Study on Detection and Perniciousness of Migrating Plasticizer in Food Packaging of Roadside Stalls

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Abstract: This article focuses on the roadside stall foods that people eat in daily life as the research object, and concludes the plasticizer migration rules and characterization methods in food contact materials. We changed the experimental methods of existing food simulants and adopted real foods. Various types of foods were extracted and purified and detected by gas chromatography-mass spectrometry to obtain data on the migration amount of plasticizers in roadside food plastic packaging. At the same time, the relationship between the level of migration and the chemical composition of packaging materials, food categories, contact time, and exposure temperature was obtained. The work intends to alert people to pay attention to unhealthy habits in daily life, and to propose a series of feasible recommendations to keep people away from the hazards of plasticizers.

Keywords: Roadside Stall Food, Plasticizer, Migration, Hazard

1. Introduction

Food toxicity of adhesives, printing inks, and other substances in plastic packaging materials has been studied previously. Modification of the properties of plastic packaging materials requires the addition of processing additives, these additives and their degradation products are harmful to the human body and cause food safety problems through migration. Among these additives, the most widely used and most toxic are plasticizers. The use of disposable plastic bags, plastic lunch boxes, and plastic cups from roadside stalls increases the risk of food being transported by plasticizers, and will cause hidden dangers to people's food safety. In this study, a total of 26 batches of samples were collected in Baoding, including disposable plastic bags, plastic lunch boxes, and plastic straws. With reference to the test method of GB/T 21928-2008, the common content of PAEs in 26 samples was detected, and the migration risk of PAEs plasticizers was tested.

2. Materials and Methods

2.1. Sample Source

A total of 26 experimental samples were randomly collected from plastic packaging for snacks in Baoding Street, including lunch boxes, plastic cups, and plastic bags.

2.2. Experimental Instruments

7890A Gas Chromatograph and 5975C Mass Spectrometer (Agilent, USA), Rotary Evaporator (BUCHI, Switzerland), XS205 Electronic Balance (Metter Toled, Germany), SK3310HP Ultrasonic Generator (Shanghai Kudos Ultrasonic Instrument Co., Ltd.) Adjustable pipette (RAININ, USA), Water Purifier (Milipore, USA).

2.3. Reagents

5 kinds of PAEs mixed standard solution (each concentration is 1000mg/L), n-hexane as solvent, including dibutyl phthalate (DBP), dihexyl(2-ethyl) phthalate (DEHP),
disobutyl phthalate (DIBP), dimethyl phthalate (DMP), and diethyl phthalate (DEP) were purchased from the American company o2si smart solutions; n-hexane (chromatographically pure) was purchased from the German GmbH company.

2.4. Experimental Protocol

2.4.1. Sampling for Content Testing and Sample Preparation

For samples with uniform material, such as transparent plastic fast food bowls, two separate samples can be randomly sampled; for non-uniform samples, such as composite cups, four separate samples can be randomly taken for sample preparation. Two of them are used for the overall test and two are used for the single-sided film extraction test (single-sided film refers to a plastic material layer that may contain a plasticizer). For sample preparation, samples less than 0.5 mm in thickness, such as disposable gloves, specimens are cut into pieces of less than 0.5 mm x 0.5 mm and mixed and weighed for pretreatment. For samples with a thickness greater than 0.5 mm and hard samples, such as rigid plastic spoons, they should be ground to single particles ≤ 0.02 g. After mixing and weighing, the samples are pretreated.

2.4.2. Sample Pretreatment for Content Testing

According to the pretreatment method of samples in GB/T 21928-2008, PAEs plasticizers in fast food and breakfast packaging were extracted. In order to improve the accuracy of the experiment, the pretreatment method in the standard was improved. The specific process was as follows: Accurately weigh 1.0 g of the prepared sample in a triangle bottle, add 25 ml of n-hexane, extract ultrasonically for 30 min, and filter through the filter paper. The above extraction process was repeated twice. The extracts were merged in a 100 ml rotary evaporation bottle. After evaporating to dryness on a rotary evaporator, n-hexane was added to a volume of 2 ml and was tested. If the solution is turbid after adding n-hexane, a syringe filter with a 0.22µm organic filter can be used before testing. In the experiment, the sample with a large phthalate content should be appropriately diluted before testing. The same method was used for the blank control test and the tests should be done under the same test conditions.

