

Determination of Phthalates in Polymer Materials – Comparison of GC/MS and GC/ECD Methods

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Abstract: The paper presents two methods for determination of phthalates in polymer materials. The methods compared were gas chromatography combined with the mass spectrometry (GC/MS) and gas chromatography with electron capture detector (GC/ECD). The GC/ECD technique was chosen for this comparison, because the ECD detector was one of few capable of detecting phthalates. In both cases the same procedure of sample preparation with ultrasonic extraction was applied. Overall recoveries were 76-100 % with relative of standard deviation (R.S.D.) values in the range 0.6-19 %. The values of limit of detection (LOD) for GC/MS method ranged from 3.46 $\mu\text{g mL}^{-1}$ to 10.10 $\mu\text{g mL}^{-1}$, depending on the determined phthalate, while in case of the GC/ECD method they were in the range from 2.97 $\mu\text{g mL}^{-1}$ to 4.29 $\mu\text{g mL}^{-1}$. The methods were applied for determination of: dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, benzyl butyl phthalate, bis(2-ethylhexyl) phthalate, diisononyl phthalate, diisooctyl phthalate in polymer material. The seventeen kinds of samples were analyzed. Most of the materials selected for the analyses were made from polyethylene (PE), polyvinyl chloride (PVC) and polystyrene (PS).

Keywords: *Gas chromatography, mass spectrometry, electron capture detector, phthalates, polymer material.*

Introduction

Each year tons of phthalates are produced in the world in various manufacturing processes. Phthalic acid esters (PAEs) are additives in plastics, mainly in polyvinylchloride (PVC) products. These compounds are excellent plasticizers because of their stability, flowability, low volatility and high molecular weight. Due to their widespread use, relatively large amounts of those compounds are released into the environment. It has been proven that phthalates are impermanently associated with the polymer matrix and can easily migrate from the plastic to the external environment, they may be leached into foods and beverages from the packing material, resulting in harmful effects on the human body and the environment. The phthalates have attracted great public attention because of the suspicion of their carcinogenic and estrogenic properties^[1]. Because of the health concern, the European Commission began restricting phthalates in 2000^[2] and U.S. government passed the Consumer Products Safety Improvement Act (CPSIA) in August of 2008.

Some phthalates are included in the priority lists of pollutants in several countries. US Environmental Protection Agency (EPA) has established the maximum admissible concentration in water of 6 mg L^{-1} for the di(2-ethylhexyl)phthalate (DEPH)^[3]. The regulations in Europe specify limits for six phthalates: di(2-ethylhexyl) phthalate, dibutyl phthalate, benzylbutyl phthalate, diisononyl phthalate, diisodecyl phthalate and di-n-octyl phthalate at the level less than 0,1 % in all toys and articles designed so that they can be put in a child's mouth^[4]. As a result of those regulations, industries have to monitor the presence and amount of those specific compounds. The identification and quantification of phthalates requires an analytical technique which

can separate each phthalate from other additives and from the plastic matrix itself. In recent years, several methods for the determination of phthalates by gas chromatography (GC)^[1,5-10] and by high performance liquid chromatography (HPLC)^[11-20] were described. Different methods of sample preparation and extraction have been used, such as liquid - liquid extraction (LLE)^[7,21], solid phase extraction (SPE)^[1,6,11,12,16,17,21], solid phase microextraction (SPME)^[8,20,22,23], supercritical fluid extraction^[21], microwave extraction^[13,21], Soxhlet extraction^[10,21,24] and ultrasonic extraction^[5,21,25].

In this paper, the studies of gas chromatography in combination with mass spectrometry detector (MS) and electron capture detector (ECD) for determination of seven kinds of phthalates, e.g. dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzylbutyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), diisooctyl phthalate (DIOP), in polymeric products for everyday use were developed. The methods were evaluated by investigating the accuracy and precision. Seventeen kinds of samples, including parts of a cable, a plug, and a garden hose were tested.

Experimental

Chemicals and materials

Methanol of HPLC isocratic grade was purchased from J.T. Baker Company (Deventer, Netherlands); methylene chloride, hexane and toluene were purchased from POCH (Gliwice, Poland). The standard mixture consisted of: dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, benzyl butyl phthalate, bis(2-

ethylhexyl) phthalate, all dissolved in methanol, each at a concentration of 500 µg mL⁻¹ (EPA 506 Phthalate Esters Mix), diisononyl phthalate, diisooctyl phthalate and Amberlite XAD-2 were purchased from Supelco Company (Bellefonte, PA, USA). Silica gel 60 for column chromatography, was purchased from Merck (Merck KGaA, Germany).

