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Simultaneous Analysis of Trace Polymer Additives in Plastic Beverage Packaging by Solvent Sublation Followed by High-Performance Liquid Chromatography

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Supporting Information

ABSTRACT: Using solvent sublation (SS), a novel pretreatment method for separating and concentrating antioxidants and ultraviolet absorbers from plastic beverage packaging was developed, and these target compounds were quantitatively analyzed by high-performance liquid chromatography (HPLC). In the pretreatment section, the effects of the sublation solvent, solution pH, NaCl concentration, nitrogen flow rate, sublation time, and light condition on the sublation efficiency were investigated in detail and the optimal conditions of the solvent sublation process were selected. The analytical method of SS−HPLC showed good linearity in the range from 0.33 to 667 ng/mL with good presenting regression coefficients ($0.9995 \geq R^2 \geq 0.9972$). Low limits of detection (LODs) of 0.34−1.25 ng/mL and limits of quantification (LOQs) of 1.13−4.15 ng/mL were achieved. The mean recoveries were in the range from 88.73 to 107.65% at 20, 30, and 40 ng/mL spiked levels, and the relative standard deviations (RSDs) were in the range from 2.16 to 10.55%.

KEYWORDS: *Solvent sublation, high-performance liquid chromatography, plastic beverage packaging, antioxidants, ultraviolet absorbers*

INTRODUCTION

Plastic, as drink or food packaging,[1] is a commonly used material for food storage and protection, which usually is in contact with food. Because antioxidants and ultraviolet (UV) absorbers[2,3] can delay the oxidation reaction of the polymer,[4−6] these polymer additives are widely used in plastic packaging. However, antioxidants and UV absorbers can migrate from plastics into the food and contaminate it during production or storage, and the related problem of food safety attracts much attention. It is obvious that research on the migration mechanism and specific migration levels (SML) of these additives is very important for the quality control of food. Before the quantitative analysis of antioxidants and UV absorbers, the sample pretreatment is the most important step for the instrumental determination, because of the trace content of these compounds in plastic packaging. Recently, several pretreatment techniques were used for sample preparation of polymer additives in plastics, such as liquid−liquid extraction,[7] ultrasonic extraction,[8,9] microwave extraction,[10] supercritical fluid extraction,[11] solid-phase extraction,[12−17] and solid-phase microextraction.[18] However, these pretreatment techniques were difficult to treat a large number of samples and spent a lot of time. Therefore, the development of a new convenient pretreatment technique is very necessary.

Solvent sublation (SS) is a kind of adsorptive bubble separation technique in which the surface active (or hydrophobic) compounds in aqueous phase are adsorbed on the bubble surfaces of an ascending gas stream and then collected in an organic layer placed on top of the aqueous phase.[19] This technique has many advantages,[20] such as high separation efficiency, high concentration coefficient, low dosage of organic solvent, soft separation process, and simple operation. With the advantages of simultaneous separation and enrichment, SS has been a good pretreatment technique of trace target compounds for environmental analysis[21−23] and food analysis.[24,25]

In the present work, the structures of antioxidants and UV absorbers have many hydrophobic groups (see Figure S1 of the Supporting Information), and they can be easily adsorbed on the bubble surface; therefore, these polymer additives are very suitable for SS. The aim of this study is to develop a pretreatment and analytical method with low limits of detection (LODs), good precision, and accuracy for the determination of trace antioxidants and UV absorbers in plastic beverage packaging. In the analytical method of solvent sublation followed by high-performance liquid chromatography (SS−HPLC), SS was used to separate and concentrate the polymer additives from beverage simulants and then the flotation products were determined by HPLC. The new method was applied to 17 plastic beverage packagings with good results.

MATERIALS AND METHODS

Apparatus. A PHS-3C pH meter (Shanghai, China) was used to determine the pH of the solution. A KH-100E supersonic wave purifier (Kunshan, China) and a GP225D electron balance (Sartorius, Germany) were used. The chromatographic separation were carried

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out on a Shimadzu LC-20A system, including two LC-20A solvent delivery units, a SPD-M20A UV−vis photodiode array detector (DAD), a SCL-20A system controller, and a Class-VP-LC workstation (Shimadzu, Kyoto, Japan).

