

Gas Chromatography/ Mass Spectrometry

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Determination of the Migration of Phthalate and Polycyclic Aromatic Hydrocarbon from Food Contact Plastic Bags by GC/MS

buns, oil cake and soybean milk are typically packaged in plastic. Leftovers, supermarket cooked food and even beer, are also packaged with plastic bags. Plastic packaging is very convenient but plasticizers and other additives dissolve and migrate into food during processing, heating and packaging, which can result in food contamination and permanent damage to human health and the environment.

This application demonstrates a method for the determination of 16 phthalates (PAEs) and 16 polycyclic aromatic hydrocarbons (PAHs) leaching from plastic bags using the PerkinElmer Clarus® SQ 8 GC/MS with electron ionization (EI) source. The method is based on the Chinese National Standards GB 31604.1-2015, GB 31604.30-2016 and GB 5009.265-2016.¹⁻³ Toluene is used as a solvent to extract the target compounds from the food simulants.

Introduction

Plastic bags are widely used in food packaging due to cost and flexibility, for example breakfast items such as hot steamed

Experimental

The PerkinElmer Clarus 680 SQ 8 GC/MS operating in electron ionization (EI) mode was used to perform these experiments with the conditions presented in Table 1. SIFI MS mode was used to analyze samples qualitatively and quantitatively with the operating parameters for SIM mode shown in Table 2.

A PerkinElmer Elite 5MS column (30 m × 0.25 mm × 0.25 μm) was used to separate the compounds. Five food simulants are used in this study (shown in Table 3) according to GB 31604.1-2015, General rules for food contact materials and articles.

Calibration standards (sixteen PAE and sixteen PAH mixture) were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. Chromatographic grade toluene (HPLC grade, Fisher Scientific) was used for all standard dilutions and as a solvent to extract target compounds from simulants. The concentration ranges for the standards are 0.05 mg/L – 10 mg/L for PAEs and 5 μg/L -100 μg/L for PAHs. Plastic bags (polyethylene) were obtained from a local breakfast store and vegetable market. Each bag was cut into 0.6 dm² pieces and submerged in 10 mL of food simulants with the storage conditions for each plastic in the five food simulants shown in Table 4. The glass containers for the food simulants were sealed to prevent loss due to evaporation.

After the migration test, the plastic pieces were removed from the simulants. The isooctane simulant was placed directly into vials for analysis without further preparation. A toluene extraction was performed for the other stimulants using the following procedure; add 2 mL of toluene to the simulants followed by mechanical shaking. The extract was then separated under centrifuge with the toluene layer sampled for analysis by GC/MS.

Table 1. Analytical parameters.

GC Parameters	
Injector Type	Capillary injector with capillary splitless deactivated glass liner with deactivated wool
Inlet Temp	280 °C
Carrier Gas Flow	1 mL/min
Split Flow	Splitless
Injection Volume	1 μL
Initial Oven Temp	50 °C
Oven Hold	1.0 min
Ramp	20 °C/min
2 nd Oven Temp	220 °C
Oven Hold	1.0 min
Ramp	5 °C/min
3 rd Oven Temp	250
Oven Hold	1.0 min
Ramp	20 °C/min
4 th Oven Temp	290 °C
Oven Hold	5.0 min
MS Parameters	
Ionization	EI
GC Inlet Line Temp	290 °C
Ion Source Temp	260 °C
Function Type	SIFI
Mass Range	45 to 450 amu
Scan Time	0.05 s
Solvent Delay Time	3 min

The spike recovery experiment was carried out by spiking 10 mL of food simulants to give expected concentrations of 0.2 mg/L and 5 mg/L PAE and 20 μg/L PAH in toluene.

Table 2. Operating parameters for SIM MS mode.

Compound Name	Quantitation Ion (m/z)	Dwell Time (s)	Retention Window (min)
Naphthalene	128	0.1	4.70 - 6.13
DMP	163	0.03	6.50 - 8.00
Acenaphthylene	152		
Acenaphthene	154	0.05	7.65 – 8.60
DEP	149		
Fluorine	166	0.03	9.00 – 12.20
Phenanthrene	178		
Anthracene	178		
DIBP	149		
DBP	149		
DMEP	149		
BMPP	149		
Fluoranthene	202		
DEEP	149		
DPP	149		
Pyrene	202	0.03	12.70 – 16.40
DHXP	149		
BBP	149		
DBEP	149		
Benz[a]anthracene	228		
Chrysene	228		
DCHP	149		
DEHP	149		
DPhP	225		
DNOP	149		
Benz[b]anthracene	252	0.03	16.80 – 20.20
Benz[k]anthracene	252		
Benzo[a]pyrene	252		
DNP	149		
Indeno(1,2,3-cd)pyrene	276	0.03	20.60 – 23.00
Dibenz[a,h]anthracene	278		
Benzo[g,h,i]perylene	276		

Table 3. Food simulants.