Apparatus and equipment

The GC/MS analysis was performed on a Perkin Elmer Clarus 500 gas chromatograph equipped with a Clarus 500 mass detector (PerkinElmer, USA). Gas chromatographic analyses were also carried out using the Perkin Elmer Clarus 500 gas chromatograph equipped with an electron capture detector (⁶³Ni ECD). Capillary columns Elite – 5MS (5% diphenyl, 95% dimethylpolysiloxane) of 30 m length × 0.25 mm ID with film thickness 0.25

µm, (PerkinElmer, Shelton, USA) were employed for separation of analytes in both methods.

Standards and spiked samples

Standard mixture of five phthalates in methanol at concentration 500 µg mL⁻¹ was stored at 4°C. Standards of diisononyl and diisooctyl phthalates were prepared in methanol at concentration of 784 µg mL⁻¹ and stored at 4°C. Suitable working solutions with concentration in the range of 6.12-250 µg mL⁻¹ were prepared as standards before the use for calibration curves.

Sample collection

For the purpose of this paper, seventeen kinds of polymer materials, like plastic parts of a plug, cables, a garden hose, containers, pipes and pellets, were analyzed. Most of the materials selected for the analyses were made from polyethylene (PE), polyvinyl chloride (PVC) and polystyrene (PS). Seven kinds of phthalates (DMP, DEP, DBP, BBP, DEHP, DIOP, DINP) were screened and determined by GC/MS and GC/ECD methods.

Extraction

The phthalates are removed from the polymer surface with a solvent in which they are soluble. In this

case methylene chloride was chosen as the best solvent for the extraction of those compounds. The polymer samples were cut with scissors into pieces of less than 4 mm², to improve extraction efficiency. Approximately 10 g of each grated sample was transferred to a glass conical flask and soaked in 75 mL of methylene chloride, followed by sonication for 1 hour. Due to the high efficiency of extraction, the extract contained substantial amounts of the monomers which are soluble in methylene chloride. The extract purification step by open liquid chromatography with the use of SiO₂ was introduced^[26].

Conditions of the analysis

The column temperatures for gas chromatograph with a mass spectrometer and gas chromatograph with ECD detector were programmed to increase from 40 to 290°C at 20°C min⁻¹ and from 290 to 310°C at 20°C min⁻¹ and held 9 min; the temperature of an injector was 250°C. In case of GC/MS, the temperature of ion source was 230°C and EI mass spectra were obtained at 70eV. The temperature of ECD detector was 310°C. An overview of the GC/MS and GC/ECD parameters was given in Table 1.

Qualitative analysis was performed on GC/MS chromatograph by comparing the retention times and the mass spectra registered for the compounds corresponding to the particular peaks in the chromatogram with the mass spectra found in reference libraries. The chromatogram of the standard mixture is presented in Figure 1. Also, qualitative analysis was performed on a GC/ECD chromatograph. Phthalates were identified by their retention times (Figure 2).

In the case of GC/MS, quantitative analysis was performed using selected ion monitoring method (SIM), choosing one or two ions typical for each compound (Table 2).

A direct injection calibration curve was generated based on the standard injections in a solvent solution. Detector signals, measured in arbitrary units (peak areas), were plotted versus the amount of analyte injected, expressed in mass units (µg). Quantification of target compounds had to be done within the linearity range of the calibration curve, and in order to determine this range for the detector, several standard solutions have been prepared

Table 1. Gas chromatographic, mass spectrometric and electron capture detector parameters used for analysis of phthalates in selected polymer materials.

