Parabens analysis in cosmetics by ultrasonic extraction coupled with HPLC detection

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Keywords: parabens; daily cosmetics; ultrasonic extraction; HPLC

Abstract. Parabens extracted from five kinds of daily cosmetics by ultrasonic extraction were detected by high performance liquid chromatography. The optimal extraction solvent was dichloromethane. And the extraction time was 15 min. The linear range was from 0.01 to 50.0 mg/L. Parabens were found in 3 kinds of samples. The spiked recoveries of paraben in five kinds of samples were 96.36%-110.96% with the relative standard deviations of 0.3%-6.6%. The proposed method is fast and accurate. It can be used for the detection of parabens in daily cosmetics.

Introduction

Parabens are widely used as anti-microbial agent in food, medicine, cosmetics and toiletries [1,2]. Parabens have a broad spectrum and excellent antisepsis capabilities, which are commonly used as preservatives in cosmetics. It is also an internationally recognized antiseptic [3]. The antimicrobial activity will improve with the increase of the alkyl chain length. But the solubility will decrease correspondingly [4]. In addition, more than two kinds of the parabens are often used at the same time to achieve synergies [5]. Personal care products, such as hand cream, facial cleanser and moisturizer, are widely used in people's daily lives. But parabens may be added into these products during the production. It can be absorbed through the skin into the body.

Routledge et al firstly discovered the estrogenic activity of parabens [6]. Darbre et al reported the concentrations of parabens in breast cancer tumor tissues of 20 patients [7]. Apparently the parabens were one of the reasons to cause breast cancer [8]. Moreover, it could produce inhibition effect to mitochondrial respiratory capacity and influence reproductive potential of humanity [9]. Therefore, parabens should be strictly controlled within limitation. *Hygienic standard for cosmetics* (2007 Edition, China) restricts the parabens preservatives limited dose. The upper limit of mass percentage of single ester was 0.4% and the upper limit of mixed esters was 0.8%. In this paper, a fast and sensitive detection of parabens method was developed to detect parabens in personal daily cosmetic by ultrasonic extraction coupled with HPLC analysis.

Materials and methods

Apparatus and reagents.

Dionex Ultimate 3000 HPLC system (Dionex Corporation, USA) with a DAD detector, autosampler and C18 column (J & K Scientific LTD, 5 μm, 4.6 mm × 250.0 mm); PS-20 Jie Kang ultrasonic cleaning agents (ultrasonic Equipment Co., Ltd. Dongguan Jie Kang).

Methyl paraben, ethyl paraben, propyl paraben and butyl paraben were purchased from Aladdin LTD. Methanol and acetonitrile were HPLC grade. The other reagents were analytical grade.

Sample preparation.

0.10g sample was dissolved by 10 mL solvent. Then it was extracted for 15 min by ultrasonic extraction. Then the supernatant was filtered through 0.45 μm membrane. The filtrate was injected for HPLC analysis.

Chromatographic conditions.

The mobile phase was 60% acetonitrile solution. The flow rate was 1.0 mL/min. The detection wavelength was 254 nm. The column temperature was set at 30 ℃. The injection volume was 20

μL.

Results and discussion

Optimization of the extraction conditions.
1) Optimization of the extraction solvent.
0.10 gnourishing & hydrating toner sample was dissolved in 10mLextraction solvent. The extraction solvents were tested with carbon tetrachloride, methanol, dichloromethane, ethanol, and acetone, respectively. Each sample was extracted 15 min by ultrasonic bath. After extraction, 1mL supernatant was filtered with membrane and then blown with nitrogen to near dryness. The residue was dissolved in 1 mL methanol. The solution was injected for HPLC analysis. The results were shown in Fig. 1. The best result could be obtained when the extraction solvent was dichloromethane. And methyl paraben could be determined in the sample. The concentration was 11.07 mg/L. Therefore, the dichloromethane was chosen as the optimal extraction solvent.
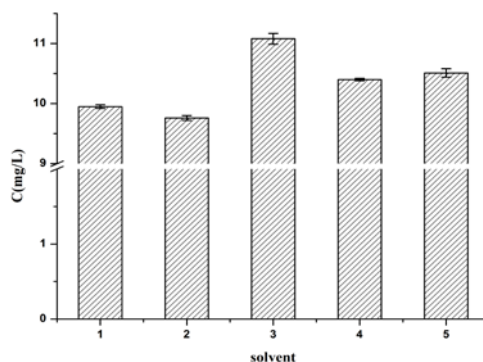

Fig. 1 Effects of different extraction solvents on extraction efficiency
1: carbon tetrachloride; 2: methanol; 3: dichloromethane; 4: Ethanol; 5: acetone

2) Optimization of extraction time.
0.10 g Nourishing & Hydrating Toner sample was dissolved in 10 mL dichloromethane. Ultrasonic time was set 5,10,15,20 and 25 min, respectively. The analysis results were shown as Fig. 2. With the increasing of ultrasonic time, the extraction efficiency of methyl paraben was improved and the extraction equilibrium was achieved at 15 min. So, the extraction time was selected as 15 min.
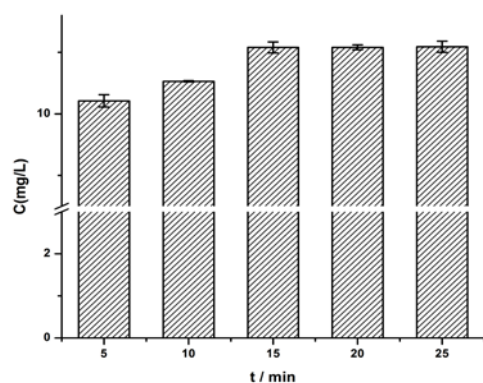