Type of Food	Food Simulants	
Aqueous	pH ≥5	10% Ethanol (v/v)
	pH <5	4% Acetic acid (v/v)
Alcoholic	The amount of Ethanol ≤20% (v/v)	20% Ethanol (v/v)
	20% < The amount of Ethanol ≤50% (v/v)	50% Ethanol (v/v)
Oil and food with oil on the surface	Isooctane *	1 μL

* Vegetable oil is the simulant for oil and food with oil on the surface which can be replaced by 95% ethanol (v/v), hexane, n-heptane and isooctane. Here isooctane is used as a simulant.

Table 4. Storage conditions.

Time (Hours)	Temperature (°C)		
0.5	20	40	70
2	20	40	70
6	20	40	70

Results and Discussion

The overlaid extracted ion chromatograms (Figure 1) show the elution of the PAEs and PAHs. The calibration curves were plotted as the peak area versus the amount of analyte and the obtained determination coefficients (r^2) for all compounds were over 0.997, showing the reliability of the analysis in the concentration range. Table 5 and 6 summarize the results for linearity of PAEs and PAHs.

In this study, hexane, dichloromethane and toluene were the solvents evaluated for extraction efficiency. Hexane showed lower extraction efficiency than toluene and dichloromethane because of the weak polarity of the solvent. The dichloromethane layer was under the simulants layer since dichloromethane is denser than the simulants and as such it proved difficult to transfer the extract into autosampler vials. Therefore, toluene was chosen as a solvent in this paper. The recoveries per storage conditions were calculated to be in the range of 85.5 – 116.0% for most

PAEs and all PAHs (Table 7 and 8). The slightly polar compounds such as DEP, DMP and DMEP showed lower recoveries. Three phthalates, DIBP, DBP and DCHP, were detected under the different storage conditions and there was a measurable increase in leaching with increased storage time and storage temperature. The strongest leaching result was obtained in 50% of ethanol when comparing the other food simulants. Figure 2 shows the obtained total ion chromatograms of the phthalates. The phthalate extract was obtained using a migration test with samples heated at 40 °C in 50% ethanol for different times. The migration of PAEs in plastic bags summarized (Table 9) is very low even when the simulants were stored at high temperature for an extended time. Specific migration limit (SML) in the Chinese national standard for phthalates are 0.3 mg/kg for DBP, 1.5 mg/kg for DEHP, 0.01 mg/kg for DAP and 9.0 mg/kg for DINP.⁴ The amount of DBP is lower than the SML. The other two phthalates weren't prescribed SML in Chinese standard. No PAHs were detected from any of the simulants.

Table 5. PAEs results for retention time and linearity.

Compound Name	Retention Time (min)	Quantitation Ion (m/z)	Linearity	
			Calibration Curve	r^2
DMP	7.24	163	24916.6x - 716.13	0.9991
DEP	8.08	149	27373.9x - 1027.87	0.9990
DIBP	9.57	149	40998.3x - 2395.72	0.9992
DBP	10.11	149	48816.0x - 3210.09	0.9990
DMEP	10.34	149	24828.4x - 1956.98	0.9982
BMPP	10.88	149	24774.7x - 2348.26	0.9994
DEEP	11.18	149	11755.0x - 1044.41	0.9989
DPP	11.51	149	52400.1x - 3993.44	0.9993
DHXP	13.32	149	51978.3x - 5754.94	0.9993
BBP	13.41	149	20601.9x - 2406.26	0.9992
DBEP	14.70	149	8662.19x - 1362.36	0.9990
DCHP	15.25	149	36741.1x - 4353.72	0.9992
DEHP	15.47	149	32189.0x - 2720.40	0.9993
DPhP	15.55	225	22867.3x - 2229.54	0.9993
DNOP	17.91	149	46799.4x - 8164.74	0.9989
DNP	19.56	149	50894.5x - 7911.87	0.9991

Table 6. PAHs results for retention time and linearity.

