Determination of 12 acrylate compounds in plastic food contact materials via high performance liquid chromatography

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Abstract. A high performance liquid chromatography (HPLC) method was used to determine 12 acrylate compounds in plastic food contact materials. The plastic food contact material samples were extracted by ultrasonic with methanol. The mixed solution of water and acetonitrile was used as mobile phase for gradient elution. The samples were separated by ZORBAX SB-AQ column (250 mm×4.6 mm, 5 μm), and analyzed by diode array detector (DAD). The results showed that under the optimal chromatographic conditions, the 12 acrylate compounds had good linear relationships in the range of 0.01-10.0 mg/L, the correlation coefficient of the standard curves were higher than 0.999, and the detection limits (LODs) were 0.03-0.08 mg/kg. The recovery rate was between 85.4% and 110.7%, and the relative standard deviation was from 1.6% to 5.2%. The method was simple and accurate, and can be used for the analysis and detection of 12 acrylate compounds in plastic food contact materials.

1 Introduction

Acrylate compounds are the general term of esters of acrylic acid and its homologues, which are an important chemical raw material mainly used for the production of adhesives, synthetic resins, rubber and plastics [1-3]. Acrylate compounds have anesthetic effect, obvious stimulation and sensitization effect on the skin. Oral administration will strongly stimulate the oral cavity and digestive tract, which may cause dizziness, dyspnea and neuroticism [4,5]. In the process of using, harmful substances in plastic food contact materials will be transported into the human body through food. The national standard GB/T 9685-2016 has made clear provisions on the specific migration amount of various acrylates and methacrylates [6], but there is still no relevant standard for detecting acrylates and acrylates monomers in food contact materials in China.

At present, the main methods for the determination of acrylate compounds include gas chromatography [7], gas chromatography-mass spectrometry [8], high performance liquid chromatography [9], etc. These methods are mainly used for quantitative analysis of a single or a few acrylate compounds. Due to the low boiling point and high volatility of acrylates, it is easy to produce self-polymerization reaction at high temperature. Therefore, it is difficult to achieve the ideal peak shape and recovery rate of acrylate compounds by gas chromatography or gas chromatography-mass spectrometry.

In this paper, a high performance liquid chromatography (HPLC) method was used to analyze and detect 12 acrylate compounds in plastic food contact materials, which can avoid the influence of high

temperature on target substances in gas chromatography. This method is simple, accurate and reliable, and can provide technical support for the detection of acrylate compounds in plastic food contact materials in the future.

2 Materials and methods

2.1. Materials and reagents

12 acrylate standards were all supplied from Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade acetonitrile was purchased from Merck (Darmstadt, Germany). The water used in the experiment was ultra-pure water.

2.2 Instruments and equipment

Agilent 1260 high performance liquid chromatograph (with DAD detector), Agilent, USA; SQP Electronic analytical balance, Sedris, Germany; Bilon-2000 CT ultrasonic cleaner, Shanghai Bilang Instrument Co., LTD.

2.3 Methods

2.3.1 Preparation of standard solution

The standard substance of 25.0 mg was accurately weighed to volumetric flask of 25 mL, then dissolved and volume-stabilized with methanol to prepare a standard solution (1000 mg/L). The mixed standard working solutions of 0.1 mg/L, 0.5 mg/L, 1.0 mg/L, 5.0

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mg/L and 10.0 mg/L were prepared with methanol by step dilution method for HPLC analysis.

2.3.2 Sample pretreatment

The typical samples of 2 g were weighed and cut into small pieces with an area of no more than 5 mm×5 mm, and mixed evenly. The 0.5 g sample was accurately weighed into a 25 mL colorimetric tube, and 10 mL methanol was added for ultrasonic extraction at room temperature for 30 min. The supernatant was taken through 0.45 μ m organic filtration membrane for UPLC analysis.

2.3.3 Chromatographic condition

A ZORBAX SB-AQ column (250 mm ×4.6 mm, 5 μ m) was used to analysis. The mobile phase A was water and the mobile phase B acetonitrile. The column temperature was 40°C, the injection volume was 20 μ L, the detection wavelength was 210 nm, and the flow rate was 1.0 mL/min. Gradient elution procedure: 0-6.5 min, 20%-40%B; 6.5-17 min, 40%-65%B; 17-17.2 min, 65%~100%B; 22-22.2 min, 100%-20%B, then kept for 6 min.

3 Result and analysis

3.1. Selection of chromatographic conditions

The effect of chromatographic column on the separation of acrylate compounds was investigated. It was found that ZORBAX SB-AQ column had the best separation effect on 12 target compounds, so this column was selected for subsequent experiments.

Fig. 1. Chromatogram of standard solution of 12 acrylate compounds (the peak numbers were the same as table 1)

Due to the weak polarity of acrylate compounds, the peak time in reversed-phase column was not too fast, and there was no need to add acid and salt in the mobile phase. Therefore, acetonitrile-water system was more suitable. The maximum ultraviolet absorption of

acrylates compounds was around 210 nm, therefore 210 nm was selected as the best measurement wavelength. Under the optimal conditions, 12 acrylate compounds were able to achieve better baseline separation, and the chromatogram was shown in Figure 1.