Figure 1 shows the SS apparatus. The flotation column is a glass cylinder equipped with a sintered glass disk (G_4 porosity) at the bottom to generate small bubbles. The flotation column, with an inner diameter of 4.5 cm and a capacity of 400 mL, is designed for flotation. The sintered glass disk is connected to a N_2 gas cylinder equipped with a pressure regulator by a fine pressure needle valve for controlling the gas flow. In the separation procedure, sample solution is transferred to the flotation column and then a suitable organic solvent is added to the top of the sample solution with a volumetric pipet; after flotation, deionized water is added to the top of the cylinder to make the organic phase rise to the narrow section, which has an inner diameter of 2.0 cm and a capacity of 15 mL, from which it can be easily removed. Moreover, a soap-bubble flow meter is used to accurately measure the gas flow rate.

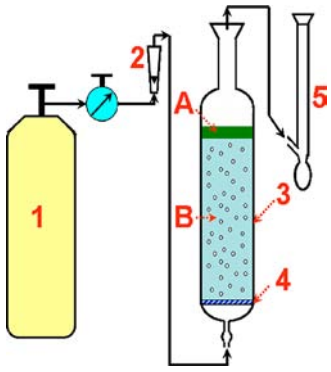

Figure 1. SS apparatus: (1) nitrogen cylinder, (2) pin-type flow meter, (3) flotation column, (4) sintered glass disk (G4 porosity), and (5) soap-bubble flow meter.

Chemicals and Solutions. The standards of polymer additives were shown in Table S1 of the Supporting Information. Butylated hydroxyanisole (BHA) (>99%), Chimassorb 81 (>98%), Irganox 1010 (>98%), 2,4-di-*tert*-butylphenol (DBP) (>99%), Irganox 1330 (>99%), Tinuvin 328 (>98%), and Tinuvin 326 (>98%) were purchased from Sigma-Aldrich (Steinheim, Germany). 2,6-di-*tert*-butyl-4-methylphenol (BHT) (>99%) was purchased from Alfa Aesar (Karlsruhe, Germany). Cyanox 2246 (>99%) and Irganox 1035 (>98%) were purchased from TCI (Shanghai, China). Isoamyl alcohol, *n*-octanol, *n*-hexane, *n*-butanol, sodium chloride, acetic acid, hydrochloric acid, and sodium hydroxide (Beijing Chemical Reagent Factory, China) were all of analytical reagent grade. Acetonitrile of HPLC grade was supplied by Dikma (Lake Forest, IL). Tetrahydrofuran of HPLC grade was supplied by J. T. Baker (Deventer, Netherlands). Water was supplied by Wahaha Pure Water (Zhejiang, China).

A standard mixture solution of 10 polymer additives (50 μg/mL) was prepared in a mixture of acetonitrile/tetrahydrofuran (1:1, v/v) and was used to optimize the separation conditions of SS.

The selected plastic beverage packages were acquired in the local supermarket (see Table S2 of the Supporting Information). In the migration tests, the plastic sample (approximately 12 dm^2) was put in 2 L of simulant. The migration test conditions were 10 days at 40 °C using the following beverage simulants:[13,26] distilled water for normal beverages and acetic acid solution (3%) for acidic beverages. An amount of 300 mL of aqueous beverage simulant was used for the concentration procedure of SS.

SS Procedure. In the optimization of SS parameters, 1.00 mL of the standard mixture solution was added in 300 mL of distilled water, and the aqueous solution was used for the procedure of SS. After separation and concentration, the flotation product was determined by HPLC. The influence of the sublation solvent (*n*-octanol, isoamyl alcohol, *n*-hexane, and *n*-butanol), solution pH (1, 2, 3, 4, 5, 6, 7, and 8), NaCl concentration [0.16% (0.5 g), 0.33% (1 g), 0.66% (2 g), 1.64% (5 g), 3.23% (10 g), 6.25% (20 g), 11.76% (40 g), 16.67% (60 g), and 21.05% (80 g)] in aqueous solution, nitrogen flow rate (10, 20, 30, 40, 50, 60, 70, and 80 mL/min), flotation time (10, 20, 30, 40, 50, 60, 70, 80, and 90 min), and light condition in the separation process (natural light and dark) were studied to yield the maximum separation efficiency.

