



Determination of 5 Photoinitiators, 6 Plasticizers and 9 Primary Aromatic Amines in Plastic and Canned Food Contact Materials by Gas Chromatography-Mass Spectrometry

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A practical and simple method was developed for determination of five photoinitiators, six adipate-based plasticizers and nine primary aromatic amines in three ink-printed plastic composite bags, one polyvinyl chloride film and two metal cans using ultrasonic extraction coupled with gas chromatography-mass spectrometry. The correlation coefficient (R^2) of standard curve was ≥ 0.9973 and limits of detection of the method ranged from 0.80 to $10 \mu\text{g kg}^{-1}$. The recoveries and precision was satisfactory. The results indicated that the di(2-ethylhexyl) adipate was prevalent exist in studied food contact materials and the content ranged from 0.19 to $1.01 \times 10^5 \text{ mg kg}^{-1}$. Benzophenone concentration ranged 0.020 to 0.065 mg kg^{-1} . Aniline concentration ranged 0.020 to 0.27 mg kg^{-1} .

Keywords: Food contact materials, Photoinitiators, Adipate-based plasticizers, Primary aromatic amines.

INTRODUCTION

As an important aspect of food safety, food contact material safety has attracted increasing attention in recent years. Potential risks of additives in food contact materials were assessed by some institutions with modern analytical techniques. The photoinitiators, the plasticizers and the azo colorants are frequently used three kinds of additives.

The photoinitiators are widely used for printing the external face of the food contact materials¹. UV-cured inks containing benzophenone-based derivatives have gradually replaced the traditional volatile solvent inks due to their less organic solvent residue, low toxicity and less environmental impact². The carcinogenicity, reproduction toxicity and skin contact toxicity of benzophenone was demonstrated in the animal test by Rhodes *et al.*³. The adipate-based plasticizers are often added to the polymer materials to modify its properties such as flexibility, processibility and extensibility⁴. Some researches indicate that they could interfere with the hormone secretion of body and cause cancer and mutation if they accumulate too much in the body⁵. Azo colorants have been extensively used for producing multi-colored textiles, leather and some food contact plastics⁶. Primary aromatic amines are decomposed from residual aromatic isocyanate which is reduced from azo colorants⁷. Primary aromatic amines are strong human carcinogens.

Since these compounds possess relatively low molecular weights, they can permeate through the materials and migrate to the packaged contiguous food or food simulants⁸. Especially adipate-based plasticizers can easily diffuse to those with high fat content⁹. The specific migration limits (SMLs) set by EU are 0.01 mg kg^{-1} for primary aromatic amines^{10,11}, 18 mg kg^{-1} and 3 mg/dm^2 for di(2-ethylhexyl)adipate. The limit of di(2-ethylhexyl)adipate in water is 0.4 mg L^{-1} set in 2011 by Edition of the Drinking Water Standards and Health Advisories¹². The maxima total migration limit of benzophenone and MM from food packaging printing inks is 0.6 mg kg^{-1} set by European Union Standing Committee on the food chain and animal health (SCFCAH)¹³.

In recently years, there are many reports on the determination and migration of the photoinitiators, the plasticizers and primary aromatic amines from food contact materials into various food and food simulants^{4,9,14-16}. Sample pretreatment methods commonly employed include solid phase microextraction^{17,18}, solid phase extraction¹⁹, microwave extraction^{20,21}, solution precipitation extraction²², soxhlet extraction^{5,23} and ultrasonic extraction¹⁵. Frequently used determination methods include GC/GC-MS^{9,15,24}, high performance liquid chromatography^{25,26}, high performance liquid chromatography-mass spectrometry (HPLC-MS)^{7,27} and Fourier transform infrared (FT-IR) spectroscopy²⁸. To the best of our knowledge, each of these works just reports the determination of only one kind of compounds in food contact materials respectively.

Because some of these three kinds of compounds are common migrants, it is important to develop a universal method for their determination. Herein a GC-MS method coupled with ultrasonic extraction is developed for determination of 20 compounds in 3 plastic composite bags, 1 polyvinyl chloride film and 2 metal cans. The optimized ultrasonic extraction is low-cost and fast with satisfactory recovery. This method provides good precision and recovery. Five target compounds were found in the real samples. This method is sensitive enough to determine these compounds migrating from food contact materials to food simulants.

