Study on migration of two acrylate monomers in plastic food contact materials

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Abstract. The migration rules of acrylate monomers in plastic food contact materials were studied in this work. The migration rules of two acrylate monomers from food packing materials to four different stimulants including pure water, 4% acetic acid, 10% ethanol and isooctane were investigated by supercritical fluid chromatography (SFC) technology. The effects of food simulation species, concentration of ethanol, migration time and migration temperature on the migration amount of acrylate monomers were studied. The results showed that the migration of acrylate monomers in different food simulants were in the order: 10% ethanol>4% acetic acid>isooctane>water. Moreover, acrylate monomers were more likely to migrate in high concentration of ethanol. In the same food simulation, the migration of acrylate monomers increased with the increase of temperature and time. This study can provide theoretical basis and technical support for food safety control in the process of production, storage and transportation.

1. Introduction
Acrylate compounds are important raw materials for the synthesis of acrylic resin. In recent years, acrylic resin has been widely used in many fields, such as medical treatment, coating, plastic packaging materials, etc., because of its excellent color retention, light resistance, ultraviolet resistance, and oxidation resistance [1-3]. During the application of acrylate compounds in food packaging materials, acrylate monomers have strong irritation and corrosive effects on eyes, skin and respiratory tract, and may cause organ damage such as liver and lung as food packaging materials may come into contact with food directly or indirectly [4,5]. Long-term exposure to acrylate compounds has been shown to be toxic or carcinogenic. The European Union regulation (EU) No. 10/2011 and China's national standard GB/T 9685-2016 have made clear provisions on specific migration amounts of various acrylates and methacrylates [6,7], but China still has no relevant standards for testing acrylates and acrylates monomers in food contact materials.

The detection techniques of acrylate substances mainly include high performance liquid chromatography [8], gas chromatography [9] and gas chromatography mass spectrometry [10], etc. Due to the high volatility and low molecular weight of acrylates, liquid chromatography has been used to eliminate the interference of solvents and other impurities. At present, there are mainly the following challenges in liquid chromatography detection of acrylate: (1) low detection efficiency; (2) high analysis cost; (3) large consumption of organic solvents. However, most of the existing reports focus on the detection methods of acrylate, but few studies on its migration rules.
2. Experimental and Methods

2.1. Materials and Reagents
The standards were methacrylate (MAA) and methyl methacrylate (MMA), which were all supplied from Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade acetonitrile was purchased from Merck (Darmstadt, Germany). Food grade CO₂ (99.99%) was obtained from Tonghui Gas (Chongqing, China). Acetic acid, ethanol and isooctane were analytically pure, purchased from Chongqing Chuandong Chemical Company Limited.

2.2. Instruments and Equipment
The analysis of acrylates monomers were performed on Ultra-Performance Convergence Chromatography (UPC²) equipped with PDA detector (Waters, Milford, USA). The N-EVAP-112 nitrogen blower (Organomation, USA) and BILON-2000CT ultrasonic cleaner (Bilang, Shanghai) were used in the sample pretreatment stage.

2.3. Methods

2.3.1. Preparation of standards. The standard substance of 10.0 mg was accurately weighed to volumetric flask of 10 mL. The standard substance was dissolved and volume-stabilized with methanol to prepare a standard solution with a concentration of 1000 mg/L, and stored in cold storage at 4°C. The mixed standard working solutions of 1.0 mg/L, 5.0 mg/L, 10.0 mg/L, 50.0 mg/L and 100.0 mg/L were prepared with methanol by step dilution method, which were stored in a refrigerator at 4°C in dark condition for analysis.

2.3.2. Migration test.
(1) Migration in different stimulants. The plastic sample was cut into small pieces with weight less than 0.2 g. The pieces were divided into four equal parts and put into the glass bottle. Different food simulants including distilled water, 4% acetic acid, 10% ethanol and isooctane of 20 mL were separately added to the glass bottle. The samples were immersed hermetically under the condition of 40°C constant temperature water bath. The soak solution was taken at the same time point respectively, and the average value was taken in parallel for three times in each group of experiments.

(2) Migration in different ethanol concentration, temperature and time. The small plastic pieces samples were immersed in 10% ethanol at different concentration of ethanol, temperature and time for migration, and the average value was taken in parallel for three times in each group of experiments.

2.3.3. Chromatographic conditions. The analysis was carried out with ACQUITY UPC² HSS C18 SB column at temperature of 30°C. The mobile phase was a co-solvent of supercritical CO₂ and acetonitrile. The detection wavelength was set at 210 nm and the back pressure was performed at 1800 psi. The sample size was 3 μL. The elution gradient of mobile phase was 0~1 min, 0.8%~1.5% B; 1~2 min, 1.5%~25% B; 2~3 min, kept 25% B; 3-3.5 min, 25%~0.8% B. The flow rate was maintained at 1.2 mL/min.

