The Analysis of Organic Contaminants in Printing Paper Food Packaging Materials

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Abstract: A survey of 13 printed paper materials intend for food contact and 1 hand sheet sample made of wood pulp in laboratory has been undertaken. Extracted with hexane by Accelerated Solvent Extraction (ASE) with sequential analysis by Gas Chromatography Mass Spectrum（GC-MS）to identify organic compounds in the samples. It shows that there are a mount of organic contaminants，such as alkanes, alkylbenzenes, esters, especially the phthalates, phenols antioxidant, ketones, alcohols, naphthalene, alkenes and so on. In this paper, kinds of compounds with a potential to migrate to foods were quantified, such as Dibutylphthalate (DBP), 1, 2-Benzenedicarboxylic acid-bis (2-methylpropyl) ester (DiBP), Di-(2-ethylhexyl)-phthalate (DEHP), 1, 2-diethyl- Benzene and so on. For comparative purpose, 4 corresponding blank samples which were not printed were analyzed as described above. Results show that contents of selected compounds in the printed ones are higher than the blank ones. Therefore, 8 types of printing inks which used for the printed samples above were tested to make sure the main sources of these compounds. It demonstrates that printing inks are the main sources of the selected compounds that may cause risk to the food safety. Consequently, controlling the quality of printing inks is the best way to ensure the security of paper food packaging materials and the consumers' health.

Keywords: paper food packaging materials; food safety; organic contaminant; Gas Chromatography Mass Spectrum (GC-MS); printing ink

1. Introduction

Stimulated by the energy and the ecology-driven, more and more paper and boards were used for the food packaging materials for the degradable and environment-friendly characteristics. On the other hand, food-packaging regulations require that packaging materials must be safe. Therefore, potential contaminants in the packaging materials must be excluded to ensure the safety-in-use of food packaging, especially for food direct packaging. The safety and quality of food contact plastic materials has been studied extensively for several decades and are controlled in Europe through overall migration limits which set the upper boundary for mass transfer [1], whereas extensive research into fiber-based food contact materials has been conducted only for the last decade, and also results showed that there were many types of organic contaminants with potential to migrate into packaged food [2-7]. However, there have been few reports about sources of these compounds in the paper-based packaging materials [8].

The work reported in this paper will determine and quantify the selected compounds that may cause potential risk to food safety and consumer health in 13 types of printed food contact paper materials, and also 4 corresponding blank ones and 1 hand sheet. Later, 8 kinds of printing inks which were applied for the printed samples above were analyzed in more details to make sure whether the selected compounds originated from them or not.

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2. Experimental

2.1. Materials and Samples

Hexane was analytical reagent grade and was purchased from Kelong (Chengdu, China). Sea sand (0.65-0.85mm) was purchased from the company of Guoyao Group chemical reagent (China) and EPA matrix spike (in hexane, 2000 mg. L^{-1}) from Supelco Company (America) including Dimethylphthalate (DMP), Diethylphthalate (DEP), DBP, Butylphenylphthalate (BBP), DEHP and Dioctylphthalate (DNOP).

The details of the ink samples in this study are listed in **Table 1**, and they were supplied by two big different printing ink factories in China. P1was the hand sheet made of wood pulp in the laboratory, P2-P12 and p13-p18 were printed by Ⅱ inks and Ⅰ inks respectively. Paper food packaging materials were supplied by the factories A, B and C respectively.

2.2. Preparation of Samples

For the paper samples, the printed parts were cut into small pieces about 0.5cm×0.5cm and then put into aluminum foil bags for the next extraction tests.

According to the national standard <The methods for the determination of heavy metals-Pb, Hg, Cd and Cr, Part Ⅱ>, a mount of ink samples were coated to the watch glasses, after desiccated in oven, the dried inks were scraped off and crumbled, then they were put into aluminum foil bags for the next step.

Table1. Details of ink samples in the test

NO.	Properties	Color	Explanatory comment
Ⅰ	Air drying and Water-based ink	YMCK[a]	Use in offset and relief printing process for food packaging paper
Ⅱ	UV cured and Water-based ink	YMCK	Use in offset and relief printing process for food packaging paper

a. Y-Yellow, M-Magenta, C-Cyan, K-Black

2.3. ASE Extraction and GC-MS analysis

5g paper (0.5g ink) samples and a certain mount of sea sand were put into extraction pools with the volume of 66mL (34mL), mixed intensively, extracted with hexane by Accelerated Solvent Extraction (ASE 300，Dionex company, America), and then the extracts were concentrated with rotary evaporator(RE-52AA, Shanghai Yarong, China) to 1mL to analyze with GC-MS(DB-5MS and Trace DSQ respectively, Electron Thermo Company) using full scanning.

Injections of 1μL were made splitless mode at 250℃ and helium was used as carrier gas (flow rate 1mL/min). The initial column temperature was 80℃, then raised at 5℃/min to 220℃, and finally programmed at 10℃/min to 280℃ (held for 2 min). The mass spectrometer used electron ionization at 70 eV. The source temperature was 230℃ and the scanning range was 30-450amu (atomic mass units).