EXPERIMENTAL

The sources and detailed information of studied compounds are presented in Table-1. Hexane (HPLC grade, >99.9 %, CAS No. 110-54-3), ethyl acetate (HPLC grade, >99.9 %, CAS No. 141-78-6) and methanol (HPLC grade, >99.9 %, CAS No. 67-56-1) were purchased from J & K Chemical, Ltd. (Beijing, China), Tedia company inc Co., Ltd. (Connecticut, USA) and Oceanpak Alexative Chemical Co., Ltd. (Goteborg, Sweden), respectively. Acetonitrile (HPLC grade, >99.9 %, CAS No. 75-05-8), dichloromethane (HPLC grade, >99.9 %, CAS No. 75-09-2) and *tert*-butyl methyl ether (HPLC grade, >99.9 %, CAS No. 1634-04-4) were all purchased from Shanghai Anpel Scientific Instrument Co., Ltd. (Shanghai, China). Citric acid (analytical grade, >95 %, CAS No. 5949-29-1) and sodium hydroxide (analytical grade, >96 %, CAS No. 1310-73-3) were all supplied by Guangdong Guanghua Chemical Factory Co., Ltd. (Guangzhou, China). Sodium hydrosulfite (analytical grade, >88.0 %, CAS No. 7775-14-6) was supplied by National Medicine Group Chemical Co., Ltd. (Beijing, China).

GC-MS was performed with an Agilent 7890A GC coupled with a 5975C MS detector (Agilent, USA) and 7693 autosampler (Agilent, USA). The GC was equipped with a HP-5 MS UI capillary column (30m × 0.25 mm × 0.25 μm, Agilent, USA). Injection mode was splitless and the injection

volume was 1 μL. The flow rate of helium gas (>99.999 %) was 1 mL min⁻¹. The front inlet temperature was 280 °C. The temperature of ion source and quadrupole were 230 and 150 °C, respectively. The oven temperature was programmed as follows: started at 60 °C (held for 2 min), raised to 130 °C at 10 °C min⁻¹ (held for 1 min), raised to 200 °C at 10 °C min⁻¹ (held for 0.5 min) and raised to 280 °C at 20 °C min⁻¹ (held for 2.5 min), in a total run time of 22 min. The electron-impact (EI) ionization mode (70 eV) was used in mass spectrometry. The quantification was performed in selected ion monitoring (SIM). The characteristic ions and quantitative ions were presented in Table-1.

An ultrasonic cleaning machine (AS10200BT, Tianjin Autoscience Instrument Co., Ltd. Tianjin, China) was used for sample pretreatment. Ultrapure water was produced by ultrapure water system (UPHW-I-90T, Chengdu ultrapure technology Co., Ltd.). A rotary evaporator (Hei-VAP, Heidolph, Germany) and a nitrogen stream instrument (Zymark Turbo Vap LV, Caliper Co., Ltd., USA) were used for the concentration of the samples. The volumetric glassware were used throughout in order to decrease the pollution of plasticizers.

Samples: The tested samples are food contact materials including three ink-printed plastic composite bags (all about 600 cm² area and 0.075 mm thickness, single layer), one polyvinyl chloride cling film (0.025 mm thickness, single layer) and two metal cans (about 200 and 450 mL volume, respectively) with inner coating. They were all bought from local market randomly. The melt or adhesive sealed was removed before extraction.

Solution preparation: 10 mg of each compound was dissolved in 10 mL of methanol, respectively to get stock solution of single compound of 1000 mg L⁻¹, which was stored in brown glass-stopper bottles at 4 °C. The mixed stock solution of 20 compounds of 10 mg L⁻¹ was obtained by adding 100 μL of each stock solution of single compound to a 10 mL bottle. Five standard solutions of 50, 100, 200, 500 and 1000 mg L⁻¹