Fig. 2 Effects of extraction time on extraction efficiency

Analytical method.
The parabens standard solution was prepared in methanol solution. The concentrations were of 0.01, 0.1, 1.0, 5.0, 10.0, 25.0, 50.0 mg/L. The linear equations for four analytes were listed in Table 1. The results showed that four kinds of parabens had a good linear relationship in the concentration of 0.01-50.0 mg/L.

Table 1 Linear equations of four paraben analytes

Analytes	Linear equations	Correlation coefficient (r)
methyl paraben	Y=2.09 X +0.06	0.9999
ethyl paraben	Y=2.04 X +0.13	0.9999
propyl paraben	Y=1.78 X +0.05	0.9999
butyl paraben	Y=1.75 X +0.02	0.9999

Real sample analysis.

Under the optimized conditions, five real samples of nourishing &hydrating toner, beauty &softening emulsion, men's facial cleanser, nourish hand cream, spearmint toothpaste, were extracted and analysized by HPLC. The results showed that methyl paraben in nourishing & hydrating tonerwas11.07 mg/L (RSD=3.9%, n=5), and methyl paraben and propyl paraben in the beauty & softening emulsion were 17.84 mg/L (RSD=1.5%, n=5) and 6.82 mg/L (RSD=5.7%, n=5), respectively; and methyl paraben in men's facial cleanser was 9.34 mg/L (RSD=3.4%, n=5). The contents were lower than the legislation of "*Hygienic Standard for Cosmetics*" (2007 edition, China). To further verify the reliability of the method, spiked recovery experiments were carried out on five samples. The spiked level was set at the level of 1.0 mg/L for four parabens in five samples. The recovery results were shown in Table 2. The recoveries of four parabens were between 96.36% and 110.96%. The relative standard deviations were between 0.3% and 6.6%. The chromatogram of nourishing & hydrating toner sample was shown as Fig. 3.

Table 2 Cosmetics of Four kinds of parabens recoveries

Daily cosmetics	Methyl paraben			Ethyl paraben			Propyl paraben			Butyl paraben		
	Found (mg/L)	Spiked (1.0 mg/L)		Found (mg/L)	Spiked (1.0 mg/L)		Found (mg/L)	Spiked (1.0 mg/L)		Found (mg/L)	Spiked (1.0 mg/L)	
		Recovery /%	RSD /%		Recovery /%	RSD /%		Recovery /%	RSD /%		Recovery /%	RSD /%
a	11.07	106.15	5.9	0	107.28	2.8	0	109.82	0.7	0	107.32	2.1
b	17.84	108.16	4.9	0	103.52	1.1	6.82	106.05	6.6	0	101.44	3.5
c	9.34	96.36	2.1	0	109.58	1.6	0	109.87	0.3	0	110.01	1.5
c	0	109.25	0.6	0	110.43	1	0	109.65	0.7	0	109.34	1.9
e	0	109.51	0.8	0	109.19	0.6	0	110.46	0.3	0	110.96	0.3

a: Nourishing & hydrating toner, b: Beauty & softening emulsion, c: Men's facial cleanser, d: Nourish hand cream, e: Spearmint toothpaste
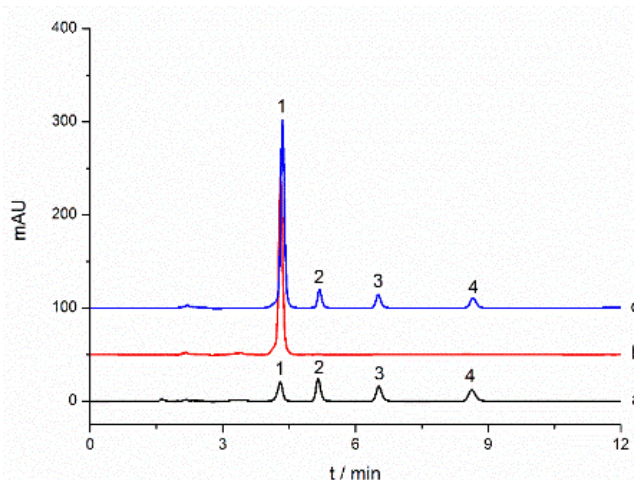

Fig. 3 HPLC analysis of nourishing & hydrating toner sample

a. 1.0 mg/L standard solution, b. sample by HPLC analysis directly, c. spiked sample by HPLC analysis, 1: methyl paraben, 2: ethyl paraben, 3: propyl paraben, 4: butyl paraben

Conclusions

A method of detected parabens in daily cosmetics by ultrasonic extraction coupled with high performance liquid chromatography was established. And it was used for parabens analysis in five daily cosmetic samples. Two parabens had been found in three daily cosmetic samples. The spiked recoveries of paraben in five samples were 96.36% -110.96%, and the relative standard deviations were 0.3%-6.6%. The method is simple and rapid. It is suitable for the analysis of parabens in daily cosmetics.

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