Parameter	GC/MS	GC/ECD
Injector temperature (°C)		250
Injection volume (µL)		1,0
GC temperature program		40°C (hold 3 min.) 290°C (20°C min. ⁻¹) 310°C (20°C min. ⁻¹ hold 9 min.)
GC carrier gas: He (ml min ⁻¹)		1,0
EI		
Ion source (°C)	230	
Quadrupole (°C)	150	
Electron energy (eV)	70	
ECD detector temperature (°C)		310

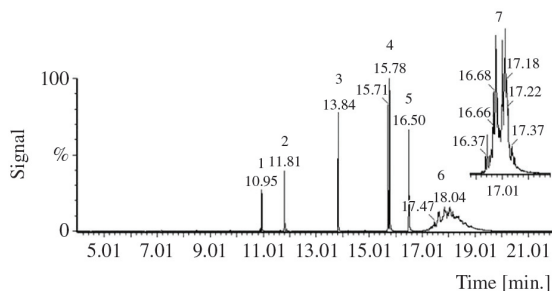


Figure 1. The chromatographic result of the GC/MS analysis of a phthalate standard at the concentration of 500 $\mu\text{g mL}^{-1}$ obtained by full – scan mode; 1- DMP, 2 – DEP, 3- DBP, 4 – BBP, 5-DEHP, 6- DINP, 7- DIOP.

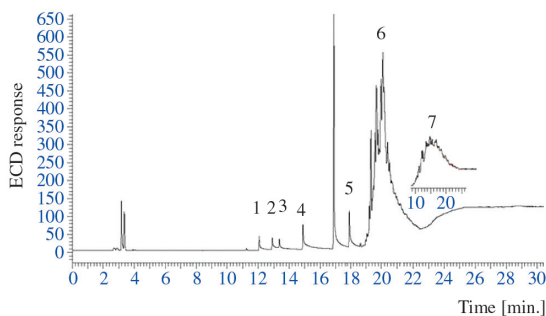


Figure 2. The chromatographic result of the GC/ECD analysis of a phthalate standard at the concentration of 500 $\mu\text{g mL}^{-1}$; 1- DMP, 2 – DEP, 3- DBP, 4 – BBP, 5- DEHP, 6- DINP, 7-DIOP.

Table 2. Selected ions for each of the seven phthalates by GC/MS studies m/z values.

	m/z	Retention time (min)
DMP	77, 92, 135, 163, 194	10.65
DEP	121, 149, 191, 209	11.52
DBP	104, 149	13.84
BBP	91, 132, 149, 206	15.40
DEHP	113, 149, 167, 279	16.15
DIOP	71, 113, 149, 167, 279	16.75
DINP	71, 149, 167, 293	18.05

and injected at different concentrations. The calibration range for five phthalates (DMP, DEP, DBP, BBP, DEHP) was from 10 to 40 $\mu\text{g mL}^{-1}$ for low concentrations and from 50 to 500 $\mu\text{g mL}^{-1}$ for high concentrations, for DINP and DIOP one calibration range from 784 to 6,12 $\mu\text{g mL}^{-1}$ was obtained. For each compound in both methods calibration curves were obtained by linear regression of the peak area against the concentration injected. As an example of a calibration curve, the curve of dimethyl phthalate at lower concentration for the GC/MS method is presented in Figure 3.

Recovery determination

No certified reference material for phthalate analysis exists. To determine the recovery of analytes, the reference materials were made. Amberlite XAD-2, which

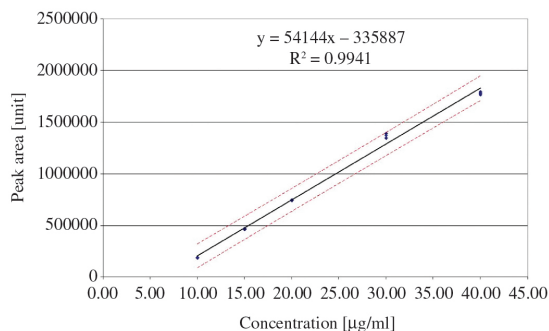


Figure 3. Calibration curve of dimethyl phthalate at range of concentration from 10 to 40 $\mu\text{g mL}^{-1}$; the solid line – calibration curve, the dotted line – deviation of calibration curve.

is a hydrophobic crosslinked polystyrene copolymer resin, and plasticizer pellets made from PVC free from the target compound, were used as a templates for phthalates extraction optimization. A sample of Amberlite XAD-2 and plasticizer were extracted three times with methylene chloride and dried until the solvent was completely removed. The 10 g of dried samples were spiked with 50 μL of a standard mixture containing DINP phthalate. In order to select the most efficient extractant/solvent for extraction of phthalates, the reference materials were extracted with methylene chloride, hexane and toluene. The obtained results are shown in Table 3.