For the analysis of plastic beverage packaging, an optimal method of SS was applied. Sodium chloride (80 g) was added in 300 mL of the beverage simulant, and the solution pH was adjusted to 3 with hydrochloric acid solution. The solution was transferred to the flotation column (as shown in Figure 1); the nitrogen gas flow rate was fixed at 60 mL/min; and then 10.00 mL of *n*-butanol was added on the top of the aqueous column. After 60 min, the flotation product (*n*-butanol phase) was transferred to a 10 mL volumetric flask and marked with *n*-butanol. Finally, the flotation product was determined by HPLC. All of the procedures of SS were performed in the dark and at room temperature.

In the separation and concentration step, the recovery of polymer additive was used to optimize the SS parameters. The recovery (R) can be calculated using the following equation:

$$R = \frac{C_t}{C_0} \times 100\% = \frac{10A_t}{A_0} \times 100\%$$

where C_t is the concentration of the organic phase after flotation and C_0 is the concentration of the organic phase supposing that 100% of the target compounds in the aqueous phase was floated into the organic phase. To simplify the calculation, the integral area of HPLC is used: A_t is the HPLC integral area of the organic phase after flotation, and A_0 is the HPLC integral area of the target compounds in the standard mixture solution.

HPLC Analysis. The 10 analytes were completely separated by a column 150 × 4.6 mm packed with Zorbax Eclipse XDB C18, 5 μm particle size (Agilent, Santa Clara, CA), maintained at 30 °C. The conditions of the chromatographic method were as follows: 55:45 acetonitrile/water to 85:15 acetonitrile/water in 4 min, to 100% acetonitrile within the next 21 min, and kept at this level for another 20 min. The detection wavelength was 276 nm. The injection volumes of flotation products and standard solutions were all 10 μL. All chromatographic analyses were performed at 30 °C.

Using the mentioned HPLC conditions, the 10 standards of polymer additives were separated with good resolution (Figure 2). The quantification was based on at least a nine-point external calibration graph obtained by plotting the individual peak areas against the concentration of calibration standards.[27,28]

RESULTS AND DISCUSSION

Optimization of SS Parameters. There are some restrictions for choosing a suitable sublation solvent. The sublation solvent should have high affinity with the polymer additives, be of low density and low volatility, and have low background interference in HPLC analysis. The effect of the sublation solvent (*n*-octanol, isoamyl alcohol, *n*-hexane, and *n*-butanol) on the recovery of SS was investigated in detail (Figure 2 and Figure S2 of the Supporting Information). The experimental results showed that all of the 10 polymer additives can be transferred into isoamyl alcohol and *n*-butanol but only 6 polymer additives can be observed in the HPLC chromatograms of *n*-octanol and *n*-hexane. Figure S2 of the Supporting Information indicated that the recoveries of 10 polymer additives were similar in isoamyl alcohol and *n*-butanol: isoamyl alcohol was higher than *n*-butanol for BHA, DBP, BHT, and Cyanox 2246; isoamyl alcohol was lower that *n*-butanol for Irganox 1035, Irganox 1010, and Irganox 1330; and for Chimassorb 81, Tinuvin 326, and Tinuvin 328, the difference was very small. However, in comparison to isoamyl alcohol, *n*-

