Determination of Total Specific Migration of Acrylic Acid and Acrylic Esters in Food Contact Materials

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Abstract: In this study, we selected a total specific migration indicator including 12 acrylic acid and acrylic esters, i.e. SML (T) 22 from national food safety standard. After comparison, methyl acetate was selected as the extracting agent, which was applicable for the treatment of acidic and aqueous simulants. The HP - INNOWAX polarity column was applied to separate the 12 compounds and the solvent. The GC - MS was utilized for qualitative and quantitative analysis with optimization of extraction duration, temperature program, scanning mode as well as the carrier gas flow rate and the sampling volume. The 12 acrylic compounds present good separation in 12 minutes, and the analytical duration is greatly shortened. The linearities in different simulants range from 0.047 mg/L to 11.43 mg/L, while the detection limits are from 0.009 mg/L to 0.666 mg/L. The actual products analysis shows that the recoveries are between 81.2% and 81.2%, and the RSDs (n = 6) are within 5.15%. This developed analysis method is fast, economical, non-toxic, with low detection limit, high precision and high accuracy. It has good applicability and is easy to promote to use.

1 INTRODUCTION

Acrylic acid and acrylic esters are volatile with serious odor, and have certain nerve toxicity and reproductive toxicity. They can contaminate the atmosphere and the water (Wang et al., 2002), and are also significantly harmful to human body. Thus the world health organization's international agency for research on cancer has listed acrylic acid and its esters as carcinogens in category 2 or 3. At the international level, such as the European Union (European Commission, 2011), as well as the Japan (Ministry of Health, Labour and Welfare, 2011) has issued regulations to limit those monomer residues. Chinese National Health and Family Planning Commission (NHFPC) together with Food and Drug Administration has also announced a series of FCMs related national food safety standards in 2017 (see the national food safety standards bulletin No.15 of 2016).

According to GB 4806.6 2016 (NFHPC, 2016), GB 9685-2016 (NFHPC, 2016), the total specific migration limit indicator [SML (T) 22], quantified in acrylic acid containing 12 species of acrylate monomers, 1 species of poly-acrylic acid salt and 1 species of acrylic polymer is limited to under 6 mg/kg. Nowadays all the common FCMs on the market such as resin, plastic, paint and coating, paper, ink, adhesives, etc., should meet the national standard limit requirement. Content determination of acrylic acid and its esters first started from the production in chemical industry process, monomer residue from textile production, air pollution and waste liquid pollution (Gu et al., 2002; Shi et al., 2003; Liu et al., 2013a; Liu et al., 2011b; Shentu et al., 2008), and were mainly carried out by using gas chromatography (GC) analysis method. Wang Jianling et al. (Wang et al., 2016; Dong et al., 2013; Ma et al., 2013) separated 12 acrylic monomers in GC instrument with non-polar chromatographic column and carried out the detection of migration content for water-based FCMs simulants. Lai Ying and Lin Rui (Lai et al., 2015) using a purge and trap sampling method, solved the direct sampling problem of water-based simulants in gas chromatography, while the shortcoming is that the acrylic acid could not be trapped. Li ying and Li Chengfa (Li et al., 2014a; Li et al., 2015b; Li et al., 2016c;), respectively utilized the solid-phase micro-extraction-GC-MS method, the head space GC-FID method, and the high performance liquid chromatography (HPLC) method to determine a

variety of acrylate and methyl acrylate migration, but these methods require complex operation, and qualitative ability are poor. Moreover the general LC is unable to separate geometric isomers with similar polarity.

Due to the bigger differences of polarity and boiling point between the 12 acrylic monomers and the existence of isomers, it is difficult to separate them in a single method. From home and abroad, a mature analysis method which can directly separate Chinese regulatory acrylic esters and can be used to determine the total specific migration has not yet been reported. We separated the 12 compounds and the solvent by polarity column with the GC - MS, and optimized the extraction time, temperature program, scan mode and sampling volume, carrier gas flow rate, etc.. The method presents feasible and precise characteristics in determining 12 acrylic acid and acrylic esters so as to calculate the total specific migration limit thereafter.