Compound Name	Retention Time (min)	Quantitation Ion (m/z)	Linearity	
			Calibration Curve	r^2
Naphthalene	5.50	128	43.42x - 142.42	0.9994
Acenaphthylene	7.37	152	28.55x - 97.55	0.9968
Acenaphthene	7.55	154	19.71x - 67.34	0.9967
Fluorine	8.18	166	18.66x - 68.49	0.9985
Phenanthrene	9.31	178	29.60x - 125.86	0.9988
Anthracene	9.38	178	27.02x - 107.53	0.9991
Fluoranthene	11.09	202	30.87x - 151.234	0.9994
Pyrene	11.53	202	32.62x - 151.56	0.9992
Benz[a]anthracene	14.79	228	20.00x - 126.54	0.9991
Chrysene	14.90	228	26.35x - 163.96	0.9995
Benz[b]anthracene	18.34	252	16.43x - 106.02	0.9975
Benz[k]anthracene	18.42	252	23.84x - 162.02	0.9986
Benzo[a]pyrene	19.09	252	15.74x - 99.15	0.9991
Indeno(1,2,3-cd)pyrene	21.46	276	10.65x - 82.70	0.9973
Dibenz[a,h]anthracene	21.57	278	11.39x - 84.94	0.9983
Benzo[g,h,i]perylene	22.07	276	14.33x - 94.20	0.9992

Table 7. PAEs recoveries (%) (n=3).

Compound Name	4% Acetic Acid		10% Ethanol		20% Ethanol		50% Ethanol		Isooctane	
	0.2 ppm	5 ppm	0.2 ppm	5 ppm	0.2 ppm	5 ppm	0.2 ppm	5 ppm	0.2 ppm	5 ppm
DMP	88.5	110.4	95.5	97.1	106.0	108.0	-	86.0	85.4	110.6
DEP	-	-	-	94.7	-	85.7	-	-	85.8	86.6
DIBP	92.5	103.7	100.5	99.0	103.0	94.1	111.5	104.0	104.3	98.6
DBP	105.5	102.5	100.0	98.9	102.5	93.9	116.0	106.0	105.1	97.6
DMEP	85.5	97.4	89.0	93.1	90.5	86.0	-	-	103.6	98.0
BMPP	87.0	104.7	99.5	98.7	103.0	95.2	114.5	113.0	100.2	97.4
DEEP	87.0	103.4	95.5	98.9	99.5	92.6	89.5	88.2	99.7	95.4
DPP	88.5	101.4	95.5	97.9	101.0	93.3	113.0	106.0	99.6	95.0
DHXP	88.5	104.7	98.0	97.7	97.0	92.8	106.5	111.2	100.3	95.0
BBP	85.7	108.3	98.0	100.9	100.5	95.8	110.5	110.8	99.5	95.6
DBEP	85.5	104.4	98.0	98.3	111.5	91.9	113.8	110.0	90.3	94.0
DCHP	88.0	103.0	100.0	98.2	103.5	94.6	113.5	108.0	95.1	95.0
DEHP	94.5	104.1	103.0	97.2	109.5	93.4	112.2	114.0	88.6	93.6
DPhP	85.5	104.1	95.5	98.0	100.5	93.0	106.5	102.7	100.4	95.0
DNOP	88.0	101.7	101.0	96.5	107.0	89.5	108.5	111.0	95.2	95.4
DNP	88.5	102.8	100.5	98.2	105.0	91.3	104.5	114.0	89.9	93.0

Table 8. PAHs recoveries (%) (n=3).

Compound Name	4% Acetic acid	10% Ethanol	20% Ethanol	50% Ethanol	Isooctane
Naphthalene	96.89	107.00	103.80	102.40	95.00
Acenaphthylene	95.50	92.75	91.20	89.00	100.20
Acenaphthene	88.65	86.35	85.80	88.25	93.50
Fluorine	98.90	92.45	102.90	96.50	96.76
Phenanthrene	97.50	97.00	105.75	106.15	96.75
Anthracene	92.70	93.70	96.50	105.60	100.55
Fluoranthene	95.60	91.55	94.50	93.80	103.40
Pyrene	96.50	93.40	95.50	104.10	98.05
Benz[a]anthracene	89.50	87.55	86.85	85.30	90.65
Chrysene	98.50	94.25	94.00	106.75	101.85
Benz[b]anthracene	91.80	91.60	101.25	110.90	89.10
Benz[k]anthracene	99.85	91.55	94.30	103.25	92.25
Benzo[a]pyrene	100.20	95.95	98.00	106.70	93.95
Indeno(1,2,3-cd)pyrene	88.50	97.10	95.90	104.35	93.30
Dibenz[a,h]anthracene	95.70	98.35	104.25	113.75	95.75
Benzo[g,h,i]perylene	87.15	90.70	91.90	94.20	94.35

Table 9. The migration of PAEs in plastic bags.