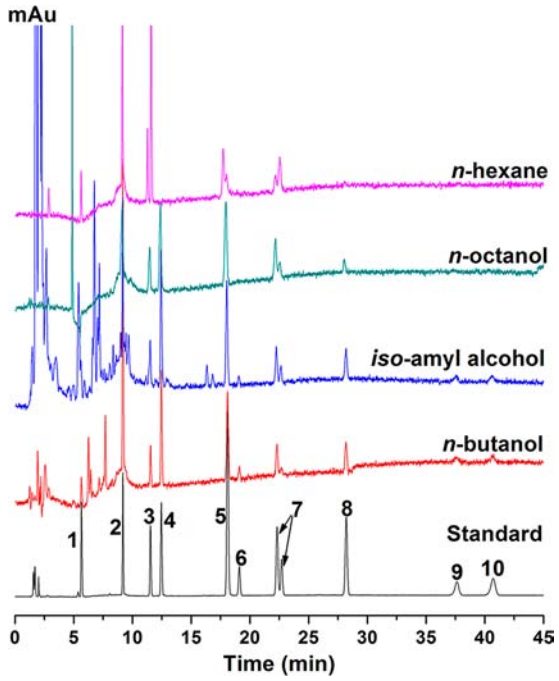

Figure 2. Effect of sublation solvents: pH, 7; m_{NaCl}, 0 g; flow rate, 40 mL/min; and flotation time, 30 min (1, BHA; 2, DBP; 3, BHT; 4, Cyanox 2246; 5, Chimassorb 81; 6, Irganox 1035; 7, Tinuvin 326; 8, Tinuvin 328; 9, Irganox 1010; and 10, Irganox 1330).

butanol gives lower background interference in the HPLC analysis. Therefore, *n*-butanol was selected as the sublation solvent.

In the adsorptive bubble separation technique, the solution pH is very important to increase the solubility of the target compound in the sublation solvent.[19,20] As shown in Figure 3,

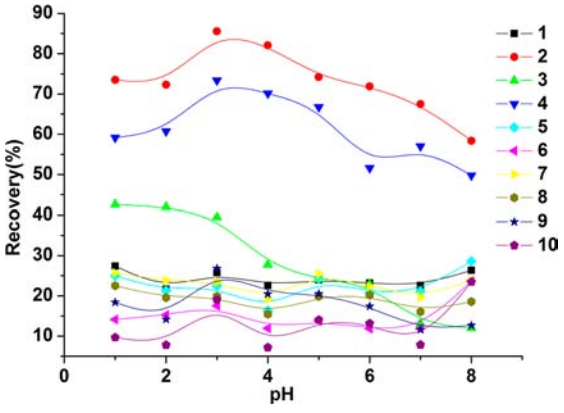

Figure 3. Effect of solution pH on SS: sublation solvent, *n*-butanol; m_{NaCl}, 0 g; flow rate, 40 mL/min; and flotation time, 30 min (1, BHA; 2, DBP; 3, BHT; 4, Cyanox 2246; 5, Chimassorb 81; 6, Irganox 1035; 7, Tinuvin 326; 8, Tinuvin 328; 9, Irganox 1010; and 10, Irganox 1330).

the solution pH significantly influenced the recovery of DBP, BHT, and Cyanox 2246: the maximum value was observed at pH 3−4 for DBP and Cyanox 2246 and pH 1−3 for BHT. Because the phenolic hydroxyl groups cannot ionize at low solution pH, the target molecules can dissolve more easily into the organic phase. However, the solution pH could almost not affect the other six polymer additives. Because of the steric effect of the big molecule (Irganox 1010, Irganox 1330, and Irganox 1035) and the intramolecular hydrogen bond (see Figure S3 of the Supporting Information), the phenolic hydroxyl groups of these polymer additives do not easily release a hydrogen ion. In the present work, pH 3 was selected and applied in the next few experiments.

The solubility in water is a problem for the sublation solvent of *n*-butanol (7.7% by weight, 20 °C), although it is the best sublation solvent. In the normal experiments, *n*-butanol should be continuously added to the sublation column to maintain a suitable volume of the *n*-butanol phase on the top of the aqueous solution. In this section, NaCl was added to reduce the *n*-butanol solubility in water, and the effect of NaCl addition on the consumption volume of *n*-butanol was shown in Figure S4 of the Supporting Information. With the increase of NaCl addition, the consumption volume of *n*-butanol was significantly reduced. When the addition was more than 60 g in 300 mL of the aqueous solution, the consumption of *n*-butanol tended to balance (approximately 12−13 mL). Moreover, NaCl addition can also increase the recovery of polymer additives (Figure 4), because of the reduction of solubility in the aqueous

