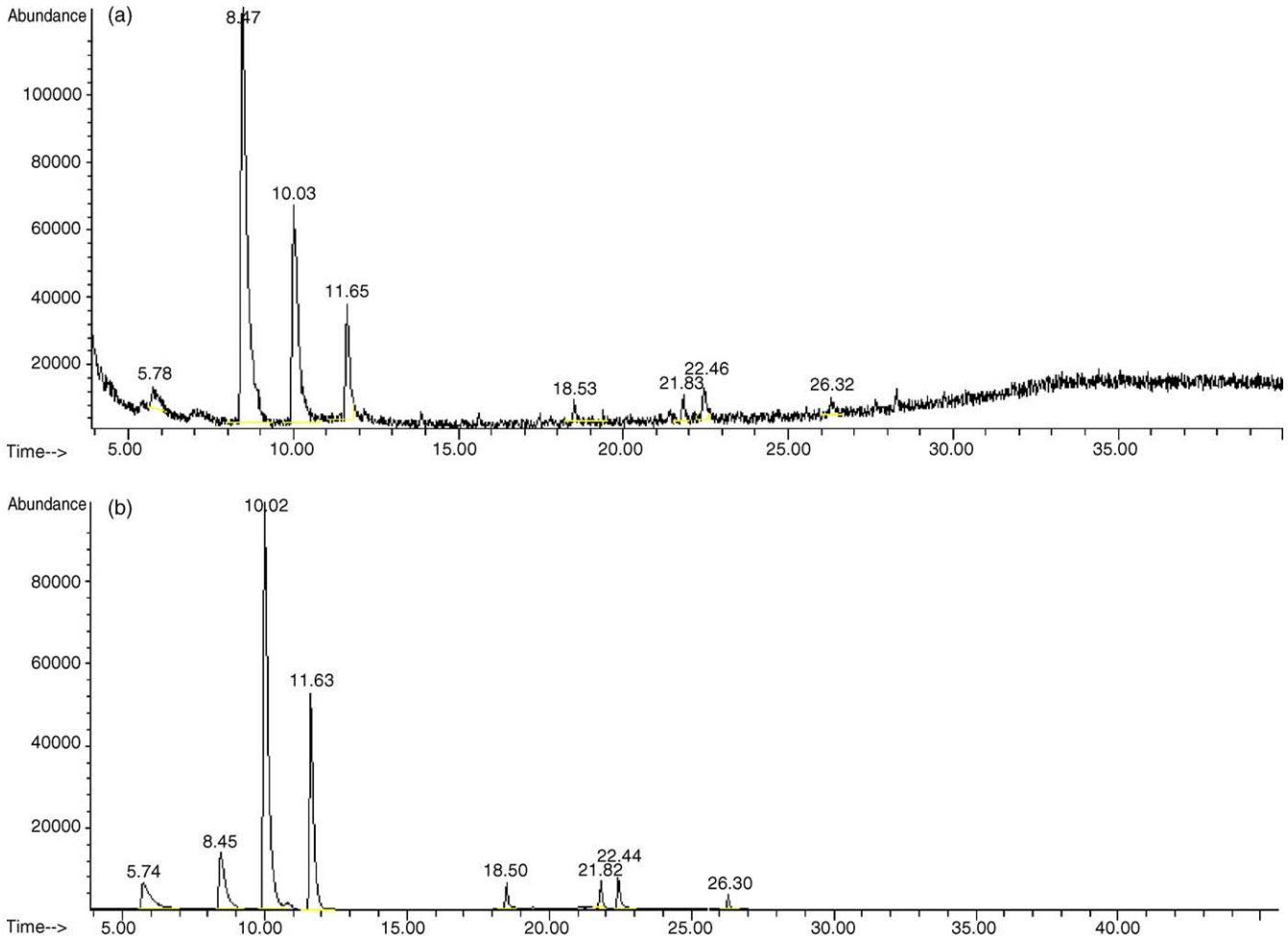

Fig. 2. The total ion chromatogram of the eight phthalates at the concentration of 1 mg/L obtained by full-scan mode (a) and selected-ion monitoring mode (b).

Table 4
Effects of condition, wash, elute solvents on LC-C18 SPE clean-up spiked packaging bag of DEP (100.0 ug/kg) determined by GC–MS

Condition	Wash	Elute	Average recovery (%)
A, C	C	A	46.5
B, C	C	A	90.5
A, C	C	50% A, C	32.4
B, C	C	50% A, C	81.8
20% A, C	C	A	45.2
5% A, C	C	A	52.7

A: CH_3CN, B: CH_3OH, C: H_2O.

as reported in literature [22], ultrasonication is more feasible and fast after samples treated under low temperature.

3.1.3. Optimization of SPE clean-up procedure

In order to eliminate the influence from the matrix by effective clean-up procedure, LC-C18 columns were applied to the studied samples. Different condition, wash, and elute agents were used for the evaluation of the clean-up efficiency. All the 25 kinds of the studied hexane extracts were spiked with phthalates before loading on to the SPE columns, and the retention capacity of the different condition, wash, and elute agents was compared. Representative results of DEP spiked polyethylene packaging bag were illustrated in Table 4. As was shown in Table 4, the optimum recovery of DEP occurred when LC-Si column was conditioned with methanol, water, washed with water and eluted with CH_3CN.