Extraction efficiency confirmation for real samples

A five real samples of polymer material (plasticizer pellets), pre-prepared in accordance with the procedure described above, weighing 20 g were divided into two equal parts A and B. In samples A the phthalates were determined in according to the *Extraction* procedure. For some variations in this study, to improve real sample quantification accuracy, internal standard of DINP (52.2 $\mu\text{g g}^{-1}$) phthalate has been added to B samples before extraction, to partially compensate for individual matrix or extraction effects. This should improve correlation between reported amount and real sample concentration. The results, comparing extraction recoveries from A and B samples, are shown in Table 4.

Real samples

Seventeen kinds of polymeric materials were tested. In order to determine phthalates in plastic products various items were bought randomly. The products that were used as samples included plastic parts of a plug, cables, a garden hose, containers, pipes and pellets. Most of the materials selected for the analysis were made from polyethylene, polystyrene and polyvinyl chloride. In accordance with the procedure outlined above, after cutting and homogenizing, the samples were extracted. The obtained extract was filtered, purified and analyzed.

Results and Discussion

The preliminary study of extraction efficiency of phthalates from polymeric materials has shown that the best recovery of DINP from the reference materials was

obtained using methylene chloride. In case of this solvent DINP recovery from both reference materials were about 100 % with R.S.D 2.7-3.3%. For the other solvents, like hexane and toluene, the recovery reached a value below 70 % for reference materials made from Amberlite XAD-2 and plasticizer pellets (Table 3). Methylene chloride was chosen for the further analysis of real samples. To

confirm extraction efficiency of phthalates from real polymer materials, the plasticizer pellet samples (B) with DINP (52.2 µg g⁻¹) as an internal standard, and plasticizer pellet samples (A) without internal standard were extracted in accordance with above described procedure. The almost 100 % extraction efficiency of DINP phthalate was confirmed for the real polymer material (Table 4).

Table 3. Effects of solvents on extraction of phthalates in the prepared reference materials spiked with DINP (78.4 µg g⁻¹) determined by GC/MS-SIM.

Isolation	Reference		DINP (found µg g ⁻¹)	Average	
	material	Solvent		recovery (%)	R.S.D. (%)
Ultrasonication	Amberlite	Dichloromethane	93.4	101.1	2.71
		Hexane	50.3	64.1	11.84
	XAD-2	Toluene	53.2	67.82	3.26
Ultrasonication	Plasticizer pellets	Dichloromethane	77.6	99.7	3.32
		Hexane	46.3	62.3	15.61
		Toluene	51.4	65.6	4.12

Table 4. Comparison of extraction recoveries from A samples (plasticizer pellets), and B samples with DINP (52.2 µg g⁻¹) internal standard, determined by GC/MS-SIM.

Isolation	Sample	Solvent	DINP (found µg g ⁻¹)	R.S.D. (%)
Ultrasonication	A	Dichloromethane	74.6	3.57
			74.3	2.98
			74.9	3.14
			74.7	3.64
			74.5	3.28
	B		126.3 (52.2 + 74.1)	3.32
			126.7 (52.2 + 74.5)	3.84
			126.4 (52.2 + 74.2)	3.71
			127.1 (52.2 + 74.9)	3.56
			126.8 (52.2 + 74.6)	3.19

A- real polymer samples (plasticizer pellets). B – real polymer samples (plasticizer pellets) + DINP internal standard (52.2 µg g⁻¹).

Table 5. Average recovery obtained by the extraction of phthalates from reference materials with methylene chloride (R, %).

Phthalates	Amberlite XAD-2		Plasticizer pellets	
	Recovery [%]	R.S.D [%]	Recovery [%]	R.S.D [%]
DMP	98.2	18.9	96.7	20.1
DEP	100.0	7.9	99.3	10.5
DnBP	100.0	10.3	99.8	11.1
BBP	76.2	1.7	71.6	3.7
DEHP	100.0	1.3	99.1	2.4
DIOP	109.7	0.4	99.8	1.1
DINP	101.1	2.7	99.7	4.3

Table 6. Regression coefficients for GC/MS and GC/ECD methods.