Compound Name	Food Simulants	Amount (mg/kg)								
		70 °C			40 °C			20 °C		
		0.5 Hour	2 Hours	6 Hours	0.5 Hour	2 Hours	6 Hours	0.5 Hour	2 Hours	6 Hours
DIBP	4% Acetic Acid	0.064	0.092	0.111	0.003	0.005	0.008	0.003	0.004	0.004
	10% Ethanol	0.071	0.091	0.173	0.006	0.006	0.008	0.003	0.004	0.004
	20% Ethanol	0.147	0.188	0.247	0.010	0.016	0.017	0.004	0.007	0.009
	50% Ethanol	0.197	0.238	0.266	0.007	0.017	0.020	0.006	0.007	0.010
	Isooctane	0.201	0.256	0.287	0.005	0.011	0.016	0.005	0.006	0.007
DBP	4% Acetic Acid	0.208	0.219	0.280	0.008	0.011	0.014	0.008	0.009	0.009
	10% Ethanol	0.184	0.199	0.230	0.010	0.010	0.011	0.003	0.004	0.004
	20% Ethanol	0.317	0.347	0.490	0.020	0.022	0.019	0.010	0.009	0.010
	50% Ethanol	0.628	0.815	1.033	0.020	0.029	0.031	0.014	0.017	0.018
DCHP	Isooctane	0.420	0.493	0.578	0.012	0.023	0.027	0.008	0.011	0.013
	4% Acetic Acid	0.009	0.009	0.012	-	-	-	-	-	-
	10% Ethanol	0.004	0.008	0.048	-	-	-	-	-	-
	20% Ethanol	0.007	0.009	0.010	-	-	-	-	-	-
DCHP	50% Ethanol	0.299	0.317	0.456	0.011	0.011	0.035	0.010	0.008	0.011
	Isooctane	0.130	0.404	0.682	-	-	-	-	-	-