2.4.3. Selection of Migration Conditions and Migration Test

In view of that disposable fast food boxes and breakfast packaging contact with the food, namely hot packaging, storage at room temperature, and within a short time, but the food types are complex and most of them contain oils and fats. The migration test was based on GB/T 23296.1-2009. The harsh conditions of 100°C and 1 h were selected to simulate the contact situations of foods within the packaging. In the experiment, o-octane was used instead of vegetable oil for migration tests to investigate the risk of PAEs migration in samples. The test conditions were 60°C for 1 h. In the experiment, the samples with PAEs were selected, and soaked using the filling method. The iso-octane was heated to 60°C by a water bath. A certain volume takenby measuring cylinder was filled into the sample and sealed with cling film. (In the experiment, the cling film should avoid to contact with the soaking solution). After putting in a constant temperature oven at 60°C for 1 h, mix the soaking solution with a glass rod, and take the solution for testing. If the soaking solution is turbid, it needs to be filtered with a syringe filter before testing.

2.4.4. Detection Method

The gas chromatography-mass spectrometry method was used to quantify the PAEs in the collected samples. According to the chromatographic and mass spectrometric detection conditions in GB/T 21928-2008. In order to increase the accuracy of quantiative determination, two standard curves were established in the experiment. The high concentration standard curve was established with reference to the standard curve in GB/T 21928-2008, i.e. 0.5, 1.0, 2.0, 4.0, and 8.0 mg/L; the low concentration standard curve, i.e. 0.2, 0.4, 0.6, 0.8, 1.0 mg/L, was used for quantification of PAEs in low-level samples.

2.4.5. Control of Blank Background

PAEs plasticizers have a relatively high boiling point and are difficult to evaporate at room temperature. In order to reduce the errors caused by residual PAEs in glass instruments during the pretreatment process, blank values in the experiments are controlled. Refer to the standard method of SN/T2037-2007 for glassware treatment, after the glassware was washed, it was rinsed with ultrapure water three times, then soaked in acetone for 30 minutes, and finally baked at 200°C for 2 hours. Ready after cooling.

3. Results and Discussion

Based on the experiments, five commonly used plasticizers in the foods from roadside stalls were tested, and the migration of plasticizers in food packaging was obtained.

| temperature(°C) | Soybean Milk | water |
|-----------------|--------------|-------|
| DMP             | 0.01223      | 0.01310 |
| DEP             | 0.01802      | 0.02035 |
| DIBP            | 0.03760      | 0.00780 |
| DBP             | 0.01575      | 0.03560 |
| DEHP            | 0.02339      | 0.00780 |

Table 1. Migration of plasticizers at different temperatures of different foods (mg/kg).

In view of that disposable fast food boxes and breakfast packaging contact with the food, namely hot packaging, storage at room temperature, and within a short time, but the food types are complex and most of them contain oils and fats. The migration test was based on GB/T 23296.1-2009. The harsh conditions of 100°C and 1 h were selected to simulate the contact situations of foods within the packaging. In the experiment, o-octane was used instead of vegetable oil for migration tests to investigate the risk of PAEs migration in samples. The test conditions were 60°C for 1 h. In the experiment, the samples with PAEs were selected, and soaked using the filling method. The iso-octane was heated to 60°C by a water bath. A certain volume takenby measuring cylinder was filled into the sample and sealed with cling film. (In the experiment, the cling film should avoid to contact with the soaking solution). After putting in a constant temperature oven at 60°C for 1 h, mix the soaking solution with a glass rod, and take the solution for testing. If the soaking solution is turbid, it needs to be filtered with a syringe filter before testing.

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3. Results and Discussion

Based on the experiments, five commonly used plasticizers in the foods from roadside stalls were tested, and the migration of plasticizers in food packaging was obtained.

| temperature(°C) | Soybean Milk | water |
|-----------------|--------------|-------|
| DMP             | 0.01223      | 0.01310 |
| DEP             | 0.01802      | 0.02035 |
| DIBP            | 0.03760      | 0.00780 |
| DBP             | 0.01575      | 0.03560 |
| DEHP            | 0.02339      | 0.00780 |