2 TEST

2.1 Instruments and Reagents

GC - MS instrument: Japan Shimadzu GC - MS QP2010 – plus.

Electronic balance: Switzerland Mettler, 0.1 mg, XS – 204.

Whirlpool extraction apparatus: Germany IKA, Vortex Genius 3.

Ultrapure water purification system: American Millipore, Milli - Q.

Methyl acrylate (> 99.7%, Aladdin), acrylic acid (> 99.5%, Aladdin), butyl acrylate (> 99%, Aladdin), benzyl acrylate (> 97%, Aladdin), iso - propyl acrylate (> 95%, International Laboratory USA); n -

propyl acrylate (> 95%, Alfa Aesa), ethyl acrylate (> 99.5%, Dr. Ehrenstorfer GmbH), *n* - butyl acrylate (> 99.5%, Dr. Ehrenstorfer GmbH), *sec* - butyl acrylate (> 95%, Chem Service), *n* - octyl acrylate (> 95%, Chem Service), hydroxyl ethyl acrylate (> 99.5%, Chem Service), *tert* - butyl acrylate (> 99.5%, Aike import packing). Methyl acetate reagent is of chromatography grade, and the rest reagents are of analysis grade.

2.2 Analysis Conditions

2.2.1 GC Conditions

The polar chromatographic column with polyethylene glycol (PEG), HP - INNOWAX (30m × 0.25mm × 0.50μm) is adopted. The Injection port temperature (T_{injec}) is 220 ℃, the interface temperature (T_{inter}) is 250 ℃, and ion source temperature (T_{ion}) is 230 ℃. Carrier gas for high purity helium (He, purity is more than 99.999%) is used, and the carrier gas flow rate is 1.8 ml/min. Sampling volume is 1μL with splitless injection mode. Solvent delay: in pure water and acid simulation is of 4.5 min; in ethanol simulation is of 6.2 min.

Programmed temperature: the initial temperature is 40 ℃, then maintain it for 5 min; after that rise the temperature at a rate of about 20 ℃ / min to 70 ℃; then warm at a rate of about 40 ℃ / min to 180 ℃, finally at a rate of about 20 ℃ / min to keep the temperature for 1 min at 220 ℃.

2.2.2 MS Conditions

Adopt both the full scan (SCAN) and the select ion scan (SIM) at 5.1 ~ 7.0 min as well as 10.6 ~ 11.0 min for data collection, while only the full scan

Table 1: Characteristic ions of 12 acrylic acid and acylate monomers

No.	Monomer name	CAS No.	Quantitative ion (*m/z*)	Qualification ion (*m/z*)
1	methyl acrylate	96-33-3	55	85, 27
2	ethyl acrylate	140-88-5	55	56, 99
3	*iso* - propyl acrylate	689-12-3	55	73, 43
4	*tert* - butyl acrylate	1663-39-4	55	57, 41
5	*n* - propyl acrylate	925-60-0	55	73, 27
6	*sec* - butyl acrylate	2998-08-5	55	73, 99
7	*iso* - butyl acrylate	106-63-8	55	56, 73
8	*n* - butyl acrylate	141-32-2	55	56, 73
9	*n* - octyl acrylate	2499-59-4	55	70, 27
10	acrylic acid	79-10-7	72	55, 45
11	2 - hydroxy acrylate	818-61-1	55	73, 86
12	benzyl acrylate	2495-35-4	55	91, 117

(SCAN) mode for the rest of testing duration. SCAN range: *m/z* 25 - 200. Quantitative ions are shown in Table 1.

2.3 Preparation of Calibration Solution

Weighed respectively 0.100 g standard solution of acrylic acid and acrylic esters in a 10 ml volumetric flask, and filled methyl acetate to the volume to obtain the mixed standard stock solution at the concentration level of 10000 mg/L. Continued to dilute step by step with methyl acetate to concentrations of 0.5, 1.0, 5.0, 10.0, 20.0, 50.0 mg/L.