TABLE-1
DETAILED INFORMATION OF 20 STUDIED ADDITIVES

Standards type	Chemical name	mw ^a	CAS No.	Source	CI	QI
Photoinitiator	Benzophenone	182.2	119-61-9	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	105, 77	105
	4-Methylbenzophenone	202.3	134-84-9	J & K Chemical, Ltd. (Beijing, China)	119, 196	119
	Ethyl-4-dimethylaminobenzoate	193.2	10287-53-3	J & K Chemical, Ltd. (Beijing, China)	148, 193	148
	1-Hydroxycyclohexyl-phenylketone	204.3	947-19-3	J & K Chemical, Ltd. (Beijing, China)	99, 81	99
	2-Ethylhexyl-4-dimethylamino-benzoate	276.4	21245-02-3	AccuStandard, Inc. (New Haven, USA)	165, 148	165
Plasticizer	Di(2-ethylhexyl) adipate	370.6	103-23-1	Pure Chemical Analysis Co., Ltd. (Boenew, Belgium)	129, 112	129
	Diisobutyl adipate	258.4	141-04-8	Pure Chemical Analysis Co., Ltd. (Boenew, Belgium)	129, 185	129
	Diethyl adipate	202.3	141-28-6	Pure Chemical Analysis Co., Ltd. (Boenew, Belgium)	111, 157	111
	Dibutyl adipate	258.4	105-99-7	Pure Chemical Analysis Co., Ltd. (Boenew, Belgium)	129, 241	129
	Dinonyl adipate	398.6	151-32-6	Pure Chemical Analysis Co., Ltd. (Boenew, Belgium)	129, 185	129
	<i>bis</i> (1-Butylpentyl) adipate	398.6	77916-77-9	Fluka Cheme GmbH, Buchs Sigma-Aldrich (Augsburg, Germany)	129, 111	129
Primary aromatic amines	4-Aminoazobenzene	197.2	60-09-3	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	92, 197	92
	<i>o</i> -Anisidine	123.2	90-04-0	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	80, 108, 123	108
	<i>o</i> -Toluidine	107.2	95-53-4	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	106, 107	106
	Aniline	93.1	62-53-3	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	93, 66	93
	4-Aminobiphenyl	169.9	92-67-1	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	169, 168	169
	3,3'-Dichlorobenzidine	253.1	91-94-1	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	252, 253	252
	4-Amino-2',3-dimethylazobenzene	225.3	97-56-3	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	106, 225	106
	4-Chloroaniline	127.6	106-47-8	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	127, 129	127
	<i>bis</i> -(4-Aminophenyl) methane	198.3	101-77-9	Dr. Ehrenstorfer GmbH (Augsburg, Germany)	198, 197	198

^amolecular weight; Characteristic ions (CI); Quantitative ion (QI)

were daily prepared by diluting the mixed stock solution with acetonitrile.

Citric acid/sodium hydroxide buffer salt solution: 12.526 g citric acid and 6.320 g were dissolved in 1000 mL of ultrapure water. Sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) solution: 5 g sodium hydrosulfite was dissolved in 25 mL of ultrapure water to get solution of 200 mg mL^{-1} . The column of diatomite (14.5 g/60 mL, Agilent, USA) was used for remove water.

Validation of method: A signal-to-noise ratio (S/N) of three in the pure solution is used to estimate the instrumental limit of detection (LODi) and of ten is used to estimate the instrumental limit of quantification (LOQi), while a signal-to-noise ratio (S/N) of three in the matrix (plastic composite bag 1 and can 1 for all the three kinds of additives, polyvinyl chloride film only for plasticizers) is used to evaluate the methodological limit of detection (LODm) and of ten is used to evaluate the methodological limit of quantification (LOQm). The recovery and repeatability of the method were verified by spiking standard solution in the blank materials with three levels (50, 100, 200 $\mu\text{g L}^{-1}$) of 20 standards in six replicate experiments.

Sample preparation: The following procedure was used to treat the samples for the determination of photoinitiators and adipate-based plasticizers. Pieces of approximately 1 cm^2 area of each samples were cut and $0.5000 \pm 0.001 \text{ g}$ was weighted. Then they were soaked in 20 mL acetonitrile in a glass bottle (50 mL) and ultrasonically extracted for 0.5 h in an ultrasonic system. The extract was collected in a 100 mL round-bottom flask. 5 mL acetonitrile was used to wash the flask and it was merged with the extract. This step was repeated 3 times. The resulting solution was evaporated to approximate dryness at $45 \text{ }^\circ\text{C}$ by rotary evaporator. The residue was dissolved to 1 mL with acetonitrile (for polyvinyl chloride, the solution was diluted 20000 times with acetonitrile) and filtered through $0.45 \mu\text{m}$ nylon membrane filter prior to the analysis by GC-MS.

The following procedure was used to treat the samples for the determination of primary aromatic amines²⁹. Pieces of approximately 1 cm^2 area of each samples were cut and $1.0000 \pm 0.0001 \text{ g}$ was weighted. Then they were soaked in 25 mL dichloromethane in a glass bottle (50 mL) and ultrasonically extracted for 0.5 h. The extract was collected in a 100 mL round-bottom flask. 5 mL dichloromethane was used to wash the flask and it was merged with the extract. This step was repeated 3 times. The resulting solution was evaporated to approximate dryness at $35 \text{ }^\circ\text{C}$ with rotary evaporator. The residue was transferred to a reactor (20 mL) using 2 mL methanol and was dispersed by ultrasound. 15 mL citric acid/sodium hydroxide buffer salt solution was heated to $70 \pm 2 \text{ }^\circ\text{C}$ and then added to the reactor. The reactor was sealed for 0.5 h at $70 \text{ }^\circ\text{C}$. Then 3 mL sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) solution (200 mg mL^{-1}) was added and oscillated adequately and sealed for 0.5 h at $70 \text{ }^\circ\text{C}$. The reaction solution was cooled rapidly in 2 min. Afterwards 0.2 mL sodium hydroxide (NaOH) (10 % (w/v)) solution was added to the reaction solution and oscillated adequately, then the reaction solution was transferred to the column of diatomite and was hold for 15 min. 10 mL *tert*-Butyl methyl ether was used to dissolve the residue in the reactor. *tert*-Butyl methyl ether was transferred with undissolved