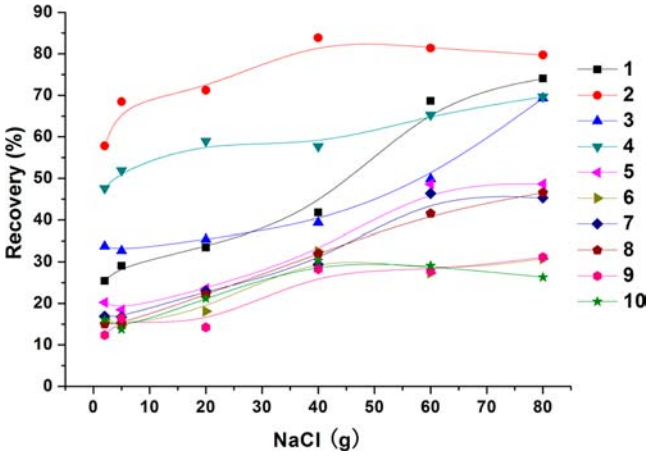

Figure 4. Effect of NaCl addition on SS: sublation solvent, *n*-butanol; pH, 3; flow rate, 40 mL/min; and flotation time, 30 min (1, BHA; 2, DBP; 3, BHT; 4, Cyanox 2246; 5, Chimassorb 81; 6, Irganox 1035; 7, Tinuvin 326; 8, Tinuvin 328; 9, Irganox 1010; and 10, Irganox 1330).

phase. The maximum recoveries were obtained with the NaCl addition of 60−80 g in the aqueous phase, which was similar to the effect of NaCl addition on the consumption volume of *n*-butanol. According to the experimental results, 80 g of NaCl was added to 300 mL of aqueous solution.

The gas flow rate plays an important role in the SS process: as the bubbles rise through the gas diffuser, the hydrophobic analytes are adsorbed on the gas−liquid interface and then extracted into the organic phase on the surface of the sample solution. Generally, the rate of gas−liquid interfacial area generation can be increased by generating smaller bubbles via a gas diffuser with smaller porosity or by increasing the gas flow rate. [25] As shown in Figure 5, the recoveries increased with the rise of the flow rate and the best nitrogen flow rate was observed at 60 mL/min. However, it is recommended that too high of a gas flow rate should be avoided because of a turbulent mixing at the solvent−aqueous solution interface. Such a mixing can promote the re-dissolution of the analytes in the aqueous phase. At the same time, *n*-butanol can also easily dissolve into the aqueous phase at a high nitrogen flow rate.

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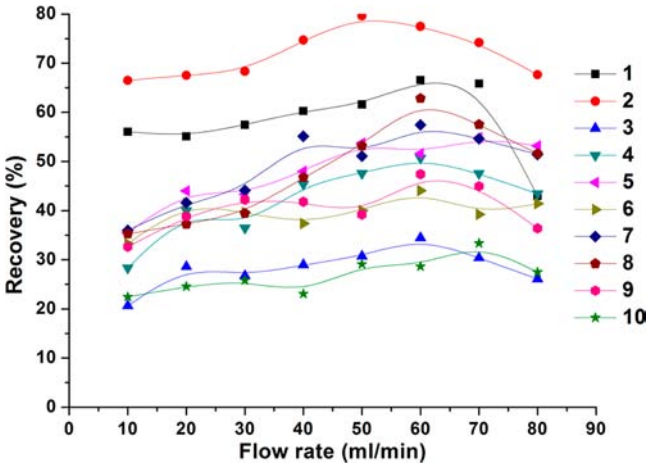

Figure 5. Effect of the nitrogen flow rate on SS: sublation solvent, *n*-butanol; pH, 3; m_{NaCl}, 80 g; and flotation time, 30 min (1, BHA; 2, DBP; 3, BHT; 4, Cyanox 2246; 5, Chimassorb 81; 6, Irganox 1035; 7, Tinuvin 326; 8, Tinuvin 328; 9, Irganox 1010; and 10, Irganox 1330).