Prepared five different blank simulants of 4% acetic acid, water, 10% ethanol, 20% ethanol, 50% ethanol according to the requirements of GB 5009.156 2016. Measured out 6 copies, 4mL of each simulants above into 10 mL centrifugal tubes, and respectively added 0.5, 1.0, 5.0, 10.0, 20.0, 50.0 mg/L mixed standard solutions of 0.4 mL, and produced a series standard working solutions of 0.05, 0.10, 0.50, 1.00, 2.00, 5.00 mg/L with 6 duplicate samples each. The extraction procedure was according to step 2.4 extraction operation.

2.4 Total Specific Migration

2.4.1 Migration Test Conditions

Conditions are selected in accordance with GB 31604.1-2015. Considering method detection limit applicability, the more gentle migration test conditions are selected as the migration incubating at 40 ºC for 2h.

2.4.2 Food Simulants Selection

In order to analyze as much food simulants as possible, the 4%acetic acid, pure water, 10% ethanol, 20% ethanol, 50% ethanol were chosen. Fat simulant was not considered due to the solvent influence in baseline separation.

2.4.3 Extraction Operation

Move 4.0 mL migrating solutions or standard working solutions in 10 mL centrifugal tubes with plug. To the centrifugal tube respectively add 0.5 g sodium chloride and 4 mL methyl acetate, and add 1 mL saturated sodium sulfate for 50% ethanol simulant only, then extract all by vortex (1500 g/min) for 5 min. Carefully take the supernatant fluid after stratification for 2 min. Samples are ready to be analyzed with GC − MS after filtration by 0.45μm filter membrane.

2.4.4 Calculation of Total Specific Migration

Total specific migration based on acrylic acid is the summation of specific migration of 14 target compounds; this paper provides the specific migration analysis method of 12 species of acrylic compounds.

3 RESULTS AND DISCUSSIONS

3.1 Extraction Operation

3.1.1 Selection of Extractant

As there are 12 target compounds containing many different species as acid, ester, hydro-ester, benzene ester co-existing in the analysis system, and the acrylic acid is highly acidic, the solubility for target compounds must be considered as well as the immisciblity for liquid-liquid extraction process between extraction agent and aqueous water, which actually leave very few options of the solvents. Small molecule esters and ethers with medium polarity or weak polarity may be applicable in theory. After test, methyl acrylate (which possesses the minimum polarity in the 12 monomers) can only be separated with methyl acetate solvent, and is unable to be separated with such medium polar solvent as ethanol, ethyl ether, methyl *tert* - butyl ether, and is susceptible to be interfered by ethyl acetate. Moreover, in non-polar solvents such as n-hexane and isooctane, poor baseline separation effect is shown (seen in Figure 1 to Figure 2). Ultimately, methyl acetate is chosen as the extraction solvent for tests thereafter.
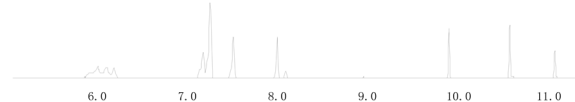

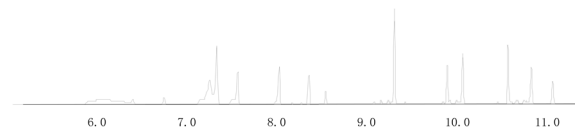Figure 1: Separation of acrylates in hexane.

Figure 2: Separation of acrylates in *iso* - octanet.

3.1.2 Optimization of Extraction Duration

Take each of 4 ml 4% acetic acid simulant for 6 copies into 10 ml centrifugal tubes with plugs, add 0.4 mL standard solution at the concentration of 10 mg/L, then add 4 ml of methyl acetate, sodium chloride 0.5 g. Respectively extract for 1 min, 2 min, 5 min, 10 min to determine the average response. The results show that the response growth of 12 monomers is no longer obvious after 5 min; therefore extraction time is selected as 5 min for test.

