

Organic Compounds in Paper and Plastic Food Packaging

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Abstract. Additives, printing ink and other chemicals in packaging may influence safety of the food. Standard solutions of eight organic compounds were prepared. By gas chromatography and mass spectrometry technology, benzene, isopropyl alcohol, ethyl acetate, ethyl benzene, cyclohexanone, *m/p*-Xylene, *o*-Xylene and butyl acetate in biscuit paper carton and jujube plastic bag were determined and analyzed. Linear calibration curves of the eight compounds were obtained with correlation coefficients of more than 0.9827, detection limits were in the range of 0.003-0.009 mg/m², recoveries ranged from 84% to 96% with RSD less than 3.8%. The results show that organic compounds in biscuit paper carton and jujube plastic bag are respectively 0.266 mg/m² and 0.37 mg/m². Benzenes in the two packages are respectively 0.167 mg/m² and 0.289 mg/m². Content of benzenes in the gravure printing inks used in the jujube plastic bag is obviously much more than that in the offset printing inks used in the biscuit paper carton.

Introduction

Plastic is polymer material made from synthetic resin monomer as raw material, adding an appropriate amount of stabilizers, plasticizers, antioxidant, coloring, pesticides and preservatives in process [1]. Due to light weight, convenient transportation and sales, good chemical stability, easy processing, good adornment effect and ideal protection effect, plastic packaging materials are widely used in food industry. However, there are some problems in terms of health and safety in food plastic packaging materials. The problems mainly are harmful monomer, oligomers, additives and organic compounds produced in process. These poisonous and harmful chemical pollutants may dissolve and migrate from packaging materials, resulting in contamination of food. Eventually, they may cause harm to people's physical and mental health.

During manufacturing process of paper packaging materials, there are wax, fluorescent whitening agent, sizing agent, organic chloride, curing agent, fungicide, organic solvents and surfactant. These compounds may migrate from materials to food.

There are a lot of harmful solvents such as benzene, toluene, xylene, ethyl acetate, butyl acetate, isopropyl alcohol, *n*-propyl acetate and *n*-butyl acetate in solvent-based printing inks. Among them, benzene solvents may cause greatest harm to human [2,3].

Scholars in domestic and foreign countries have made some researches on harmful compounds in food packaging materials [4-13]. In this paper, a gas chromatography and mass spectrometry method is used to analyze organic compounds in offset printed biscuit paper box and gravure printed jujube plastic bag in order to manufacture safe and reliable food packaging.

Experiment

Sample Preparation

Biscuit paper box, white cardboard, offset printing ink: yellow ink, magenta ink, cyan ink and black ink, fountain solution; jujube plastic bag, polyethylene (PE), polyester (PET), gravure printing ink:

yellow ink, magenta ink and cyan ink, binder. These materials were provided by Xi'an ZhiCheng packaging company. 5 cm×5 cm of packaging materials were clipped in accordance with location of printing pattern, manually cut into strips with dimensions of 5 cm×0.5 cm. Then these strips were put into headspace bottles. About 5 mg of printing ink, fountain solution and binder were put into headspace bottles respectively. The headspace bottles were put into headspace equipment to test.

Chemicals and Standard Solutions

Benzene, isopropyl alcohol, ethyl acetate, ethyl benzene, cyclohexanone, *m/p*-Xylene, butyl acetate and *o*-Xylene, (purity>99%, Tianjin, China) were prepared. Standard solutions of the eight reagents in methyl alcohol at a series density of standard solution (0.01%, 0.02%, 0.04%, 0.05%, 0.06%, 0.08%, 0.1%) were obtained for external calibration.

Equipment and Chromatographic Conditions

Headspace gas chromatography and mass spectrometry system (Clarus 600, PerkinElmer, USA) fitted with TurboMass software was used for experiment and data acquisition.

Balance temperature was 85 °C, balance time was 40 min. Oven temperature was held at 35 °C for 6 min, then raised at 18 °C/min up to 210 °C; carrier gas, He (purity>99.999%) at a constant flow rate of 2.0 mL/min.

MS conditions were as follows: ion source temperature, 210 °C; Interface temperatures, 220 °C. Quality scan range: *m/z* 35-400; ion source voltage, 70eV.

Results and Discussion

Determination of Standard Sample

Standard solutions of 1μL were spiked into headspace bottles to test compound under the experimental conditions. Fig. 1 shows retention time of isopropyl alcohol, ethyl acetate, benzene, butyl acetate, ethyl benzene, *m/p*-xylene, *o*-xylene and cyclohexanone is respectively 1.79 min, 2.51 min, 3.03 min, 6.20 min, 6.86 min, 6.99 min, 7.31 min and 7.39 min. Peak area as vertical coordinate, quantity concentration of compound as horizontal coordinate, regression equations of the eight compounds were calculated. Linear calibration curves of the eight compounds were obtained with correlation coefficients of more than 0.9827, detection limits were in the range of 0.003-0.009 mg/m², recoveries ranged from 84% to 96% with RSD less than 3.8%. The results are shown in Table 1.