3.2. Standard curve and detection limit

According to the working conditions of the instrument, the mixed standard solution series was determined, and the mass concentration of each compound was linearly regressed by the peak area of each compound. The results showed that the mass concentrations of the 12 acrylate compounds were linear in the range of 0.1-10 mg/L, and the correlation coefficient were more than 0.999. The detection limit of the method was calculated by 3 times signal-to-noise ratio ($S/N \geq 3$), and the method verification results were shown in Table 1.

Table 1. Linear equation, correlation coefficient (R^2), and determination limit (LOD) of 12 acrylate compounds.

No.	Compound	Linear equation	R^2	LOD (mg/kg)
1	acrylic acid-2-hydroxyethyl ester	$y=36.9x+1.22$	0.9993	0.08
2	2-hydroxyethyl-2-methyl-2-acrylate	$y=81.3x+2.54$	0.9995	0.03
3	methyl acrylate	$y=61.8x+1.95$	0.9993	0.03
4	methyl methacrylate	$y=81.5x+2.53$	0.9993	0.03
5	ethyl methacrylate	$y=79.2x+4.46$	0.9993	0.03
6	2-acrylate-1,1-dimethylethyl ester	$y=34.2x+0.61$	0.9993	0.08
7	n-butyl acrylate	$y=33.2x+0.76$	0.9993	0.08
8	phenyl acrylate	$y=98.2x+3.27$	0.9994	0.03
9	phenyl methacrylate	$y=117.7x+3.76$	0.9993	0.03
10	butyl methacrylate	$y=63.3x+5.01$	0.9991	0.03
11	phenyl methacrylate	$y=103.2x+5.73$	0.9993	0.03
12	2-octyl acrylate	$y=21.8x+0.87$	0.9997	0.08

3.3. Precision and recovery

Blank plastic food contact material samples were selected for standard recovery and precision testing, with the standard level of 0.1, 1.0 and 10.0 mg/L, respectively, and each concentration level was repeated for 6 times. The experimental results (Table 2) showed that the recoveries (R) of 12 acrylate compounds were in the range of 85.4%-110.7% and the relative standard deviation (RSD) was 1.6%-5.2% at the three standard

levels, which could meet the actual detection requirements.

Table 2. Recoveries and RSDs (n=6) for acrylate compounds

No.	Com-pound	0.1 mg/kg		1.0 mg/kg		10.0 mg/kg	
		R/%	RSD /%	R/%	RSD/ %	R/%	RSD /%
1	acrylic acid-2-hydroxyethyl ester	90.5	3.8	94.2	2.1	98.4	1.9
2	2-hydroxyethyl-2-methyl-2-acrylate	88.3	3.1	97.1	3.3	99.7	2.5
3	methyl acrylate	91.0	2.7	104.9	2.0	103.4	2.1
4	methyl methacrylate	108.6	4.6	90.3	3.8	101.2	2.7
5	ethyl methacrylate	87.9	2.5	103.2	2.3	100.9	1.8
6	2-acrylate -1, 1-dimethylethyl ester	110.7	3.1	106.6	2.6	94.3	1.9
7	n-butyl acrylate	85.4	5.2	92.1	3.7	98.6	2.3
8	phenyl acrylate	107.7	4.7	103.7	3.6	104.5	2.4
9	phenyl methacrylate	106.4	4.0	94.9	2.9	96.7	2.7
10	butyl methacrylate	92.3	2.4	97.8	2.0	101.1	1.9
11	phenyl methacrylate	93.5	3.6	90.5	3.3	104.2	1.6
12	2-octyl acrylate	90.8	4.2	102.9	3.4	99.6	2.5

3.4. Actual sample test

Plastic food contact materials with different materials (PE, PC, PET, etc.) were selected for actual sample analysis, and 20 actual samples were detected by this method. The results showed that a certain amount of acrylate compounds residue was detected in two samples. Sample 1 contained methyl methacrylate, phenyl

methacrylate and 2-octyl methacrylate, and sample 2 contained ethyl methacrylate and phenyl methacrylate at contents ranging from 1.40-3.41 mg/kg, and the contents of each substance were listed in Table 3.

Table 3. Average contents (mg/kg) of acrylate compounds in commercial samples

No.	Compound	Sample 1	Sample 2
1	acrylic acid-2-hydroxyethyl ester	—	—
2	2-hydroxyethyl-2-methyl-2-acrylate	—	—
3	methyl acrylate	2.31	—
4	methyl methacrylate	—	—
5	ethyl methacrylate	—	2.06
6	2-acrylate-1,1 dimethylethyl ester	—	—
7	n-butyl acrylate	—	—
8	phenyl acrylate	—	—
9	phenyl methacrylate	—	—
10	butyl methacrylate	—	—
11	phenyl methacrylate	3.20	3.41
12	2-octyl acrylate	1.40	—

“—” related to below the limit of detection

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4 Conclusions

In this study, a HPLC method for the determination of 12 acrylate compounds in plastic food contact materials was established by investigating and optimizing the chromatographic conditions. This method could realize the effective separation of 12 acrylate compounds, and the detection limit, standard recovery and precision could meet the requirements of actual samples. This method was easy to operate, sensitive and accurate, and could provide a new technical reference for the analysis and detection of acrylate compounds in plastic food contact materials in the future.

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