residue to the column of diatomite and this step was repeated twice. The column was eluted with 10 mL *tert*-butyl methyl ether, which was repeated 6 times. The eluate was collected in a 100 mL round-bottom flask. The eluate was evaporated to approximate dryness at $45 \text{ }^\circ\text{C}$ with rotary evaporator and concentrated to dryness by gentle stream of nitrogen. The residue was dissolved by 2 mL acetonitrile and filtered through $0.45 \mu\text{m}$ nylon membrane filter prior to the analysis by GC-MS.

Statistical analysis: Statistical analyses were carried out using Minitab 15 (Minitab Inc., State College, PA, USA) and statistical product and service solutions (SPSS) 13.0 (IBM spss Inc., New York, USA) analytical software. $P < 0.05$ was identified as being statistically significant at a 95 % confidence level.

RESULTS AND DISCUSSION

Stability of studied compounds: It has been observed that instability of the calibration standard solution may lead to significant deviation of the results. Standard solution of 1 mg L^{-1} was determined for ten consecutive days. All the 20 compounds were stable except for *bis*-(4-aminophenyl) methane and 4-aminoazobenzene. The stability study of benzophenone, di(2-ethylhexyl) adipate, *bis*-(4-aminophenyl) methane and 4-aminoazobenzene are shown in Fig. 1. *bis*-(4-amino-phenyl) methane and 4-aminoazobenzene were stable for just about 7 days at $-4 \text{ }^\circ\text{C}$.

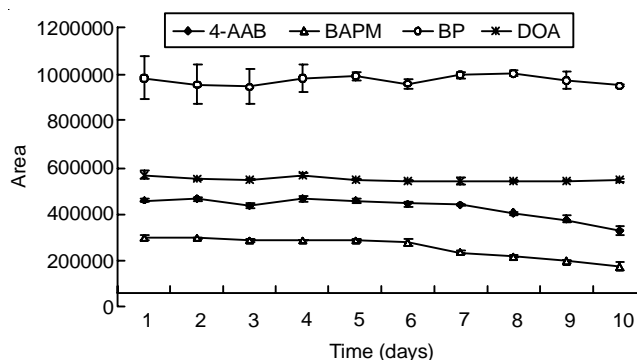


Fig. 1. Stability of calibration standards [benzophenone, di(2-ethylhexyl) adipate, 4-aminoazobenzene and *bis*-(4-aminophenyl)methane] in 10 days ($1000 \mu\text{g L}^{-1}$) ($n = 3$)

Validation of optimized method: The developed method was validated by studying the limit of detection, limit of quantitation, linearity, recovery and repeatability (Tables 2 and 3). Fig. 2 shows the chromatogram of standard solution of $100 \mu\text{g L}^{-1}$ of 20 compounds. Compared with the limit of detections reported in other paper^{2,28}. The limit of detections of this method is lower which is in favor of the determination of these compounds. The recoveries of 20 compounds ranged from 51 to 116 % and relative standard deviation from 1 to 19 % (Table-3). It was obvious that recoveries were poor for primary aromatic amines. According to the regulation of EU²⁹, the requirement of the recoveries of some primary aromatic amines in the textiles should $\geq 50 \%$. Therefore the recoveries ranging from 51 to 74 % were acceptable.

Analysis of real samples: The concentrations of 20 compounds in real samples were shown in Table-5. Five compounds

TABLE-2
RETENTION TIME, LINEARITY EQUATION, CORRELATION COEFFICIENT, LODs AND LOQs OF 20 COMPOUNDS (n=6)