Phthalate	GC/MS		GC/ECD	
	500-50 µg mL ⁻¹	40-10 µg mL ⁻¹	500-50 µg mL ⁻¹	40-10 µg mL ⁻¹
	r ²	r ²	r ²	r ²
DMP	0.999	0.994	0.999	0.991
DEP	0.994	0.994	0.995	0.992
DBP	0.988	0.996	0.986	0.996
BBP	0.988	0.999	0.958	0.993
DEHP	0.999	1.000	0.983	0.994
	784-12.3 µg mL ⁻¹		784-6.12 µg mL ⁻¹	
DIOP	0.997		0.991	
DINP	0.992		0.993	

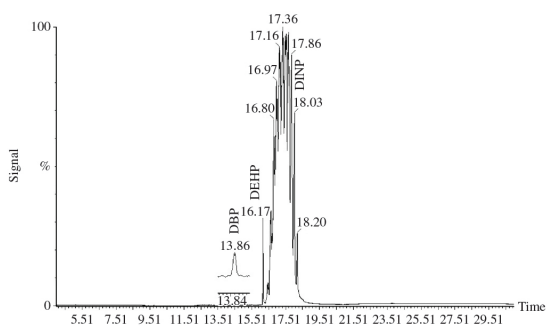


Figure 4. Chromatogram of plasticizer sample (GC/MS).

In samples A the average concentration of DINP was $74.6 \mu\text{g g}^{-1}$, with R.S.D in range from 2.98 to 3.64 %. The concentration of DINP internal standard added to B samples was $52.2 \mu\text{g g}^{-1}$, and $126.7 \mu\text{g g}^{-1}$ was an average determined concentration of DINP in those samples. These results shown that, also in case of the

B samples, average concentration of DINP phthalate was $74.5 \mu\text{g g}^{-1}$ and it confirmed almost 100 % extraction efficiency for the real polymer samples. It was shown that recoveries for each compound were very high - near 100%, only in the case of benzylbutyl phthalate it was equal to 76% (Table 5).

Application of the Elite-5MS column with GC/MS and GC/ECD chromatographs enables a very

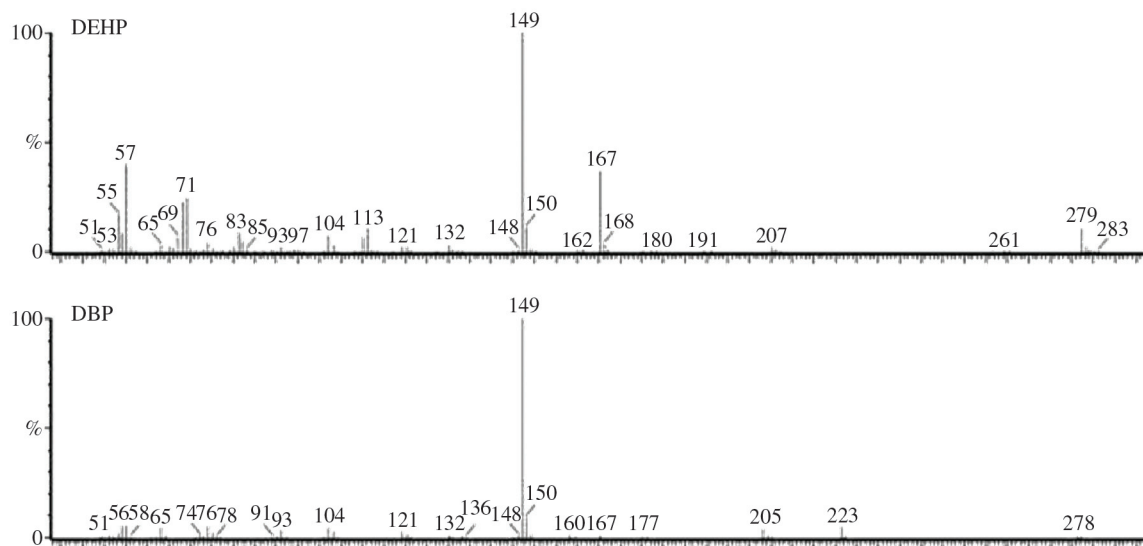


Figure 5. Comparison of spectral data for DBP and DEHP from the standard solution.