3. Results and Discussion

3.1. Calibration Graphs and Precision

The calibration graphs were plotted under the optimum conditions of GC-MS. Details about it are given in **Table 2**.

3.2. Identification and quantification of substances in paper samples

Compositional analysis screens for potentially hazardous substances thought likely to migrate into food. As we all know, the higher content, the more likely that the substance will migrate into food. Most of the chromatographic peaks from the extracts could not be identified from the commercial mass spectra library. However, the exact identification of the substances was not essential at this stage. Here in this paper, the substances in extracts with large peak areas were analyzed and this approach significantly reduced the number of unknown peaks that had to be identified.

Table2. Regression equations for the calibration graphs and their correlation coefficients

Compositions in the standard solution	Retain time /min	Regression equation	correlation coefficients (R^2)
DMP	14.16	Y=171151X+279712	0.9995
DEP	17.12	Y=690198X-1E+07	0.995
DBP	24.32	Y=1E+06X-2E+07	0.9945
BBP	30.68	Y=9277.6X-140293	0.9989
DEHP	32.10	Y=7235.1X-17255	0.9968
DNOP	33.74	Y=34668X-464553	0.9983

From the chromatographic of P1, it can be found that there is no evidence peak at all. This can be confirmed by the fact that it is the hand sheet that made in laboratory without anything that can cause pollution. For other samples, the hydrocarbons were identified in all the samples, such as alkanes, ketones, alcohols, alkenes and so on, including printed and unprinted ones. Furthermore, some alkylbenzenes which can do harm to consumer health were tested in most of samples, for instance 1,2-diethyl- Benzene was identified in P4-P9, P11, P12, P16 and P18, hexadcylbenzene was found in P2. It was also known that alkylbenzenes can deteriorate the foodstuffs and do harm to hematological system. Moreover, esters were identified in most of the samples, especially for DBP, it can be found in all the samples, except for P1, and the peak area of it is very large also. For DIBP and DEHP, they can be tested in part of the samples, such as in all the samples except for P1, P5, P6 and P10 there are a mount of DiBP, and there are some DEHP in P2, P3, P11, P12, P13, P14 and P16. Phthalate is one of the most important plasticizers. It may cause risk to environment and people's health, and nowadays there have been a lot of studies about the migration of it to foodstuffs [9-12]. In addition to these, another compounds found in the samples was identified as aromatic hydrocarbons, such as 2, 4-bis (1,1-dimethylethyl)-Phenol , 1,6-dimethyl-4-(1-methylethyl)- Naphthalene and 2,3-dimethyl –naphthalene.

The contents of these substances were estimated by comparing their peak areas with the internal standards' peak areas. 17 out of the 18 samples studied had phthalates been identified, **Table 3**. The most common phthalates were DBP and DIBP. In addition, DEHP was found in 7 samples and had an exceptionally high content.

Aromatic hydrocarbons were found in 13 out of 18 samples, **Table 3**. The main Aromatic hydrocarbons identified in the paper samples were 2, 4-bis (1, 1-dimethylethyl) - Phenol and 1, 6-dimethyl-4-(1-methylethyl) - Naphthalene though the contents of them were not so high.

Alkylbenzenes were identified in 10 of the samples, **Table 3**. There were only traces of alkylbenzenes in the paper samples, but 3 samples had high levels of 1, 2-diethyl- Benzene. Meanwhile, 1-chloro-octadecane was found in 5 samples.

From the results described above, it demonstrates that the contents of the selected organic contaminants in the samples are all very small or can be negligible for the packaging itself, except for DEHP which has been found in P2, P3 and P11 are 2567.43 $mg.Kg^{-1}$, 2291.65 $mg.Kg^{-1}$ and 2986.32 $mg.Kg^{-1}$ respectively, while the trace of the substances can cause risk to the environment, safety of food and consumer health. So it is very important to find out the possible sources of these organic contaminants and control them.

3.3. Analysis of sources of the selected compounds in paper samples

Except for P1, numerous of volatiles have been identified in the paper samples, such as alkanes, alkenes, aldehydes, esters, alcohols, ketones and so on. The contents of them in the total are about 7.7%-98.08%. It was reported that they were largely oxidation products derived from unsaturated fatty acids present in wood pitch [13]. In addition, Soderhjelm, L et al [14] identified several aldehydes in paperboard which were assumed to be oxidation and degradation substances of lipids originating from printing inks, varnishes and additives used in the production of the board. For others which we identified in this study are phthalates, such as DBP, DIBP, DEHP and so on, 2,4-bis(1,1-dimethylethyl)- Phenol and 1,6-dimethyl-4-(1-methylethyl)- Naphthalene.