Standards type	Chemical name	Retention time (min)±SD	Linearity range: 50-1000 µg L ⁻¹		Correlation coefficient (R ²)	LOD ⁱ , LOD ^M (µg L ⁻¹ , µg kg ⁻¹)	LOQ ⁱ , LOQ ^M (µg L ⁻¹ , µg kg ⁻¹)
			Slope (±SD)	Intercept (±SD)			
Photoinitiator	Benzophenone	15.90±0.001	4652±7	-2175±194	0.9991	0.30, 0.80	1.00, 3.00
	4-Methylbenzophenone	17.42±0.002	4020±6	-1661±64	0.9977	2.00, 5.00	7.00, 20.00
	Ethyl-4-dimethylaminobenzoate	16.84±0.001	530±22	832±88	0.9994	0.50, 1.00	2.00, 4.00
	1-Hydroxycyclohexyl-phenylketone	16.64±0.002	1731±3	-2842±485	0.9995	1.00, 2.00	4.00, 7.00
	2-Ethylhexyl-4-dimethylamino-benzoate	21.32±0.001	1224±4	1680±210	0.9991	1.00, 2.00	4.00, 7.00
Plasticizer	Di(2-ethylhexyl) adipate	21.89±0.002	483±3	-1971±63	0.9976	2.00, 5.00	7.00, 20.00
	Diisobutyl adipate	16.44±0.001	1084±3	-1678±330	0.9987	1.00, 2.00	4.00, 7.00
	Diethyl adipate	12.43±0.003	1013±10	-1705±224	0.9984	2.00, 5.00	7.00, 20.00
	Dibutyl adipate	22.68±0.002	430±1	1304±201	0.9999	5.00, 10.00	20.00, 35.00
	Dinonyl adipate	17.38±0.001	706±4	-2712±190	0.9973	5.00, 10.00	20.00, 35.00
	<i>bis</i> (1-Butylpentyl) adipate	22.13±0.002	300±1	-155±14	0.9996	5.00, 10.00	20.00, 35.00
	4-Aminoazobenzene	20.25±0.001	1114±2	-1661±173	0.9992	1.00, 2.00	4.00, 7.00
Primary aromatic amines	<i>o</i> -Anisidine	9.04±0.003	2668±6	-2066±310	0.9989	0.50, 1.00	2.00, 4.00
	<i>o</i> -Toluidine	7.44±0.01	5028±9	-1415±194	0.9991	0.30, 0.80	1.00, 3.00
	Aniline	5.93±0.02	5557±28	-1643±225	0.9995	0.30, 0.80	1.00, 3.00
	4-Aminobiphenyl	17.33±0.002	2973±22	1257±96	0.9987	0.50, 1.00	2.00, 4.00
	3,3'-Dichlorobenzidine	22.49±0.02	980±3	2376±211	0.9993	1.00, 2.00	4.00, 7.00
	4-Amino-2',3-dimethylazobenzene	21.36±0.002	1121±4	-1733±281	0.9994	2.00, 5.00	7.00, 20.00
	4-Chloroaniline	9.46±0.004	3962±7	-1446±58	0.9976	0.30, 0.80	1.00, 3.00
	<i>bis</i> -(4-Aminophenyl) methane	20.56±0.004	477±2	344±92	0.9995	2.00, 5.00	7.00, 20.00

LODⁱ, LOD^M: Limit of detection (LOD) of the instrument and the LOD of the method; LOQⁱ, LOQ^M: Limit of quantitation (LOQ) of the instrument and the LOQ of the method

TABLE-3
RECOVERIES AND RSDs OF 20 CHEMICALS WITH 3 CONCENTRATIONS OF 50, 100, 200 µg L⁻¹ (n=6)

Standards type	Chemical name	Recoveries (RSDs) (%)		
		50 µg L ⁻¹	100 µg L ⁻¹	200 µg L ⁻¹
Photoinitiator	Benzophenone	103(11)	89(2)	92(5)
	4-Methylbenzophenone	101(9)	106(1)	101(4)
	Ethyl-4-dimethylaminobenzoate	113(4)	101(3)	109(5)
	1-Hydroxycyclohexyl-phenylketone	107(4)	97(1)	101(3)
	2-Ethylhexyl-4-dimethylamino-benzoate	103(5)	104(4)	112(4)
Plasticizer	Di(2-ethylhexyl) adipate	109(7)	106(0.5)	114(5)
	Diisobutyl adipate	109(5)	99(2)	102(3)
	Diethyl adipate	108(10)	83(3)	83(3)
	Dibutyl adipate	112(12)	106(6)	109(7)
	Dinonyl adipate	107(7)	108(4)	114(6)
	<i>bis</i> (1-Butylpentyl) adipate	116(6)	104(2)	112(7)
	4-Aminoazobenzene	97(6)	98(1)	108(4)
Primary aromatic amines	<i>o</i> -Anisidine	66(10)	59(16)	60(17)
	<i>o</i> -Toluidine	58(11)	51(16)	55(10)
	Aniline	67(8)	73(19)	62(14)
	4-Aminobiphenyl	92(6)	96(2)	104(3)
	3,3'-Dichlorobenzidine	91(5)	97(2)	106(4)
	4-Amino-2',3-dimethylazobenzene	101(4)	100(1)	109(4)
	4-Chloroaniline	77(14)	61(11)	63(8)
	<i>bis</i> -(4-Aminophenyl) methane	57(13)	60(9)	74(9)