3.2 Instrumental Optimization

Separations of three chromatographic columns are investigated. GC temperature program and MS scanning mode were given intensive optimization to achieve rapid qualitative and quantitative. Besides, sampling volume and carrier gas flow rate were also given appropriate consideration. Sampling volume at splitless injection mode is 1 μL since higher volume would cause detector saturation. On the premise of separation, carrier gas flow rate can be set as higher as possible to achieve faster outflow. After optimization, chromatograms of mixed standard solutions of the 12 acrylic monomers are showed in Figure 3-1 to Figure 3-6, in which the Figure 3-1 to Figure 3-5 are the SIM *m/z* 55 graph of acrylic monomers, and in which the Figure 6 is the SIM *m/z* 72 graph of acrylic acid. Since methyl acrylate cannot be separated from ethanol, data of methyl acrylate is not collected in ethanol simulants.

3.2.1 Chromatographic Column Selection

This paper tested three chromatographic columns to separate 12 target compounds. They are respectively column AT SE - 54 (30m × 0.32mm × 0.50μm), column DB - WAX (30m × 0.25mm × 0.25μm) and column HP - INNOWAX (30m × 0.25mm × 0.50μm).

Firstly, target compound methyl acrylate possesses very weak polarity as well as low boiling point, and is unable to reach the baseline separation in non-polar chromatographic column AT SE - 54 even with almost all sorts of solvent. Secondly, target compound acrylic acid and hydroxyl ethyl acrylate both present weak responses at AT SE – 54 column maybe is because of stronger polarity, and peak tailing are obvious at the same time. Based on the above, a polar chromatographic column with thicker stationary phase liquid membrane of 0.5μm HP – INNOWAX is selected.

3.2.2 GC Temperature Program

The peak of target methyl acrylate is different at different initial column temperature. Because of its low boiling point and weak polarity, its responses reduce gradually with the rising initial temperature
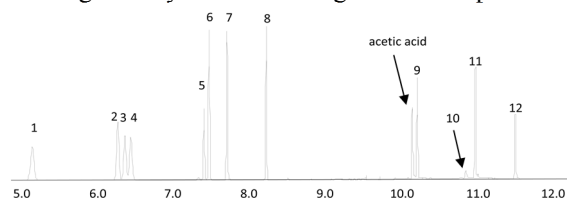
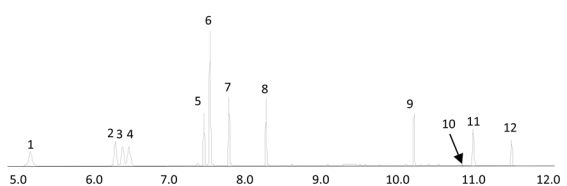Figure 3-1: 12 Acrylate monomers in 4% acetic acid.
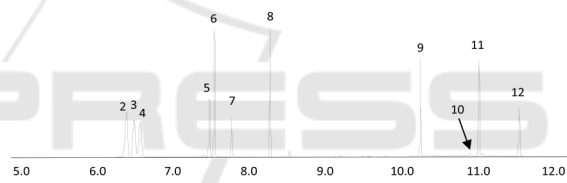
Figure 3-2: 12 Acrylate monomers in water.

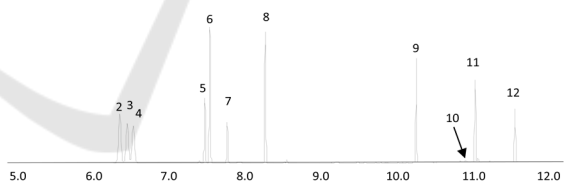Figure 3-3: 11 Acrylate monomers in 10% ethanol.