3.2. Optimum of data acquisition for GC–MS analysis

GC–MS analysis for the studied eight kinds of phthalates was operated in a scan mode. Phthalates were identified according to their retention times and mass spectra using standards. The base peak, ion ($m/z = 149$) of all the phthalates, was selected for the screening studies. The characteristic ions selected for quantitative studies were listed in Table 1.

By using SIM method, the sensitivities of detecting phthalates have been improved at least 10 times. As shown in Fig. 2a, the total ion chromatogram (TIC) of the eight phthalates at the concentration of 1 mg/L, which is obtained by full-scan mode, except DPP, DIBP, DBP, the signal-to-noise ratio of spectra of the other five phthalates, e.g. DEP, BBP, DCHP, DEHP and DOP, were not high enough for identification of the phthalates. In the case of the (TIC) obtained by SIM mode of the eight phthalates at the same concentration, shown in Fig. 2b, the baseline was quite clear and the signal-to-noise ratio of all the eight phthalates were high enough to achieve well separation and identification of the individual phthalate.

3.3. Method evaluation

To evaluate the methods, spiked samples were tested. The result showed that GC–MS–SIM technique was possible to detect phthalates at the level of 10.0 μg/kg. Overall recoveries were 82–106% with R.S.D. values at 3.8–10.2%.

Table 5
Determination of phthalates in 25 kinds of samples (mg/kg, extracted by hexane) by GC–MS–SIM method

No.	Sample	DEP	DPP	DIBP	DBP	BBP	DCHP	DEHP	DOP
1	Color drinker sucker	N.D	N.D	0.52	0.58	0.11	0.08	1.98	0.12
2	Color drinker spoon	N.D	N.D	0.40	0.42	0.08	0.15	5.16	0.19
3	Yellow drinker sucker	N.D	N.D	0.01	0.43	2.93	4.45	2.08	0.26
4	Ice cream spoon	N.D	N.D	1.95	1.18	0.54	3.35	5.63	1.72
5	Reusable plastic cup	N.D	N.D	7.25	9.84	0.44	3.01	119.35	0.68
6	Milk package bag	N.D	N.D	0.54	0.83	0.07	0.24	42.5	0.23
7	Reusable plastic fork	N.D	N.D	0.08	0.57	0.12	0.32	5.78	0.32
8	Box for microwave oven use	N.D	0.50	0.48	1.44	0.10	0.57	8.72	0.13
9	Package film	N.D	0.38	2.40	1.88	0.09	1.16	27.58	0.42
10	Convenience noodle package	N.D	1.25	0.51	0.58	0.07	0.25	3.98	0.56
11	Package bag for biscuit	N.D	0.20	7.83	6.52	5.92	15.0	1763.8	27.6
12	Cachou-1	N.D	0.04	0.17	N.D	9.98	0.35	97.16	0.49
13	Cachou-2	N.D	0.05	0.59	0.90	5.96	1.08	1.94	N.D
14	Cachou-3	0.05	0.05	0.67	0.70	0.10	0.77	2.17	0.14
15	Mixing pole	N.D	8.1	0.38	N.D	16.0	0.09	0.80	N.D
16	White drinker sucker	N.D	N.D	0.21	0.30	N.D	N.D	0.80	N.D
17	Reusable plastic bowl	N.D	N.D	0.16	0.28	N.D	N.D	0.68	N.D
18	Blue milk sucker	N.D	N.D	0.15	0.26	N.D	0.05	2.71	N.D
19	Disposable cup	N.D	N.D	1.65	1.12	N.D	0.43	2.88	N.D
20	Storage box	N.D	N.D	1.90	1.18	N.D	0.21	3.94	0.14
21	Cover of storage box	N.D	N.D	0.28	0.42	0.10	N.D	2.18	N.D
22	Disposable bowl	N.D	N.D	0.24	0.37	0.06	N.D	1.38	N.D
23	Disposable plate	N.D	N.D	0.30	0.47	N.D	N.D	2.36	N.D
24	Package bag	N.D	3.35	N.D	1.62	0.34	0.22	11.07	N.D
25	Reusable plastic plate	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D

3.4. Real samples

In order to inspect the phthalates residue in plastic products for food use, packaging bags, packaging film, containers, boxes for microwave oven use, sucking tubes, spoons, cups, plates, etc. Twenty-five kinds of products for food use were bought from the market randomly. Most of the materials were selected for the analyses were made from polyethylene (PE), fibreboard (FB), polystyrene (PS), cellophane (CL), polyvinyl chloride (PVC) and laminated aluminium polyethylene (Al-PE). Eight kinds of phthalates, e.g. DEP, DPP, DIBP, DBP, BBP, DCHP, DEHP, DOP, were screening and determined by GC–MS–SIM methods. The results were listed in Table 5. Only one of the 25 examined samples was free from phthalates. The rest 24 samples were found to contain at least three or more of these phthalates. The predominant phthalates detected were DEHP.

4. Conclusion

Studies on screening and determination of phthalates were carried out by GC–MS method. Procedures for sample preparation and analysis have been optimized. It was found that phthalates could be efficiently extracted by sonication-assisted solvent extraction system after sample treatment with liquid nitrogen. The clean-up with LC-C18 SPE was optimized when was conditioned with methanol, water, washed with water and eluted with CH_3CN. The detection limits were found to be 10.0 μg/kg. Overall recoveries were 82–106% with R.S.D. values at 3.8–10.2%. Only one of the 25 examined samples was free from phthalates. The rest 24 samples were found to contain at least three or more of these phthalates. The predominant phthalates detected was DEHP.

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