Figure S5 of the Supporting Information gives the linear relationship between the consumption volume of *n*-butanol and the nitrogen flow rate. Therefore, the nitrogen flow rate could be fixed at 60 mL/min in all of the subsequent experiments.

As shown in Figure 6, the recoveries of polymer additives increased with an increasing the flotation time. When the sublation time was ≥60 min, the recoveries reached their highest values and basically remained constant because of the achievement of the thermodynamic equilibrium. However, the long separation time may lead to the decomposition of some polymer additives, and the recoveries will be reduced. Moreover, the consumption volume of the sublation solvent is also linearly increased with the increase of the flotation time (see Figure S6 of the Supporting Information). Therefore, the sublation time could be fixed at 60 min in this work, and the consumption of *n*-butanol was less than 14 mL.

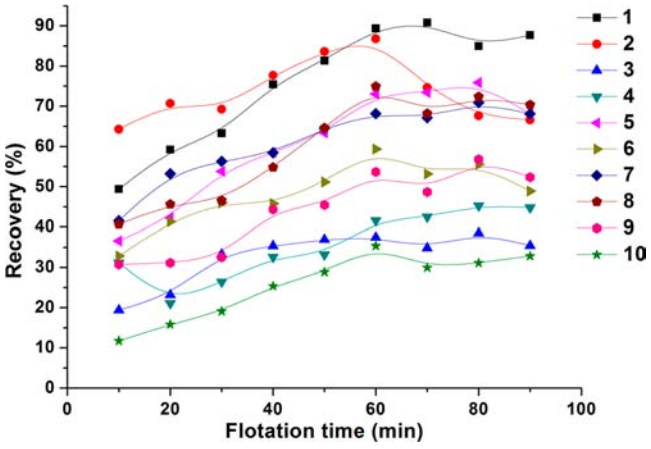

Figure 6. Effect of the sublation time on SS: sublation solvent, *n*-butanol; pH, 3; m_{NaCl}, 80 g; and flow rate, 60 mL/min (1, BHA; 2, DBP; 3, BHT; 4, Cyanox 2246; 5, Chimassorb 81; 6, Irganox 1035; 7, Tinuvin 326; 8, Tinuvin 328; 9, Irganox 1010; and 10, Irganox 1330).

The decomposition of some polymer additives (Figure 6) reminded us to study the effect of the light condition in the SS process. In this section, the separation process was performed in a black flotation column and the results were compared to the normal operation (see Figure S7 of the Supporting Information). It is obvious that the recoveries in the dark are higher than the normal recoveries. Therefore, the separation process of SS should be carried out in the dark.

On the basis of the above experiments, the optimal conditions of SS are summarized as follows: *n*-butanol as the sublation solvent, pH 3, 80 g of NaCl in 300 mL of aqueous solution, nitrogen flow rate of 60 mL/min, and flotation time of 60 min. Furthermore, all of the operations of SS were carried out in the dark.

Performance of the SS–HPLC Method. To evaluate the matrix effect of the simulants, a comparison between calibration curves obtained from standards prepared in pure solvent and calibration curves constructed using some simulants spiked with standards was performed. It was observed that the HPLC responses were nearly equivalent in both cases. The regression equations of the SS–HPLC method were obtained using the nine-point concentration of the standard as the abscissa and the integral area of the chromatogram peak as the vertical coordinate. It is shown in Table 1 that good linearity was in the range from 3.33 to 666.67 ng/mL for the 10 analytes, with the correlation coefficient greater than 0.99. The limits of detection (LODs) and the limits of quantification (LOQs) were calculated according to the directives of the International Union of Pure and Applied Chemistry (IUPAC),[29] taking LOD = $3S_B/b$ and LOQ = $10S_B/b$, where S_B and b are the signal of the blank measurement and the slope of the calibration curve, respectively. The LOD of the SS–HPLC method was in the range from 0.34 to 1.25 ng/mL, and the LOQ was in the range from 1.13 to 4.15 ng/mL. Because of the high concentration coefficient of SS, the LOD and LOQ values of SS–HPLC were better than those in the previous reports.[7−10,12,13,18] Moreover, in comparison to the conventional pretreatment techniques (liquid–liquid extraction, ultrasonic extraction, solid-phase