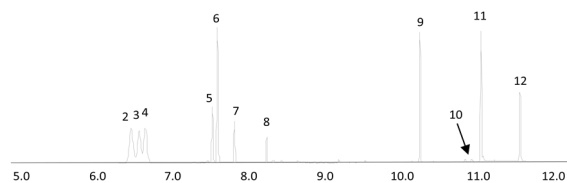Figure 3-4: 11 Acrylate monomers in 20% ethanol.
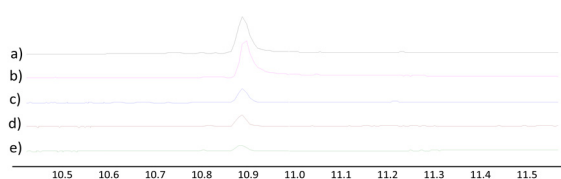
Figure 3-5: 11 Acrylate monomers in 50% ethanol.

Figure 3-6: Acrylic acid in five different simulants.

Number 1-12 represent the corresponding compounds in Table 1. a) acrylic acid in 4% acetic acid, b) acrylic acid in 10% ethanol, c) acrylic acid in 20% ethanol, d) acrylic acid in 50% ethanol, e) acrylic acid in aqueous.

despite the same other conditions, and there is even no outflow when temperature is 60 ºC above. Finally the initial temperature is set at 40 ºC. For ethyl acrylate, *iso* - propyl acrylate and *tert* - butyl acrylate, it is more difficult to separate them, thus a lower rate of warming is adopted at their outflow. Last but not the least, T_{injec}, T_{ion} and T_{inter} have influence on acrylic acid response, results show that when T_{injec} is 220 ºC, T_{ion} is 230 ºC and T_{inter} is 250 ºC, a clearer acrylic acid peak is observed (Figure 4).
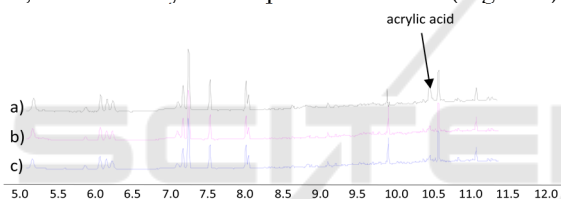

Figure 4: GC temperature optimization

a) T_{injec} = 220 ºC, T_{ion} = 230 ºC, T_{inter} = 250 ºC
b) T_{injec} = 180 ºC, T_{ion} = 230 ºC, T_{inter} = 250 ºC
c) T_{injec} = 180 ºC, T_{ion} = 200 ºC, T_{inter} = 250 ºC

3.2.3 MS Scan Mode

The vast majority of the acrylate targets in this test system is of high sensitivity, so single SCAN mode is adopted. However, for targets outflow at low temperature and the acrylic acid, sensitivity can be relatively low, so simultaneously adopting SCAN and SIM mode to collect data is recommended.

3.3 Linearity and Detection Limit

The linear ranges and the detection limits of 12 acrylic monomers in different simulants are examined. As shown from Table 2 to Table 6, the vast majority of the monomers in their corresponding linear range show a correlation coefficient of above 0.998. Method detection limits (MDL) in the calculation of 10 times the signal-to-noise ratio (10 S/N), are between 0.009 ~ 0.666 mg/L. It can be concluded that 50% ethanol stimulant has a greater matrix influence, although the detection limit could still meet the total amount requirement of under 6 mg/kg.

Table 2: Calibration curve and MDL of 12 acrylic monomers in 4% acetic acid simulant.

Compounds name	Calibration curve	Correlation coefficient R	Linear range (mg/L)	MDL (mg/L)
methyl acrylate	Y =213331.5X + 2641.579	0.99976	0.050-5.02	0.023
ethyl acrylate	Y = 279874.0X - 5950.658	0.99965	0.047-9.46	0.017
iso - propyl acrylate	Y = 210024.9X - 3753.339	0.99972	0.047-9.46	0.022
tert - butyl acrylate	Y = 206089.9X - 4562.689	0.99947	0.051-10.15	0.028
n - propyl acrylate	Y = 131143.7X - 3349.896	0.99950	0.058-11.43	0.019
sec - butyl acrylate	Y = 256910.8X - 7288.816	0.99952	0.065-11.02	0.021
iso - butyl acrylate	Y = 350907.9X - 6254.656	0.99972	0.049-9.78	0.025
n - butyl acrylate	= 270062.8X - 5771.874	0.99951	0.052-10.42	0.007
n - octyl acrylate	Y =214252.1X + 3599.324	0.99936	0.049-9.74	0.010
acrylic acid	Y = 61074.37X - 3732.911	0.99910	0.105-10.52	0.028
2 – hydroxyl acrylate	Y = 222656.2X - 4330.287	0.99879	0.053-10.52	0.011
benzyl acrylate	Y = 131496.7X - 1627.629	0.99950	0.051-10.18	0.009