Tab. 1 Regression equations, correlation coefficients, detection limits and relative standard deviations of compounds

Compound	Regression equation	Correlation coefficient	Detection limit (mg/m ²)	Recovery (%)	RSD (%)
Isopropyl alcohol	$y=532.45x-784.12$	0.9896	0.004	91	2.5
Ethyl acetate	$y=267.236x-34.56$	0.9937	0.003	89	2.8
Benzene	$y=38.74x-3681.4$	0.9985	0.005	84	2.6
Butyl acetate	$y=86.452x-542.52$	0.9939	0.004	90	2.9
Ethylbenzene	$y=134.257x-236.4$	0.9827	0.006	87	3.8
<i>m/p</i> -Xylene	$y=89.54x-5413.21$	0.9864	0.005	85	3.2
<i>o</i> -Xylene	$y=76.255x-453.9$	0.9853	0.009	94	3.1
Cyclohexane	$y=564.213x-541.8$	0.9961	0.004	96	2.7

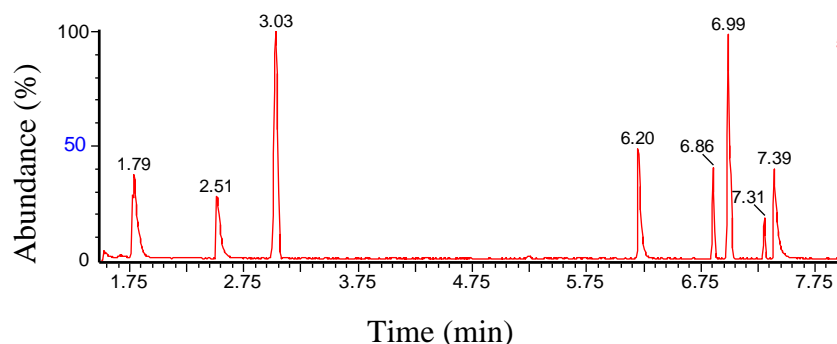


Fig. 1 Chromatogram of standard solution

Organic Compound in Food Packaging and Its Raw Materials

Chromatograms of paper carton and plastic bag are shown in Fig. 2 and Fig. 3. Content of the compounds was calculated by regression equation. The results are shown in Table 2 and Table 3.

Tab.2 Organic compounds in the paper carton and its raw materials

Sample	Isopropyl alcohol	Ethyl acetate	Butyl acetate	Benzene	Ethyl benzene	<i>m/p</i> -Xylene	<i>o</i> -Xylene	Cyclohexanone	Amount
White cardboard (mg/m ²)	0.050	0.047	0.002	0.014	0.045	0.051	0.092	-	0.301
Yellow ink (mg/kg)	11.256	0.112	0.024	0.127	0.320	0.378	0.750	-	12.967
Magenta ink (mg/kg)	3.400	0.080	0.026	0.333	0.233	0.260	0.630	-	4.962
Cyan ink (mg/kg)	10.986	0.290	0.042	1.381	0.769	0.577	2.628	-	16.673
Black ink (mg/kg)	18.490	0.341	0.095	0.372	1.170	1.006	1.974	-	23.448
Fountain solution (mg/kg)	102.237	0.150	0.016	0.073	5.223	1.051	2.441	-	111.191
Paper carton (mg/m ²)	0.055	0.042	0.002	0.011	0.038	0.040	0.078	-	0.266

-: No detected

Table 3 Organic compounds in the jujube plastic bag and its raw materials

Sample	Isopropyl alcohol	Ethyl acetate	Butyl acetate	Benzene	Ethyl benzene	<i>m/p</i> -Xylene	<i>o</i> -Xylene	Cyclohexanone	Amount
PET (mg/m ²)	0.042	0.016	0.002	0.007	0.018	0.019	0.020	-	0.124
PE (mg/m ²)	0.042	0.018	0.002	0.007	0.019	0.022	0.026	-	0.136
Yellow ink (mg/kg)	73.284	1637.451	37.612	35.235	40.746	33.847	77.493	-	1935.668
Magenta ink (mg/kg)	141.271	442.166	8.737	3.254	0.085	205.376	0.067	2531.56	3332.516
Cyan ink (mg/kg)	45.134	0.178	2.163	90.857	0.258	355.240	1348.718	-	1842.548
Binder (mg/kg)	3.411	0.028	0.122	0.017	0.534	0.695	0.860	-	5.667
Plastic bag (mg/m ²)	0.042	0.037	0.002	0.011	0.050	0.056	0.172	-	0.37