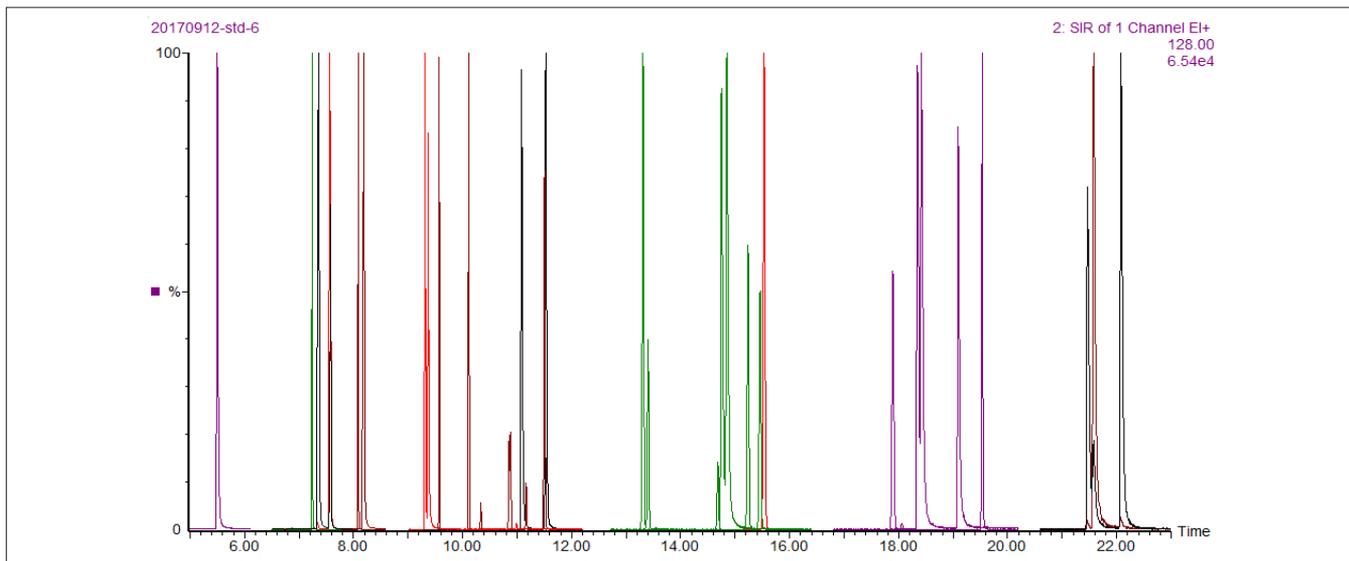


Figure 1. The overlaid extracted ion chromatogram in selected ion monitoring mode of a 5 mg/L PAE standard and 50 µg/L PAH standard.

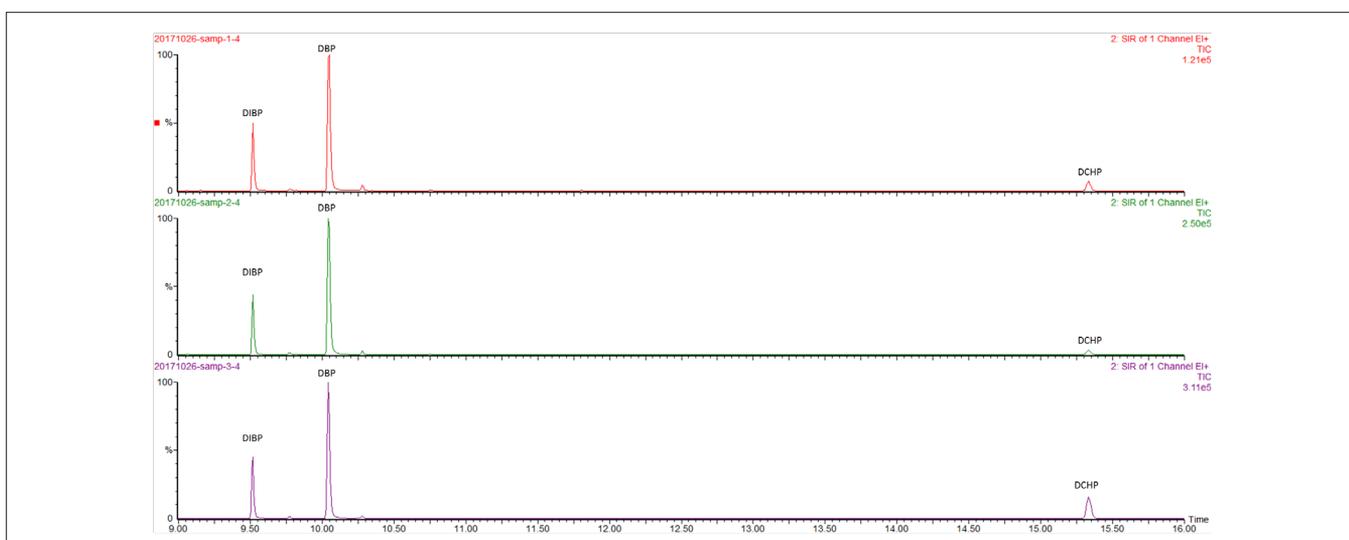


Figure 2 Total ion chromatogram of the sample at 40 °C in 50% ethanol for 0.5, 2, 6 hours. (The red one is for 0.5 hour. The green one is for two hours. The violet one is for six hours.)

Summary

In this paper, a method for the determination of 16 phthalates (PAEs) and 16 polycyclic aromatic hydrocarbons (PAHs) leaching from plastic bags was established using the PerkinElmer Clarus® SQ8 GC/MS with electron ionization (EI) source. Toluene was shown to be a suitable solvent with good recoveries for this application. The phthalate leaching from the plastic bags into food is lower than the SML in GB 9685-2008.

References

1. GB 31604.1-2015, General rules for food contact materials and Articles.
2. GB 31604.30-2016, Food contact materials and articles - Determination of phthalates and migration.
3. GB 5009.265-2016, Determination of polycyclic aromatic hydrocarbons in foods.
4. KGB 9685-2008, Hygienic standards for uses of additives in food containers and packaging materials.