Table 1. Regression Data, LOQs, and LODs for 10 Compounds Analyzed by HPLC–DAD

compound	regression equation ($y = ax + b$)	R^2	linear range (ng/mL)	LOD (ng/mL)	LOQ (ng/mL)
BHA	$y = 66.91x + 653.29$	0.9993	6.67–666.67	1.06	3.54
DBP	$y = 64.37x + 1443.87$	0.9980	3.33–666.67	0.42	1.39
BHT	$y = 72.80x + 2254.34$	0.9989	3.33–666.67	0.65	2.15
Cyanox 2246	$y = 203.91x + 5478.56$	0.9995	3.33–666.67	0.34	1.13
Chimassorb 81	$y = 205.57x + 4591.98$	0.9979	3.33–666.67	0.47	1.56
Irganox 1035	$y = 35.43x + 685.51$	0.9983	3.33–666.67	0.65	2.17
Tinuvin 326	$y = 89.33x + 1474.43$	0.9984	3.33–666.67	0.45	1.50
Tinuvin 328	$y = 100.28x + 2824.72$	0.9972	6.67–666.67	1.25	4.15
Irganox 1010	$y = 34.35x + 1235.01$	0.9974	3.33–666.67	0.56	1.86
Irganox 1330	$y = 49.01x + 1399.08$	0.9994	6.67–666.67	0.90	3.00

Table 2. Precision of the SS−HPLC Analytical Method (n = 5)

compound	concentration (ng/mL)	RSD (%)	compound	concentration (ng/mL)	RSD (%)
BHA	20, 30, and 40	2.88, 2.98, and 1.17	Irganox 1035	20, 30, and 40	6.24, 5.08, and 4.81
DBP	20, 30, and 40	4.36, 6.75, and 3.82	Tinuvin 326	20, 30, and 40	4.77, 1.31, and 2.30
BHT	20, 30, and 40	2.19, 3.98, and 4.69	Tinuvin 328	20, 30, and 40	5.85, 6.66, and 3.13
Cyanox 2246	20, 30, and 40	5.38, 2.15, and 3.53	Irganox 1010	20, 30, and 40	4.86, 3.56, and 1.01
Chimassorb 81	20, 30, and 40	5.42, 3.63, and 6.12	Irganox 1330	20, 30, and 40	3.71, 3.52, and 3.85

Table 3. Accuracy of the SS−HPLC Analytical Method (n = 3)

compound	concentration (ng/mL)	recovery (%)	RSD (%)	compound	concentration (ng/mL)	recovery (%)	RSD (%)
BHA	20	97.67	10.01	Irganox 1035	20	90.03	7.74
	30	98.05	8.76		30	98.57	9.89
	40	100.06	9.42		40	101.69	7.10
DBP	20	97.43	10.34	Tinuvin 326	20	89.34	4.28
	30	96.64	9.76		30	91.42	5.27
	40	99.79	10.12		40	93.98	2.16
BHT	20	96.98	10.38	Tinuvin 328	20	95.18	6.20
	30	91.20	7.29		30	95.81	7.18
	40	88.73	7.46		40	94.40	7.68
Cyanox 2246	20	103.79	9.83	Irganox 1010	20	99.83	10.29
	30	106.43	9.66		30	98.30	9.58
	40	107.65	8.21		40	97.89	8.77
Chimassorb 81	20	106.35	4.85	Irganox 1330	20	100.38	9.76
	30	101.34	4.36		30	99.38	10.55
	40	102.38	4.97		40	101.79	7.69