were found in 6 samples. Polyvinyl chloride film just contained di(2-ethylhexyl)adipate and it did not contain primary aromatic amines because there was no printing on the surface of the film. Plastic composite bags contained benzophenone, aniline and *bis*-(4-aminophenyl) methane, which are all from printing inks on the surface of bags. All samples contained di(2-ethylhexyl)adipate and its concentrations ranged from 0.19 to 1.01 × 10⁵ mg kg⁻¹. di(2-Ethylhexyl)adipate was frequently found in plastic bags. di(2-Ethylhexyl)adipate was found in both two metal can samples probably due to the inside coating. Benzophenone was detected from printing ink on the surface

of some samples and its content ranged 0.020 to 0.065 mg kg⁻¹. Aniline content ranged from 0.020 to 0.27 mg kg⁻¹. *bis*-(4-Aminophenyl) methane was found only in one plastic composite sample (plastic composite bag 1).

Selection of extraction solvent: Four solvents including hexane, ethyl acetate, acetonitrile and dichloromethane were compared to assess their extraction efficiency. The experiments were carried out on plastic composite bag 1 and the results are shown in Fig. 3. The extraction amount of di(2-ethylhexyl) adipate from plastic composite bag 1 with four solvents was analyzed by kruskal-wallis (K-W) test, which belong to non

TABLE-4
LIMIT OF DETECTION S OF 20 CHEMICALS BY CALCULATION AND ACTUAL MEASURED

Standards type	Chemical name	Different concentration for LOD ($\mu\text{g L}^{-1}$) calculation				Actual measured
		1000 $\mu\text{g L}^{-1}$	100 $\mu\text{g L}^{-1}$	50 $\mu\text{g L}^{-1}$	10 $\mu\text{g L}^{-1}$	
Photoinitiator	Benzophenone	0.024	0.025	0.033	0.20	0.30
	4-Methyl benzophenone	0.042	0.058	0.059	0.70	2.00
	Ethyl-4-dimethylaminobenzoate	0.06	0.066	0.068	0.33	0.50
	1-Hydroxycyclohexyl-phenylketone	0.061	0.074	0.080	0.58	1.00
	2-Ethyl hexyl-4-dimethylamino-benzoate	0.051	0.054	0.059	0.80	1.00
Plasticizer	Di(2-ethylhexyl) adipate	0.18	0.25	0.49	1.02	2.00
	Diisobutyl adipate	0.090	0.099	0.13	0.69	1.00
	Diethyl adipate	0.11	0.23	0.36	0.71	2.00
	Dibutyl adipate	0.20	0.33	0.48	2.61	5.00
	Dinonyl adipate	0.33	1.22	1.68	2.75	5.00
	bis(1-Butylpentyl) adipate	0.30	1.73	2.79	3.01	5.00
Primary aromatic amines	4-Aminoazobenzene	0.076	0.074	0.1	0.64	1.00
	<i>o</i> -Anisidine	0.056	0.074	0.082	0.32	0.50
	<i>o</i> -Toluidine	0.022	0.026	0.033	0.17	0.30
	Aniline	0.014	0.023	0.027	0.15	0.30
	4-Aminobiphenyl	0.044	0.050	0.068	0.39	0.50
	3,3'-Dichlorobenzidine	0.078	0.093	0.12	0.59	1.00
	4-Amino-2',3-dimethylazobenzene	0.064	0.063	0.095	0.87	2.00
	4-Chloroaniline	0.039	0.041	0.076	0.13	0.30
	bis-(4-Aminophenyl) methane	0.21	0.16	0.23	0.82	2.00