Table 3. Contents of organic contaminants in the tested paper samples（$mg.Kg^{-1}$）

NO.	Contents ($mg.Kg^{-1}$)						
	DBP	***DIBP***	***DEHP***	***1,2-diethyl-Benzene***	***2,4-bis(1,1-dimethylethyl)-Phenol***	***1,6-dimethyl-4-(1-methylethyl)-Naphthalene***	***1-chloro-octadecane***
P1	×	×	×	×	×	×	×
P2	41.07	21.49	2567.43	×	28.92	6.92	×
P3	28.54	15.40	2291.65	×	24.30	5.56	×
P4	7.60	6.59	×	6.10	7.28	12.02	×
P5	4.68	×	×	204.00	42.22	×	×
P6	31.33	×	×	76.79	34.79	×	×
P7	39.74	32.48	×	129.39	50.24	52.57	×
P8	28.67	26.51	×	50.89	×	×	×
P9	33.25	30.30	×	104.72	40.32	×	×
P10	26.04	×	×	×	×	×	×
P11	69.44	41.82	2986.32	32.56	78.49	×	30.77
P12	11.05	7.65	735.52	11.43	17.67	×	×
P13	44.49	29.26	243.38	×	12.76	×	6.07
P14	55.55	34.73	218.10	×	13.28	×	9.04
P15	25.21	16.70	×	×	11.92	×	5.19
P16	31.59	25.36	204.74	10.77	18.31	13.58	6.05
P17	58.10	36.53	×	×	×	41.04	×
P18	28.83	17.26	×	23.36	×	19.28	×

×: not analyzed or below the limitation of detection

For the paper samples used in this study are collected form manufactures directly, it is not known whether the processes of transportation, storage, downstream processing and printing processing of the samples will draw into the contaminants. However, printing inks of Ⅰand Ⅱwhich were used to print the paper samples have been analyzed to make sure if these contaminants originated from them.

From the results of analyses to printing inks, it shows that there are amount of volatiles in them, such as alkanes, ketones, aldehydes, alcohols and ethers, especially 2-(2-butoxyethoxy)-ethanol, and it is coincide with the report of Soderhjelm, L. and his partners [14]. But there are no ethers have been identified in the printed paper samples. It may be due to the fact that the strong volatility of ethers and they may loss in the processes of drying, transportation and storage of printed productions.

Phthalates are the important ingredients of plasticizers which used in printing inks to soften the ink film. DIBP was found in 4 printing inks of Ⅱand DBP was identified in all the printing inks except for K-Ⅰ. This is confirmed by the fact that ink film of K-Ⅰ is hard and crisp. Meanwhile, 1, 2, 3, 4-tetrahydro-1-phenyl-naphthalene and 2, 4-bis (1, 1-dimethylethyl)-phenol which thought to be hazardous to health and environment were identified in most of the printing ink samples. The contents of these substances are shown in **Fig.1**. As described in **Fig.1**, the contents of these substances in inks Ⅰare higher than in inks Ⅱ. Compare printed paper samples with unprinted ones (**Table 3**), P2 and P3, P4 and P5,

P11 and P12, it reveals that the contents of selected compounds in the printed ones are all higher than the unprinted ones, except for 1,2-diethyl- Benzene and 2,4-bis(1,1-dimethylethyl)- Phenol in P5.

Above all, part of the selected organic contaminants in printed paper samples, such as DBP, DIBP and alkylbenzenes, are come from the printing inks, also it is coincide with the discoveries before bell [5, 15-16]. For other parts of these substances, they may be originated from the process of paper making, transportation, storage and downstream processing *et al*.

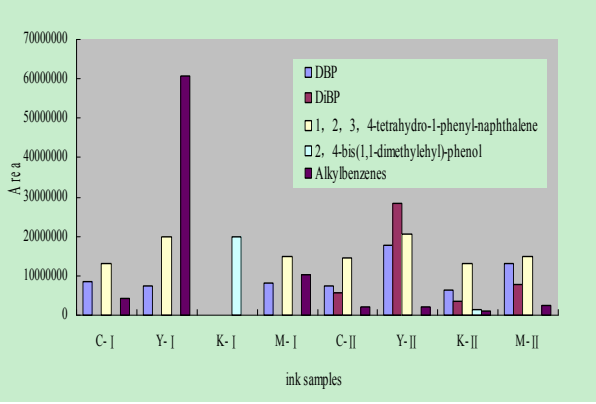

Figure1. Contents of organic contaminants in the ink samples

4. Conclusions

There are kinds of organic contaminants, such as phthalates, aromatic hydrocarbons and alkylbenzenes, in the studied paper food packaging materials which can be risk to food and consumer health. From the comparative results, it shows that the contents of these substances in the printed samples are higher than the unprinted ones. To make sure whether these substances come from the printing inks that used in printing processes or not, 8 kinds of printing inks which supplied by manufactures were analyzed. It turns out that there are some types of these organic contaminants in the printing inks. However, for other parts of these organic contaminants may come from the processes of transportation, storage, downstream processing and so on.

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