Table 1. Migration of plasticizers at different temperatures of different foods (mg/kg).
| temperature(°C) | DMP      | DEP      | DIBP     | DBP      | DEHP     |
|----------------|----------|----------|----------|----------|----------|
| 40             | 0.00416  | 0.00184  | 0.00223  | 0.00282  | 0.00979  |
|                | 0.00402  | 0.00155  | 0.00590  | 0.00472  | 0.01011  |
| 80             | 0.01462  | 0.00490  | 0.00224  | 0.00317  | 0.00756  |
|                | 0.01377  | 0.00525  | 0.00363  | 0.00677  |          |
| 20             |          |          | 0.04746  | 0.06636  | 0.04761  |
|                |          |          | 0.02593  | 0.03972  | 0.02642  |
| porridge       | 0.00785  | 0.01347  | 0.00949  | 0.00990  | 0.2555   |
|                | 0.00614  | 0.00840  | 0.00819  | 0.00865  | 0.01171  |
|                | 0.005046 | 0.005616 | 0.005326 | 0.05129  | 0.04923  |
| 40             |          |          | 0.05326  | 0.05129  | 0.04923  |
| 80             |          |          | 0.07085  | 0.06947  | 0.07032  |
|                |          |          | 0.07149  | 0.07290  | 0.07214  |
|                | 0.09266  | 0.09248  | 0.11701  |          |          |
|                | 0.09819  | 0.09626  | 0.12011  |          |          |
|                | 0.04664  | 0.04712  | 0.04415  |          |          |
| 20             |          |          | 0.04664  | 0.04712  | 0.04415  |
|                | 0.04848  | 0.04924  | 0.04852  |          |          |
| Fritters       | 0.07714  | 0.07421  | 0.07123  |          |          |
|                | 0.07125  | 0.07230  | 0.07012  |          |          |
|                | 0.09130  | 0.09213  | 0.10912  |          |          |
|                | 0.09814  | 0.09210  | 0.1234   |          |          |
| Pan Fried      |          |          | 0.07714  | 0.07421  | 0.07123  |
| Dumpling       |          |          | 0.07125  | 0.07230  | 0.07012  |
|                |          |          | 0.09130  | 0.09213  | 0.10912  |
|                |          |          | 0.09814  | 0.09210  | 0.1234   |

**Figure 1.** Comparison of plasticizer migration in 5 samples at 80 degrees centigrade.

**Figure 2.** The transfer amount of plasticizer in Fried dumplings at different temperatures.
From the experimental results, the content of plasticizer in the sample was mainly DIBP, DBP, DEHP, and the migration amount was less than 0.1 mg/kg. The migration amount was affected by factors such as temperature and food type.

4. Conclusion

In the experiment, the migration amount of plasticizers for food packaging in major roadside stalls in Baoding city was tested. Under different temperature conditions (20°C, 40°C and 80°C), the migration of DEHP increased with increasing temperature. The experimental data shows that the risk of migration of plasticizers in fat foods packaged in plastic containers is high. The risk of migration of plasticizers in food packaging in roadside stalls in Baoding is low. However, the long-term intake of plasticizers is harmful to human health. In order to avoid its harm to the human body, I give the following suggestions.

5. Feasibility Suggestion

5.1. Public

The hazards of plasticizers to the human body should be fully recognized, and the habits and behaviors of daily life should be normalized. When choosing containers, avoid using plastic food containers; try not to use plastic containers to hold oily foods, nor to use plastic containers to heat foods. Avoid prolonged contactor soaking with the plastic container. A special food container should be used when heating food with a microwave oven.

5.2. Government Functional Departments

Further improve the legal construction of food safety supervision, actively propagate and indicate relevant policies and regulations, and take the law as the basis. Food packaging manufacturers shall enforce the raw material purchase inspection system and produce them according to the limited quantity of national standards. They shall be strictly standardized according to the relevant regulations of the State for food labeling, and shall strengthen the factory inspection system to prevent unqualified products from entering the market. At the same time, relevant departments should continue to effectively promote the work of the national standards for the detection of plasticizers.

5.3. Industrial and Commercial Management Department

The national food safety regulatory authorities should further clarify the supervisory responsibilities of their respective departments, effectively integrate the supervision and administration departments such as industry and commerce, quality supervision, and public security to form a regulatory joint force to ensure that market supervision is in place.

5.4. R&D Department

Plastic packaging materials are indispensable in people's daily life. This requires strict control in production and consumption. At the same time, they should continue to increase technological investment and actively develop non-toxic and harmless “plasticizer” alternatives and eliminate harmful packaging materials to remove the hazards of plasticizers to the human body from the source.

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