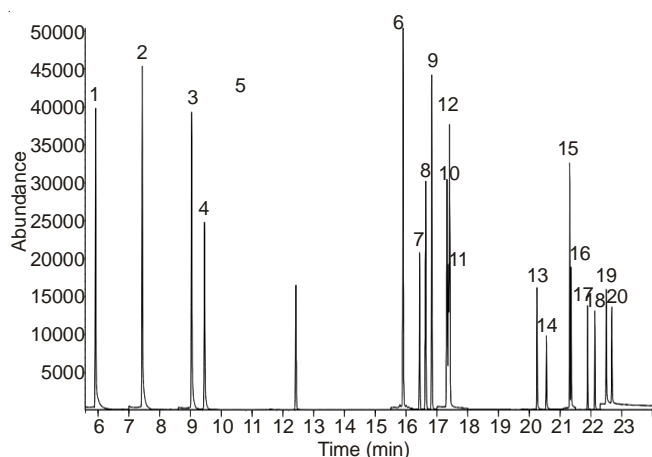


Fig. 2. GC-MS chromatogram of 20 studied compounds with each concentration of $100 \mu\text{g L}^{-1}$; (1) aniline; (2) *o*-toluidine; (3) *o*-anisidine; (4) 4-chloroaniline; (5) diethyl adipate; (6) benzophenone; (7) diisobutyl adipate; (8) 1-hydroxycyclohexyl-phenylketone; (9) ethyl-4-dimethyl aminobenzoate; (10) 4-aminoazobenzene; (11) dibutyl adipate; (12) 4-methyl benzophenone; (13) 4-aminoazobenzene; (14) bis-(4-aminophenyl) methane; (15) 2-ethylhexyl-4-dimethyl-amino-benzoate; (16) 4-amino-2',3-dimethyl-azobenzene; (17) di(2-ethylhexyl) adipate; (18) bis(1-butylpentyl) adipate; (19) 3,3'-dichlorobenzidine; (20) dinonyl adipate

parametric test at a 95 % confidence level. The heterogeneity of variance might be explained by the poor reproducibility of dichloromethane, which was caused by the low boiling point and strong polarity of dichloromethane. The extraction efficiencies of acetonitrile, ethyl acetate and dichloromethane were similar ($p = 0.733 > 0.05$ for these three solvents by K-W test) and they were apparently higher than that of hexane ($p = 0.035 < 0.05$ for these four solvents by K-W test). Because acetonitrile has puny matrix effect for GC-MS than other solvents, it was chosen as extraction solvent.

Effect of volume of solvent: Different volumes of acetonitrile (20×1 , 20×2 and 20×3 mL) were performed to obtain the optimal effect, which is less solvent and less pollution.

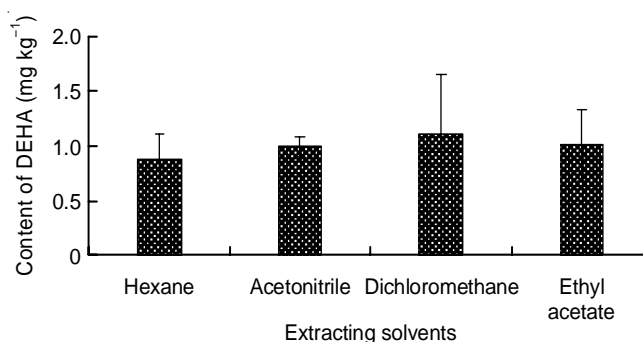


Fig. 3. Effect of different solvents on extraction of plastic composite bag 1 ($n=3$)

The experiments were carried out on plastic composite bag 1 and the results are shown in Fig. 4. The result showed that the 20×2 mL acetonitrile was effective enough to extract the compounds.

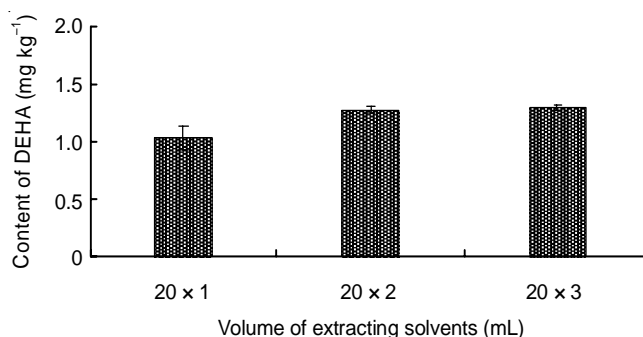


Fig. 4. Effect of extraction volume of acetonitrile on extraction of plastic composite bag 1 ($n=3$)

Matrix effect: Matrix effect was investigated by comparing the responses of the standards in pure solution with three matrices (the standards were spiked onto the food contact materials), which included plastic composite bag 1, poly vinyl

TABLE-5
 CONTENTS OF 5 PHOTOINITIATORS, 6 PLASTICIZERS AND 9 PRIMARY AROMATIC AMINES IN 4 PLASTIC COMPOSITE BAGS, 1 POLYVINYL CHLORIDE FILM AND 2 METAL CANS (n=3)