Table 3: Calibration curve and MDL of 12 acrylic monomers in aqueous simulant.

Compounds name	Calibration curve	Correlation coefficient R	Linear range (mg/L)	MDL (mg/L)
methyl acrylate	Y = 16645.87X - 1122.097	0.99917	0.050-5.02	0.137
ethyl acrylate	Y = 117359.3X - 7280.47	0.99991	0.047-9.46	0.044
iso - propyl acrylate	Y = 63144.9X - 391.7042	0.99990	0.047-9.46	0.069
tert - butyl acrylate	Y =54266.12X + 1798.745	0.99858	0.051-10.15	0.065
n - propyl acrylate	Y = 124151.3X - 9402.363	0.99984	0.058-11.43	0.039
sec - butyl acrylate	Y =179995.3X + 7001.684	0.99994	0.065-11.02	0.017
iso - butyl acrylate	Y = 167692.4X - 34947.27	0.99910	0.490-9.78	0.029
n - butyl acrylate	Y = 118731.4X - 36992.03	0.99814	0.520-10.42	0.047
n - octyl acrylate	Y = 77051.36X - 10073.97	0.99935	0.098-9.74	0.062
acrylic acid	Y = 44205.96X - 7577.23	0.99512	0.210-10.52	0.114
2 - hydroxyl acrylate	Y =45573.47X + 2370.367	0.99816	0.212-10.52	0.047
benzyl acrylate	Y = 59995.59X - 11443.8	0.99908	0.051-10.18	0.081

Table 4: Calibration curve and MDL of 11 acrylic monomers in 10% ethanol simulant.

Compounds name	Calibration curve	Correlation coefficient R	Linear range (mg/L)	MDL (mg/L)
ethyl acrylate	Y = 227635.9X - 10229.23	0.99967	0.095-4.73	0.037
iso - propyl acrylate	Y = 183979.7X - 8447.88	0.99968	0.095-4.73	0.049
tert - butyl acrylate	Y = 165710.8X - 5309.12	0.99985	0.102-5.08	0.056
n - propyl acrylate	Y = 109444.0X - 3450.485	0.99987	0.114-5.72	0.035
sec - butyl acrylate	Y = 213532.4X - 7722.765	0.99990	0.130-6.50	0.019
iso - butyl acrylate	Y = 73403.92X + 125.8798	0.99991	0.098-4.89	0.029
n - butyl acrylate	Y = 214916.0X - 7857.83	0.99980	0.104-5.20	0.016
n - octyl acrylate	Y = 158578.6X - 3158.069	0.99985	0.097-4.87	0.020
acrylic acid	Y = 11655.98X + 2324.899	0.99767	0.526-5.26	0.069
2 - hydroxyl acrylate	Y = 162818.3X + 4613.518	0.99778	0.105-5.26	0.023
benzyl acrylate	Y = 100208.2X - 1863.335	0.99990	0.102-5.09	0.038

Table 5: Calibration curve and MDL of 11 acrylic monomers in 20% ethanol simulant.