3. Results and Discussion

3.1. Influence of simulants on migration amount of acrylate monomers
In the experiment, four representative food simulants, namely distilled water, 4% acetic acid, 10% ethanol and isooctane, were used to carry out the migration experiment, and the migration rules of acrylate monomers in different simulants of PE food contact materials were studied. The results were shown in Fig. 1. Under the condition of constant temperature of 40°C, PE positive samples were completely soaked in the four simulants. After 24 h, MAA migrated in all the water-based simulants, however, no dissolution of MAA had been observed in the fatty simulants. In acid and alcohol food
simulants, two kinds of acrylate monomers showed different degree of dissolution. Both MAA and MMA had the most obvious migration in alcohol simulants with migration amount of 1.32 and 1.06 mg/kg, respectively.

![Fig.1 Migration of two acrylate monomers in different simulants (40°C, 24 h)](image)

3.2. Influence of concentration of ethanol on migration amount of acrylate monomers
Since the migration of acrylate monomers was the most obvious in alcohol simulants, the migration of acrylate monomers under different concentrations of ethanol (10%, 30%, 50%, 70% and 90%) was investigated. As shown in Fig. 2, the migration amount of MAA was significantly higher than MMA at low concentration of ethanol. With the increase of concentration of ethanol, the migration rate of both acrylate monomers increased gradually. Furthermore, the migration rate of MMA increased relatively faster in high-concentration ethanol, indicating that the migration rate of acrylate monomers was more likely to occur in the food matrix with higher ethanol concentration.

![Fig.2 The effect of ethanol concentration on migration amount of two acrylate monomers](image)

3.3. Influence of temperature and time on migration amount of acrylate monomers
The effects of migration temperature and time on the migration amount of acrylate monomer were further investigated. As shown in Fig 3a, the migration behaviour of MAA and MMA were not obvious at 4°C. As the temperature increased, the migration amount increased gradually, this is due to the higher temperature enhanced molecular thermal motion.
Fig. 3 The effect of temperature and time on migration amount of two acrylate monomers

With the extension of migration time, the migration amount of acrylate monomer in the plastic food contact material also increases rapidly (Fig 3b). When the migration time exceeded 24 h, the increase rate of MAA and MMA migration slowed down significantly, and when it reached 48 h, the migration rate reached a balance, indicating that the longer the exposure time was, the greater the risk of harmful substances contamination to food would be. Therefore, plastic food contact materials were not recommended for high temperature and long time use.

4. Conclusion

In this study, the migration rules of two acrylate monomers (MAA and MMA) in plastic food contact materials under different simulants, concentration of ethanol, migration temperature and time were studied. The results showed that the migration of acrylate monomer in alcohol simulants was the most obvious, and the migration increased with the increase of ethanol concentration. In the same food simulants, the migration amount of acrylate monomer increased with the increase of temperature and time. The experimental results can provide the theoretical basis and method basis for the safety control of food processing, production, storage, transportation and sales, together with the guidance for consumers on food safety.

Funding

This research was funded by Scientific Research Project of Chongqing Market Supervision Administration [CQSJKJ2019005].

References

[1] Zhao HY, Cao GF, Zhang XL, et al. Head-Space-Gas chromatographic determination of methyl methacrylate released from bone cement [J]. Phys Test Chem Anal Part B: Chem Anal, 2009, 45(6): 707-709.
[2] Wei Z, Huang H. Determination of residual monomer MMA in MMA-CR system by headspace sampling method [J]. Chem Bioeng, 2009, 26(8): 83-84.
[3] Sengtu XY, Zhang W. Determination of residual acrylate monomers in the coatings [J]. Dye Finish, 2008, 34(5): 33-35.
[4] Gong SG, Kong B, Tuo SX, et al. Simultaneous determination of 23 ester compounds in cigarette water-borne adhesives by liquid-liquid extraction and gas chromatography-mass spectrometry [J]. Chin J Chromatogr, 2013, 31(10): 989-994.
[5] Determination of residual acrylate monomers in adhesives by headspace gas chromatography-mass spectrometry [J]. Chin J Chromatogr, 2011, 29(12): 1179-1182.
[6] (EU) No 10/2011 Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food [S].
[7] GB 9685-2008 Hygienic standards for uses of additives in food containers and packaging materials [S].
[8] Zuo Y, Sun DZ, Luo C, et al. HPLC determination of residual amounts of 13 acrylic esters in living paper products [J]. Phys Test Chem Anal Part B: Chem Anal, 2015, 51(2): 168-171.

[9] Hu WL, Pang M, Li L, et al. Determination of acrylates in soil and sediment by head-space gas chromatography [J]. Phys Test Chem Anal Part B: Chem Anal, 2013, 49(2): 196-198.

[10] Dai XL, Li D, Chen XL, et al. Determination of nine esters compounds in water by chromatographic-mass spectrometry with purge and trap [J]. Admin Tech Environ Monitor, 2012, 24(5): 55-57.