IOP Conference Series: Earth and Environmental Science

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To cite this article: Genrong Li *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **446** 032081

Rapid determination of bisphenol A in environmental water by solid phase extraction-ultra performance convergence chromatography

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Abstract. A rapid method based on solid phase extraction-ultra performance convergence chromatography was established for the determination of bisphenol A (BPA) in environmental water. The chromatographic conditions and solid phase extraction conditions were investigated, and the rapid and effective analysis of BPA could be achieved in 4 min. The results showed that the method has a good linearity with BPA in the range of 0.20-100 mg/L with correlation coefficient (R^2) of 0.9996. Furthermore, the limit of detection (LOD) was 0.01 mg/L. The spiked recovery (R) and relative standard deviation (RSD) were 89.7%~109.2% and 2.78%~4.66%, respectively. The method is rapid, simple, accurate and reliable, which can provide technical reference for the detection of BPA in environmental water.

1. Introduction

Bisphenol A (BPA) (2,2-bis[4-hydroxyphenyl] propane) is an important raw material for the production of polycarbonate, epoxy resin and other polymers, which is widely applied in all kinds of plastic products [1-3]. BPA is a typical environmental estrogen, which can affect human metabolic process and has reproductive toxicity and carcinogenicity [4-9]. According to the investigation, one of the important ways of BPA entering human body is tap water. In addition, the byproduct of BPA produced in the disinfection process of tap water has a stronger endocrine disrupting effect. Therefore, improving the detection technology of BPA possesses great significance to human health and ecological environment.

At present, the main detection methods for BPA include high performance liquid chromatography (HPLC) [11-13], liquid chromatography-mass spectrometry (LC-MS) [14,15] and gas chromatography-mass spectrometry (GC-MS) [16-18]. Due to the low content of BPA in the environment, water samples are usually separated and enriched before analysis. At present, solid phase extraction is more commonly used because of its relatively simple operation. However, the analysis time for BPA is usually greater than 10 min.

In order to save analysis time and improve detection efficiency, this work employed the solid phase extraction-ultra performance convergence chromatography to detect BPA in environmental water. The method has the advantages of rapid analysis, simple operation, good recovery and high accuracy, which can provide technical support for the daily detection of BPA in water samples.

2. Experimental and Methods

2.1 Materials and reagents

BPA was supplied from Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade methanol, isopropanol and acetonitrile were obtained from Merck (Darmstadt, Germany). HPLC grade dichloromethane, ethyl acetate and n-hexane were purchased from Tedia (Ohio, USA).

2.2 Instruments and equipment

ACQUITY UPC^2 ultra performance convergence chromatography (Waters, USA); N-EVAP-112 nitrogen blower (Organomation, USA); BILON-2000CT ultrasonic cleaner (Bilang, Shanghai).

2.3 Methods

2.3.1 Chromatographic conditions. The analysis was carried out with ACQUITY UPC^2 Torus DIOL column with 150 × 30 mm with 1.7 μm particles at temperature of 35°C. The mobile phase was a co-solvent of supercritical CO_2 and methanol. The detection wavelength was set at 220 nm and the back pressure was performed at 1800 psi. The elution gradient of mobile phase was 0~1 min, 5%~9% B; 1~2 min, 9%~10% B; 2~2.5 min, 10%~20% B; 2.5-5 min, 20% B; 5~5.5 min, 20%~5% B. The flow rate was maintained at 1.3 mL/min.

2.3.2 Preparation of standards. Different concentrations of BPA were prepared for constructing calibration curve. Standard substance of 10.0 mg was accurately weighed to a volumetric flask, after that, the substance was dissolved in methanol and diluted to 10 mL to obtain a standard liquid with concentration of 1000 mg/L. Standard working solution of 0.2~100.0 mg/L was prepared with methanol by stepwise dilution method.

2.3.3 Method validation. Method linearity was evaluated at different concentration of BPA standard in the range of 0.2-100.0 mg/L. According to the requirements of ICH guidelines, the precision was assessed at high, medium and low concentration levels (0.2, 50.0 and 100.0 mg/kg) in seven replicates. The LODs were calculated based on 3 times of signal-to-noise (S/N) ratio.

2.3.4 Pretreatment of sample. The water sample firstly filtered with a 0.45 μm membrane to remove parts of impurities, then purified by HLB solid phase extraction column, and the eluent dried with nitrogen flow at 45°C. Lastly, dissolved the residue with methanol and diluted to volume to 1.0 mL for UPC^2 analysis.

3 Results and Discussion

3.1 Optimization of chromatographic conditions

The chromatographic column is the key factor for influencing the retention ability of the target substance. The effects of different chromatographic column types (ACQUITY UPC^2 Torus DIOL, ACQUITY UPC^2 Torus DEA, ACQUITY UPC^2 Torus 1-AA and ACQUITY UPC^2 2-PIC) on the retention ability of BPA were firstly investigated. In addition, the effects of organic solvents (methanol, isopropanol and acetonitrile), column temperatures and system back pressures on the peak shape and analysis time of BPA were compared. It was found that the peak shape of BPA was the most symmetrical on Torus DIOL chromatographic column with methanol as modifier at temperature of 35°C and back pressure of 1800 psi. The efficient detection of BPA could be realized within 4 min. The optimal chromatographic diagram was shown in Figure 1.