Table 4. Contents (mg/kg) of 10 Compounds in 17 Commercial Beverage Packages (n = 3)

sample	BHA	DBP	BHT	Cyanox 2246	Chimassorb 81	Irganox 1035	Tinuvin 326	Tinuvin 328	Irganox 1010	Irganox 1330
1	nd[a]	1.46	nd	nd	nd	1.85	nd	2.01	nd	0.29
2	16.19	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	1.11	0.86	nd	nd	nd	<LOQ	nd	nd	nd	nd
4	nd	nd	nd	7.33	nd	3.97	nd	<LOQ	nd	nd
5	31.15	nd	nd	nd	nd	nd	nd	nd	nd	nd
6	28.49	nd	nd	nd	nd	nd	nd	nd	nd	nd
7	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
8	28.63	nd	nd	nd	nd	nd	nd	nd	nd	nd
9	48.65	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
11	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
12	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
13	210.80	25.31	nd	nd	nd	nd	nd	nd	nd	nd
14	nd	nd	nd	nd	nd	92.73	20.46	13.88	nd	7.63
15	14.63	nd	nd	nd	nd	nd	nd	nd	nd	nd
16	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
17	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

[a]nd = not detected.

extraction, and solid-phase microextraction), SS also gave some special advantages, such as a soft separation process and simple operation.

The precision of the SS−HPLC method was determined by beverage simulants spiked with polymer additives at three different concentration levels of the standard mixture (20, 30, and 40 ng/mL). The precision for the 10 analystes was described as the relative standard deviation (RSD), and the test results are given in Table 2. The overall precision in simulants ranged from 1.01 to 6.75%. The accuracy experiment was carried out by determining the recovery of 10 polymer additives in the beverage simulants spiked at different concentration levels. The data in Table 3 show that the recoveries for the 10 analytes were in the range from 88.73 to 107.65% with RSDs from 2.16 to 10.55%.

Application to Real Samples. The established analytical method was applied to determine plastic beverage packaging (Table 4). Of all 17 samples, BHA was found in 8 samples with the content range of 1.11−210.80 mg/kg; DBP, Irganox 1035, and Tinuvin 328 were detected in 3 samples with the contents of 0.86−25.31, 1.85−92.73, and 2.01−13.88 mg/kg, respectively; Irganox 1330 was found in sample 1 (0.29 mg/kg) and sample 14 (7.63 mg/kg); Cyanox 2246 and Tinuvin 326 were observed in only 1 sample; and BHT, Chimassorb 81, and Irganox 1010 were not detected in the 17 samples. To confirm the accuracy of the analysis data for the real samples, a series of recovery experiments were performed for each sample (n = 3)

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and the results were satisfied with the recovery range from 80 to 120%.

On the basis of the above results, the developed SS−HPLC method can ensure the confirmation and simultaneous analysis of 10 polymer additives at a low concentration level (ng/mL) for the studied plastic beverage packaging.

In the present paper, a novel and effective pretreatment technique, SS, was applied to concentrate trace levels of polymer additives in simulants of plastic beverage packaging. Using the adsorptive bubble separation technique, a qualitative and quantitative method of SS−HPLC was successfully established for the simultaneous determination of polymer additives in plastic beverage packaging. The method was proven to be of good linearity, precision, and accuracy. The LODs and LOQs were in the range of 0.34−1.25 and 1.13−4.15 ng/mL, respectively, for 10 different analytes. Recoveries in the range of 88.73−107.65% with RSDs of 2.16−10.55% were obtained. According to refs 13 and 26, the SML additives of four compounds were reported. The developed method may be used to control the food safety and give basic data for the previous legislation improvement.

■ ASSOCIATED CONTENT

Supporting Information

Polymer additives (Table S1), commercial beverage packages and corresponding simulants (Table S2), chemical structures of 10 polymer additives (Figure S1), comparison of separation efficiency for different sublation solvents (Figure S2), intramolecular hydrogen bonds in Tinuvin 326, Tinuvin 328, and Chimassorb 81 (Figure S3), effect of NaCl addition on the consumption volume of *n*-butanol (Figure S4), effect of the nitrogen flow rate on the consumption volume of *n*-butanol (Figure S5), effect of the sublation time on the consumption volume of *n*-butanol (Figure S6), and effect of the light condition on SS ($n = 3$) (Figure S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ ABBREVIATIONS USED

SS, solvent sublation; HPLC, high-performance liquid chromatography; SS−HPLC, solvent sublation followed by high-performance liquid chromatography; LOD, limit of detection; LOQ, limit of quantification; RSD, relative standard deviation; SML, specific migration levels

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