Study on the migration of four phthalates from plastic food contact materials to food simulants

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Abstract. The ultra performance convergence chromatography method was developed to detect the migration of four phthalates (PAEs) in plastic food contact materials. Plastic food contact materials samples are immersed with oil-based (isooctane) and water-based simulants (10% ethanol, 4% acetic acid and water), respectively. The pre-treatment method of four kinds of PAEs in the simulated immersion solution was optimized. The relationship between migration behaviour and the simulants, migration temperature and migration time were studied. The results show that PAEs were more likely to migrate in oily simulants. Within a certain range, the migration amount increased with the extension of immersion time. The migration rate and amount enhanced with the temperature.

1. Introduction
With the frequent occurrence of food safety incidents, food safety has attracted more and more attention. The migration of toxic and harmful substances in food contact materials is one of the main causes of food contamination. Phthalate (PAEs) is widely used in plastic food packaging materials because of its ability to enhance the toughness, strength and ductility of plastics and its products [1-3]. PAEs and plastic matrix rely on van der Waals force and hydrogen bond combination [4], in the process of food heating and transportation, it is easy to migrate from plastic food contact materials to food, thus contaminate food and harm human health.

Recent studies have shown that PAEs is a kind of environmental hormone substance, which has endocrine disruptiveness, reproductive toxicity and carcinogenicity[5-8]. Moreover, it not easy to be discharged after ingestion. The potential harm brought to human body cannot be ignored. Therefore, many countries, such as the European Union and the United States, have given priority to the control of pollutants, and many countries have stipulated the amount of PAEs allowed to be used in some plastic food contact materials and specific migration limits. It has great significance to study the migration characteristics of PAEs in plastic food contact materials and the factors affecting migration to evaluate the safety of food contact materials. At present, most studies on PAEs in China focus on the detection of residues in food and the establishment of methods [9-10], and relatively few systematic studies on the migration rule of PAEs.

In view of this, the migration characteristics and migration rules of the four PAEs (DHXP, DNP, DEEP and DHP) in the plastic food contact materials were studied by ultra-high efficiency chromatographic method in this study, so as to provide certain safety guidance for food processing, production, transportation, storage and sales.
2. Experimental and Methods

2.1. Materials and reagents
The standards: dihexyl phthalate (DHXP), diazonyl phthalate (DNP), diethyl phthalate (2-ethoxy), dihexyl phthalate (DHP), were all purchased from Dr. Ehrenstorfer, Germany. N-hexane, ethyl acetate and dichloromethane purchased from Tedia Company, USA. Isooctane, chromatogram pure, purchased from Tianjin Damao Chemical Reagent Factory.

2.2. Instruments and equipment
The experiment was performed on ACQUITY UPC² ultra performance convergence chromatography (Waters, USA). N-EVAP-112 nitrogen blower (Organomation, USA) was used for the concentration of target compounds. BILON-2000CT ultrasonic cleaner (Bilang, Shanghai) and BSXT-06 soxhlet extractor (Lanyi, Shanghai) were used in the preprocessing.

2.3. Methods

2.3.1 Chromatographic conditions
The separation experiment was used ACQUITY UPC² HSS C18 SB column (150 mm × 30 mm, 1.8 μm) at 65℃. The mobile phase was supercritical CO₂ with a small quantity of acetonitrile. The detection wavelength was optimized at 220 nm. The best back pressure was 12.41 MPa and the injection volume was 5 μL. Mobile phase elution gradient: 0-1 min, 3%-4.5%B, flow rate: 1.5-1.2 mL/min; 1-2.5 min, 4.5%-B, flow rate: 1.0 mL/min; 2.5-3.5 min, 4.5%-15% B, flow rate: 1.0-1.5 mL/min; 3.5-4.5 min, 15%-20% B, 4.5-5 min, 20%-25% B, 5-6 min, 25%-3%B, the flow rate was always 1.3 mL/min.

2.3.2 Migration experiment
According to the requirements of GB 31604.1 -- 2015 "General Rules for The Migration Test of Food Contact Materials and Products", 2 mL simulated liquid was added to each square centimeter of food contact materials, and corresponding simulated liquid was added to the samples to carry out the migration experiment under specific conditions.

Water-based simulants: 10 mL water-based food simulators (10% ethanol, 4% acetic acid, water) were removed into the sorting funnel, respectively, then dichloromethane, ethyl acetate and n-hexane were added for extraction twice and combined with organic phase. Nitrogen was blown to near-dry at 45℃, and then constant volume to 1 mL with n-hexane and filtered through an organic membrane of 0.22 μm for UPC² analysis.

Oil simulants: 10 mL isoctane was removed into a test tube and blown to near-dry by nitrogen at 45℃. A 0.22 μm organic filter membrane was used for UPC² analysis after constant volume of n-hexane to 1 mL.

3. Results and Discussion

3.1. The effects of simulants on phthalate migration
In this study, isoctane, 10% ethanol, 4% acetic acid and water were selected to simulate fatty, alcoholic, acidic and water-based foods respectively, and the effects of different simulants on the migration of phthalates were studied. At 40℃, the plastic food contact material samples were immersed in four simulants for 24 h. Experimental results (Figure 1) show that under the same migration temperature and migration time, food contact materials in the four kinds of phthalic acid esters in 4 kinds of simulation of the overall trend of migration of isoctane > 10% ethanol > 4% acetic acid > water. Therefore, plastic packaging materials containing phthalates are not recommended for fatty and alcoholic foods.
3.2. The effect of temperature on migration amount of bisphenols
Since PAEs have the highest migration risk in isooctane, this study selected isooctane as the food simulant, and the contact time was 24 h. The migration of four phthalates in the isooctane simulant was investigated at 0-80℃. As can be seen from Figure 2, with the increase of temperature, the migration of phthalates also increases. When the temperature is lower than 30℃, the migration amount is relatively small and the migration rate does not change much. When the temperature is 30-60℃, the migration amount of phthalate increases significantly and the migration rate speeds up. When the temperature exceeds 60℃, the migration amount in the simulation slows down and gradually tends to balance. Therefore, it is not recommended to heat plastic packaging materials with phthalates directly or serve hot food.

3.3. The effect of time on migration amount of bisphenols
In order to explore the migration of phthalates of plastic food contact materials under different immersion times, the samples were immersed at 40℃ for 2, 4, 6, 8, 12, 24, 36 and 48 h, respectively. As shown in Figure 3, at the same temperature, the longer the immersion time is, the larger the migration of phthalate increases significantly and the migration rate speeds up. When the temperature exceeds 60℃, the migration amount in the simulation slows down and gradually tends to balance. Therefore, it is not recommended to heat plastic packaging materials with phthalates directly or serve hot food.
Figure 3. The effect of migration time on migration amount of 4 kinds of PAEs

4. Conclusions
In this study, an ultra performance convergence chromatography method was established for the determination of four PAEs in food contact materials. The experimental results show that the extraction efficiency of n-hexane is better than that of dichloromethane and ethyl acetate. Experiment results indicate that PAEs occur more easily in the oily food simulant, within a certain range, the migration rate increase with the temperature. Moreover, the migration amount enhance with the migration time.

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