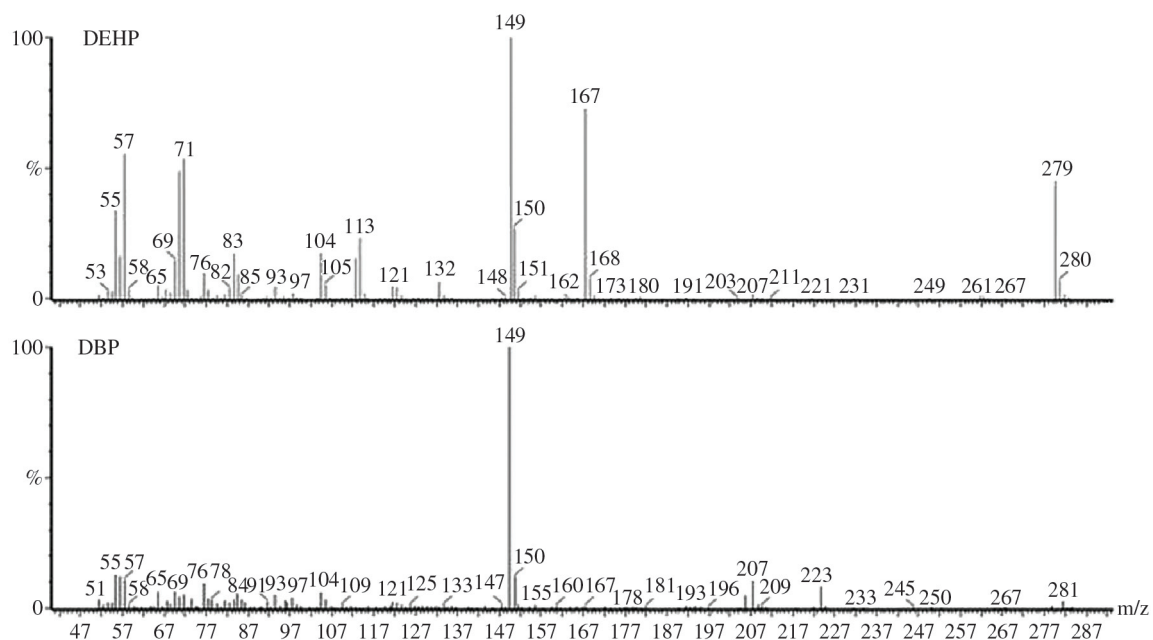


Figure 6. Comparison of spectral data for DBP and DEHP from the real sample.

good separation of particular phthalates from polymer materials. In the method for GC/MS and GC/ECD the regression coefficient in each case was greater than 0.90 (Table 6). The chromatogram of the real sample of plasticizer obtained by GC/MS is presented in Figure 4. In Figures 5 and 6 mass spectra of DBP and DEHP from the standard and from real sample are presented for comparison.

The real samples were analyzed by GC/MS, because of the possibility of double identification of analytes by retention time and mass spectrum. The repeatability

Table 7. Repeatability of the GC/MS and GC/ECD methods for each phthalate.

Phthalate	GC/MS	GC/ECD
	R.S.D. (%)	R.S.D. (%)
DMP	0.7	1.8
DEP	1.3	1.1
DBP	0.9	0.8
BBP	0.7	0.6
DEHP	0.7	1.6
DIOP	1.3	0.5
DINP	0.4	1.8

Table 8. Detection and quantification limits of the GC/MS and GC/ECD methods for each phthalate.

Phthalate	GC/MS		GC/ECD	
	LOD ($\mu\text{g mL}^{-1}$)	LOQ ($\mu\text{g mL}^{-1}$)	LOD ($\mu\text{g mL}^{-1}$)	LOQ ($\mu\text{g mL}^{-1}$)
DMP	6.31	12.62	4.29	8.59
DEP	5.41	10.84	4.18	8.37
DBP	4.27	8.55	2.98	5.96
BBP	9.02	18.05	3.69	7.38
DEHP	10.10	20.20	4.01	8.02
DIOP	5.57	11.14	2.97	5.92
DINP	3.46	6.92	2.99	5.98

Table 9. Concentration of phthalates in polymer materials (mg kg^{-1}).