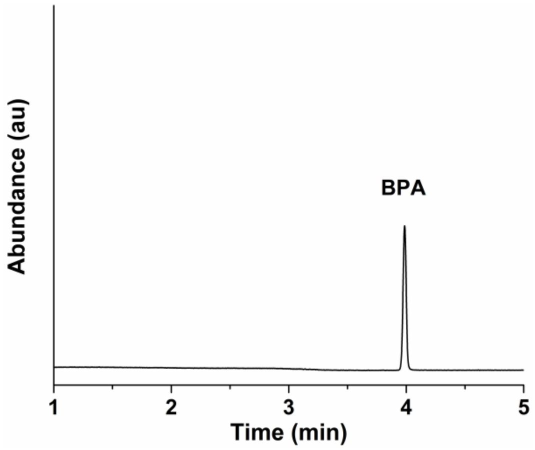

Fig. 1. Chromatogram of standard solution of BPA

3.2 Optimization of purification conditions

The effects of solid phase extraction columns (Florisil, C18 and HLB) on the recovery of BPA in water samples were investigated, and the results were shown in Figure 2. It was found that BPA was lost seriously during the elution process with Florisil column, resulting in less residual BPA in eluent and a relatively low recovery rate (<60%). The recovery of BPA tested on C18 column was more than 75%, while the most satisfying extraction effect was observed on HLB column, which could effectively eliminate the interference of impurities in water sample to BPA, and the recovery was no less than 88%. Therefore, HLB column was the optimal selection for solid phase extraction purification.

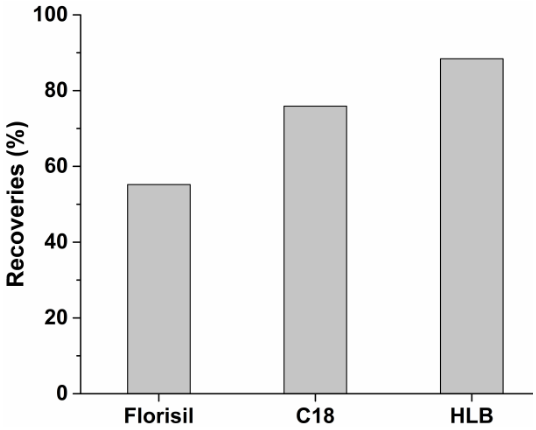

Fig. 2. Effect of solid phase extraction columns on the recoveries of BPA

3.3 Method validation

The samples were injected at a concentration of 0.2, 5.0, 20.0, 50.0, 80.0 and 100.0 mg/L, respectively, and quantified by external standard method. The chromatographic peak area Y of each substance was linearly returned to the mass concentration X. The results exhibited a good linearity between 0.05~100 mg/L, and the correlation coefficient was 0.9996. The standard solutions with high, medium and low concentration were severally added in blank water samples, and the detection limit (LOD) calculated according to 3 times of signal-to-noise ratio (S/N=3) was 0.01mg/L. The spiked recoveries and relative standard deviations (RSDs) were respectively in the range of 89.7%~109.2% and 2.78%~4.66%, suggesting that the method has good recovery and precision, which can satisfy the actual testing requirements.

Table 1 Recoveries and relative standard deviations of BPA at three spiked levels

Spiked level / (mg/L)	Recovery / %	RSD / %
0.2	109.2	4.66
50	89.7	3.05
100	98.6	2.78

3.4 Testing of environmental water and tap water actual sample

In the experiment, three environmental water samples and two tap water samples were selected. The water samples of 1 L volume were taken for enrichment first, then 10 mg/L standard solution was added to the sample to test the spiked recovery. As shown in Table 2, the experimental results presented that a certain amount of BPA was observed in all environmental water samples and one tap water sample, and the concentrations of BPA were ranged from 0.125~0.337 mg/L, indicating that the environmental water was widespread polluted, although the concentration is not high, it should be brought to the forefront.

Table 2 Contents and recoveries of BPA in real water samples

Samples	Contents /(mg/L)	Recovery / %
environmental water-1	0.186	92.7
environmental water-2	0.337	96.4
environmental water-3	0.204	103.6
tap water-1	—	93.1
tap water-2	0.125	107.8

"—" indicate below the LOD.

4 Conclusion

In the present work, a rapid method based on solid phase extraction-ultra performance convergence chromatography was developed for the determination of BPA in environmental water. By investigating the influence of chromatographic methods and purification conditions on the detection results, the rapid and effective detection of BPA can be achieved within 4 min under the optimal conditions. The recovery, precision and other technical indicators can meet the actual testing requirements. The method has the advantages of simple operation, rapid analysis, low cost and high accuracy, which can provide technical support for daily analysis of BPA in environmental water.

Acknowledgments

This work was funded by Chongqing scientific research institute performance incentive and guidance special project (cstc2018jxj100007).

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