Standards type	Chemical name	Sample (mg kg ⁻¹ ±SD)					
		Plastic composite 1	Plastic composite 2	Plastic composite 3	Polyvinyl chloride film	Metal can 1	Metal can 2
Photoinitiator	Benzophenone	0.065±0.01	-	0.009±0.004	ND	0.020±0.002	0.018±0.001
	4-Methylbenzophenone	ND	ND	ND	ND	ND	ND
	Ethyl-4-dimethylaminobenzoate	ND	ND	ND	ND	ND	ND
	1-Hydroxycyclohexyl-phenylketone	ND	ND	ND	ND	ND	ND
	2-Ethylhexyl-4-dimethylamino-benzoate	ND	ND	ND	ND	ND	ND
Plasticizer	Di(2-ethylhexyl) adipate	1.28±0.03	0.62±0.25	54.58±2.25	1.01±0.10(×10 ⁵)	0.39±0.05	0.12±0.01
	Diisobutyl adipate	ND	ND	ND	ND	ND	ND
	Diethyl adipate	ND	ND	ND	ND	ND	ND
	Dibutyl adipate	ND	ND	ND	ND	ND	ND
	Dinonyl adipate	ND	ND	ND	ND	ND	ND
	<i>bis</i> (1-Butylpentyl) adipate	ND	ND	ND	ND	ND	ND
	4-Aminoazobenzene	ND	ND	ND	ND	ND	ND
	<i>o</i> -Anisidine	ND	ND	ND	ND	ND	ND
	<i>o</i> -Toluidine	-	0.12±0.01	ND	ND	ND	ND
	Aniline	-	0.27±0.01	0.051±0.01	ND	0.023±0.002	0.020±0.0005
Primary aromatic amines	4-Aminobiphenyl	ND	ND	ND	ND	ND	ND
	3,3'-Dichlorobenzidine	ND	ND	ND	ND	ND	ND
	4-Amino-2',3-dimethylazobenzene	ND	ND	ND	ND	ND	ND
	4-Chloro aniline	ND	ND	ND	ND	ND	ND
	<i>bis</i> -(4-Aminophenyl) methane	0.35±0.15	ND	ND	ND	ND	ND

ND: No detection: Have detection but lower than limit of quantitation of this method

chloride film and metal can 1. The responses of benzophenone, 4-methyl benzophenone, di(2-ethylhexyl)adipate, diisobutyl adipate, 4-aminoazobenzene and *bis*-(4-aminophenyl) methane in the pure solution and the matrix were shown in Fig. 5. Analysis of variance and multiple comparison were performed on the responses of compounds in 4 matrices at a 95% confidence level. Results indicated that this method is free from matrix interferences for benzophenone, 4-methyl benzophenone, di(2-ethylhexyl)adipate and diisobutyl adipate ($p = 0.240$, $p = 0.652$, $p = 0.175$ and $p = 0.205$ for benzophenone, 4-methyl benzophenone, di(2-ethylhexyl)adipate and diisobutyl adipate, respectively). However, the plastic composite bag 1 and metal can 1 slightly weakened the response of 4-aminoazobenzene ($p = 0.003 < 0.05$ for pure solution and plastic composite bag 1, $p = 0.000 < 0.05$ for pure solution and metal can 1) and the metal can 1 slightly weakened the response of *bis*-(4-aminophenyl) methane ($p = 0.019 < 0.05$ for pure solution and metal can 1).

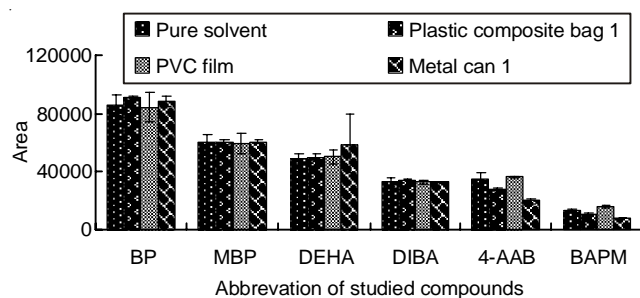


Fig. 5. Effect of different matrices on determination of 6 compounds (n=3)

Calculated limit of detections and measured limit of detections: The limit of detection was inspected by calculation from different concentrations (1000, 100, 50 and 10 $\mu\text{g L}^{-1}$),

actual measured (Table-4). The following formula was used to calculate the limit of detection of the compound:

$$\text{Limit of detections} = \frac{3c}{S/N_c}$$

where c is the concentration ($\mu\text{g L}^{-1}$) of the compound; S/N_c is the signal-to-noise ratio at the corresponding concentration.

The limit of detections of method were also determined by spiking lower and lower amounts until a S/N of 3 was observed. The result indicated that many of the limit of detections measured from the lower concentration were different from the limit of detections calculated from higher concentration of analytes.

Conclusion

An efficient GC-MS method coupled with ultrasonic extraction was developed and validated in terms of recoveries (51-116%), RSDs (1-19%). The limits of detection of method ranged from 0.80-10 $\mu\text{g kg}^{-1}$. Five of 20 compounds in six food contact materials were detected. In conclusion, this method is an excellent choice for the identification and quantification of photoinitiators, plasticizers and primary aromatic amines in food contact materials. It can also be used to determine the studied 20 compounds migrating from food contact materials to food simulants due to its low limit of detections.

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