No.	Sample	DMP	DEP	DBP	BBP	DEHP	DIOP	DINP
1	Band	N.D	N.D	28.0	N.D	1311.0	N.D	N.D
2	Plasticizer	N.D	N.D	24.0	N.D	2110.0	N.D	16200
3	Cable	N.D	N.D	7.0	N.D	3254.1	N.D	N.D
4	Plug	N.D	N.D	24.3	N.D	2446.4	N.D	N.D
5	Garden hose	N.D	N.D	0.9	N.D	178.6	N.D	N.D
6	The upper part of the garden hose	N.D	N.D	1.5	N.D	267.0	N.D	N.D
7	The middle part of the garden hose	N.D	N.D	11.0	N.D	N.D	N.D	N.D
8	Black composter	N.D	N.D	39.7	N.D	160.1	N.D	N.D
9	Gray composter	N.D	N.D	4.2	N.D	8.4	N.D	N.D
10	Gray container	N.D	N.D	11.3	N.D	26.1	N.D	N.D
11	Black container	N.D	N.D	5.6	N.D	7.6	N.D	N.D
12	Container wheel	N.D	N.D	6.1	N.D	8.4	N.D	N.D
13	Green polyethylene pellets	N.D	N.D	3.9	N.D	860.5	N.D	N.D
14	Black polyethylene pellets	N.D	N.D	9.1	N.D	12.6	N.D	N.D
15	Polyethylene pipe	N.D	N.D	N.D	N.D	1.7	N.D	N.D
16	Blue coat	N.D	N.D	13.3	N.D	N.D	N.D	N.D
17	Black coat	N.D	N.D	32.2	N.D	123.9	N.D	N.D

N.D – not determined.

of the whole analytical procedure was expressed as a relative standard deviation, and is an evaluation of the overall extraction, purification and analysis procedure. The whole process was repeated 5 times. The value of R.S.D for the GC/MS method ranged from 0.4 % for DINP to 1.3 % for DEP and DIOP. In case of the GC/ECD method repeatability was in the range from 0.5 % for DIOP to 1.8 % for DMP and DINP (Table 7). Better repeatability was estimated for GC/MS.

The limit of detection for each phthalate was estimated as three times the value of standard deviation and the limit of quantification as five times the value of standard deviation. The values of LOD for the GC/MS method ranged from $3.46 \mu\text{g mL}^{-1}$ for DINP to $10.10 \mu\text{g mL}^{-1}$ for DEHP, and in case of the GC/ECD method - from $2.97 \mu\text{g mL}^{-1}$ for DIOP to $4.29 \mu\text{g mL}^{-1}$ for DMP (Table 8). Application of the ECD detector, allowed reduction of the limit of quantification for all determined phthalates. The biggest LOQ differences were found in the case of DEHP.

The analyzes carried out have shown that, depending on the type of the polymeric material, total content of the phthalates determined according to the European regulations ranges from 1.7 mg kg^{-1} to 18334 mg kg^{-1} . The highest content of phthalates was found in samples of the plasticizer, cable and plug and it represented 1.8 %, 0.3 % and 0.2 % of polymer mass, respectively. In all the materials, except the middle part of the garden hose, and the blue coat, DEHP was detected. The concentration of DEHP ranged from $3254.1 \text{ mg kg}^{-1}$ to 1.7 mg kg^{-1} . In the case of samples obtained directly from the producers the concentration of this compound was higher than 1000 mg kg^{-1} . In the case of DBP concentration in the examined materials ranged from 39.7 mg kg^{-1} to 0.9 mg kg^{-1} . The highest content of this compound, equal to 40 mg kg^{-1} , was found in the black composter sample. DMP, DEP, BBP and DIOP were not found in the examined materials. The concentrations of phthalates

in investigated polymer materials are shown in Table 9. In the plasticizer sample the concentrations of DEHP and DINP were higher than 0,1 %. Hence this material can't be used for production of polymeric materials for children and food products.

Conclusion

The method developed for the determination of phthalates in polymer materials consists of:

- Ultrasonic extraction with methylene chloride;
- Purification the extracts on silica gel column;
- Quantitative analysis on the gas chromatograph combined with mass spectrometry and on the gas chromatograph with electron capture detector.

In this paper, two methods GC/MS and GC/ECD were compared. Optimization of the extraction method was performed by determining the recoveries of the analytes using different extractants. GC/ECD method showed lower limits of detection and quantification for phthalates than the GC/MS method. Also, mass spectrometry detection was seriously disturbed by complex matrix of polymer materials, whereas ECD provided excellent phthalates profiles without interferences. However, in the case of the GC/MS method there is a possibility of double compound identification by retention time and mass spectrum. This allows determination of phthalates other than those identified in this paper.

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