-: No detected

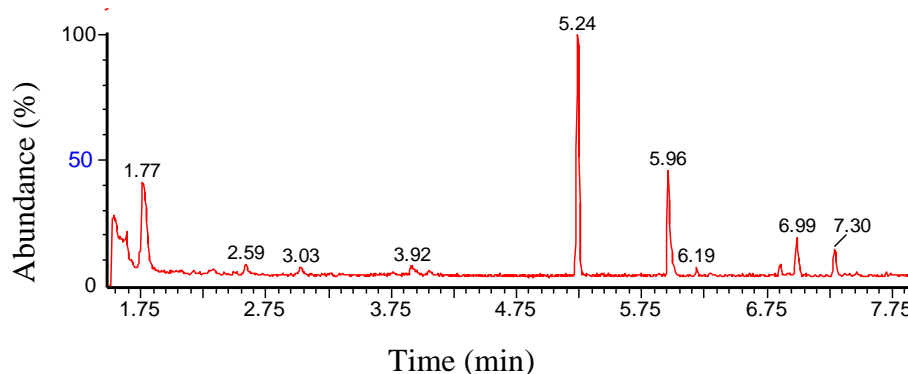


Fig. 2 Chromatogram of paper carton

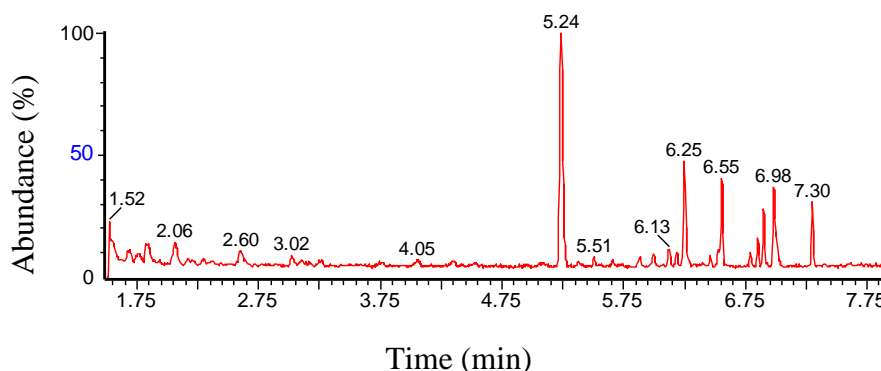


Fig. 3 Chromatogram of plastic bag

Analysis of Organic Compound in Food Packaging

Table 2 and table 3 show organic compounds in biscuit paper carton and jujube plastic bag are spectively 0.266 g/m^2 and 0.37 g/m^2 . Benzenes in the two packages are respectively 0.167 mg/m^2 and 0.289 mg/m^2 . Benzenes in yellow, magenta, cyan and black offset printing ink are respectively 1.575 mg/kg , 1.456 mg/kg , 5.355 mg/kg and 4.522 mg/kg . Benzenes in yellow, magenta and cyan gravure printing ink are respectively 187.321 mg/kg , 208.782 mg/kg and 1795.073 mg/kg . Content of benzenes in gravure printing ink is obviously much more than that in offset printing ink. In addition, white cardboard, PET, PE, fountain solution and binder contain different degree of benzenes.

Ways of Reducing Benzenes in Food Packaging

In paper and plastic packaging, benzenes exist in basic material, printing ink, fountain solution and binder. Therefore, reducing benzenes organic compound mainly lays in the processing of raw materials and improving production process.

Print Packaging with Water-based Ink. There are not volatile organic solvents in water-based ink. So, printing with water-based ink can reduce residual toxicity in the printing products and make printing equipment easy to clean. Moreover, it can reduce fire risk and hazards due to static electricity and flammable solvents. Water-based ink is “green” printing material.

Print Paper Carton by Waterless Offset Printing Technology. Ink and fountain solution in traditional offset printing technology contain various organic solvents. Waterless offset printing technology commonly prints material with soybean oil ink and aromatic-free ink, which have no impact on human and environment. So, waterless offset printing technology, prints with non-solvent-based ink instead of fountain solution, make a great contribution to environment protection.

Print Plastic Bag by Flexible Printing Technology. At present, food packaging in China is mainly printed by gravure technology. Various food packaging bags in supermarket, such as biscuit, pastry and milk powder packages, are basically printed with chlorinated polypropylene ink. While flexible printing is a main method of food packaging in Europe and other countries. Flexible printing is not as good as gravure printing in network performance. But it takes the lead in environment protection. Flexible printing will gradually replace gravure technology in the future development.

Conclusions

Organic compounds in biscuit paper carton, jujube plastic bag and their raw materials have been successfully analyzed by gas chromatography and mass spectrometry technology. Effective methods to reduce benzenes in the food packages have been put forward from the aspect of material and process.

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