Compounds name	Calibration curve	Correlation coefficient R	Linear range (mg/L)	MDL (mg/L)
ethyl acrylate	Y = 234892.1X - 3376.416	0.99970	0.095-4.73	0.049
iso - propyl acrylate	Y = 151856.8X + 3058.984	0.99972	0.095-4.73	0.061
tert - butyl acrylate	Y = 177324.5X - 6981.871	0.99979	0.102-5.08	0.064
n - propyl acrylate	Y = 94813.75X + 2609.779	0.99972	0.114-5.72	0.045
sec - butyl acrylate	Y = 182752.9X + 6723.2	0.99963	0.131-6.52	0.023
iso - butyl acrylate	Y = 64097.8X + 1010.351	0.99980	0.098-4.89	0.058
n - butyl acrylate	Y = 184409.9X + 3763.209	0.99973	0.104-5.20	0.018
n - octyl acrylate	Y = 136378.3X + 4600.976	0.99958	0.097-4.87	0.024
acrylic acid	Y = 13455.22X - 2376.646	0.99912	0.526-5.26	0.118
2 - hydroxyl acrylate	Y = 159920.3X + 8330.662	0.99937	0.105-5.26	0.026
benzyl acrylate	Y = 90564.6X + 2501.27	0.99971	0.102-5.09	0.046

Table 6: Calibration curve and MDL of 11 acrylic monomers in 50% ethanol simulant.

Compounds name	Calibration curve	Correlation coefficient R	Linear range (mg/L)	MDL (mg/L)
ethyl acrylate	Y = 147856.2X - 9376.71	0.99810	0.473-9.46	0.616
iso - propyl acrylate	Y = 124102.3X - 5827.429	0.99959	0.473-9.46	0.666
tert - butyl acrylate	Y = 117981.0X - 14046.97	0.99910	0.508-10.15	0.650
n - propyl acrylate	Y = 111935.8X - 38669.92	0.99642	0.572-11.43	0.466
sec - butyl acrylate	Y = 245926.4X - 50416.27	0.99902	0.551-11.02	0.215
iso - butyl acrylate	Y = 52864.83X - 4071.117	0.99931	0.489-9.78	0.524
n - butyl acrylate	Y = 150361.6X - 2456.627	0.99990	0.521-10.42	0.176
n - octyl acrylate	Y = 114555.1X - 3421.28	0.99963	0.487-9.74	0.186
acrylic acid	Y = 6659.213X - 1258.587	0.99919	0.526-10.52	0.196
2 - hydroxyl acrylate	Y = 141481.7X - 2373.479	0.99971	0.526-10.52	0.199
benzyl acrylate	Y = 77315.0X - 4021.075	0.99968	0.509-10.18	0.368

3.4 Recovery and Precision

A plastic lid of ABS material is used to incubate with the five food simulants under 40 ºC, respectively for 2 h. Then take each the migrated solutions of 4 ml, and add respectively 0.10, 1.0, 5.0 mg/L mixed standard solution extract according to the extraction operation in step 2.4. Six duplicate samples at three concentration levels were required. Recovery and precision at the three levels were then tested. Results show that the recovery rate of acrylic acid and esters in both acid and water simulants ranges in 81.2% ~ 108.3%, while the relative standard deviation (RSD, n = 6) of which is within 5.15%.

4 CONCLUSIONS

The National Food Safety Standard involved limit indicator [SML (22)], a total specific migration calculated by acrylic acid contains 12 acrylic monomers, which are rather difficult to quantify by a single system due to their large differences of physical and chemical properties. In fact common LC column cannot separate the four butyl acrylate isomers. In this study, with the most commonly used GC-MS in the testing laboratories, we establish aan instrumental analysis method for determination migration with acid and aqueous food simulants. This method has the characteristics of rapidity and non-toxicity, with low detection limit and high precision. But in some simulants containing large amount of ethanol, the methyl acrylate peak is significantly hindered by residual ethanol solvent. Another conclusion maybe deduced from the results as well, that is the ethanol also has different degree of influence on other monomers' outflow.

Subsequently, attempt of multiple liquid-liquid extraction will be made to possibly reduce the ethanol residual for improved GC analysis; or study of using headspace sampling will be continued to explore probably reduced interference of high concentrations of ethanol simulants.

ACKNOWLEDGEMENTS

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