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Review

A review of the extraction and chromatographic determination methods for the analysis of parabens

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ABSTRACT

Parabens are a family of most widely used antimicrobial preservatives in food ingredients, cosmetic consumer products and pharmaceutical preparations. But several recent studies have cautioned that exposure to parabens may have more harmful consequences on animal and human health than what we realized previously, which made the analysis of parabens necessary. In this paper, we reviewed main sample preparation methods and chromatographic analysis methods proposed in formerly published works dealing with the analysis of parabens in different matrices. The sample preparation methods included ultrasonic assisted extraction, supercritical fluid extraction, pressurized liquid extraction, solid phase extraction, solid phase microextraction, liquid phase microextraction, dispersive liquid–liquid microextraction, stir bar sorptive extraction and matrix solid phase dispersion. The chromatographic analysis methods involved liquid chromatography, gas chromatography, and capillary electrophoresis.

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Abbreviations: UAE, ultrasonic assisted extraction; SFE, supercritical fluid extraction; RSD, relative standard deviation; PLE, pressurized liquid extraction; SPE, solid phase extraction; MWCNT, multi-walled carbon nanotube; MIP, molecularly imprinted polymer; MISPE, SPE using MIP as sorbens; SPME, solid phase microextraction; HS, headspace; LPME, liquid phase microextraction; DLLME, dispersive liquid–liquid microextraction; SBSE, stir bar sorptive extraction; PDMS, polydimethylsiloxane; MSPD, matrix solid phase dispersion; HPLC, high performance liquid chromatography; UV, ultraviolet; MS, mass spectrometry; DAD, diode array detector; MS/MS, tandem mass spectrometry; GC, gas chromatography; FID, flame ionization detection; CE, capillary electrophoresis; MEKC, micellar electrokinetic chromatography.

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1. Introduction

Alkyl esters of p-hydroxybenzoic acid, also known as parabens, are widely used as antimicrobial agents in food products, pharmaceutical preparations, cosmetic and toiletries consumer products [1,2]. This family of chemicals mainly includes methylparaben, ethylparaben, n-propylparaben, iso-propylparaben, n-butylparaben, iso-butylparaben and benzylparaben, and their $\log D_{\mathrm{ow}}$, $\mathrm{p}K_{\mathrm{a}}$ and aqueous solubility are shown in Table 1 [3]. It had been found that antimicrobial activity increased as the chain length of the ester group of paraben increased [4]. However, esters of longer alkyl chains are of limited applications due to their lower solubility in water [5]. To reach a satisfied activity, parabens are usually used as mixtures according to their antibacterial synergistic effect [6]. Among all parabens, methylparaben and propylparaben are often used together [7].

Parabens have been added to food for a very long time, and the use of parabens has steadily increased in many more food categories over the years. They are employed in several foods including processed vegetables, baked goods, fats and oils, seasonings, sugar substitutes, coffee extracts, fruit juices, pickles, sauces, soft drinks and frozen dairy products at concentrations between 450 and 2000 mg kg^{-1} [4].

Formerly, parabens were used to being considered as safe preservatives, because they can be rapidly absorbed and metabolized into p-hydroxybenzoic acid, which is less toxic than the parent compounds, and are therefore consumed in large quantities [8]. In order to reduce the harm of parabens to human health, parabens are regulated in several countries. European Union permits their use with a maximum concentration of 0.4% (w:w) for each one and total maximum concentration of 0.8% (w:w) for the mixtures in the finished cosmetic product (Cosmetic Directive 76/768/EEC) [9]. In Japan, the daily intake permitted for per person is 1.06 mg [10].

The popular use of paraben preservatives arises from their low toxicity, broad spectrum of antibacterial activity, chemical stability, worldwide regulatory acceptance, biodegradability and low cost [11]. However, several recent studies have cautioned that exposure to parabens may modulate or disrupt the endocrine system and thus may have harmful consequences on animal and human health than what we realized previously [12]. For example, parabens have been shown that they also exhibited estrogenic activity in addition to their antibacterial activity with the potential to alter either in a beneficial or harmful manner [13]. Besides, parabens were proved to have possibility to lead to breast cancer because of prolonged dermal expositions to deodorants which contained parabens [14]. Some recent studies have also reported adverse reproductive effects of parabens [15]. It can be seen from all these works that the analysis of parabens becomes very important and imperative under such circumstances.

In this paper, we presented a review of the most common sample preparation methods, including ultrasonic assisted extraction, supercritical fluid extraction, pressurized liquid extraction, solid phase extraction, solid phase microextraction, liquid phase microextraction, dispersive liquid–liquid microextraction, stir bar sorptive extraction and matrix solid phase dispersion, and chromatographic analysis methods, including liquid chromatography, gas chromatography, and capillary electrophoresis, which have been reported and used to analyze parabens. Some of methods used for the analysis of parabens are summarized in Table 2. Analytical procedures for the analysis of parabens with various techniques were shown in Fig. 1.

2. Sample preparation methods

Sample preparation is one of the most critical steps. In this step, the parabens are separated from the matrices and are preconcentrated to improve the selectivity, sensitivity, reliability, accuracy, and reproducibility of the analysis [16]. The traditional methods that were commonly used before, including Soxhelt extraction and heating under reflux, are generally operated with large amounts of organic solvents and long times. In order to realize effective and eco-friendly sample preparation, many emerging extraction technologies are becoming more and more popular. Sometimes, in the case of very dirty or highly complex samples, this step also includes a clean-up step to facilitate the analysis and prevent the deterioration of the chromatographic system and detector used. Moreover, sample preparation is the most labor-intensive and time consuming step and is also the main source of error of an analytical method [17].

2.1. Extraction methods

2.1.1. Ultrasonic assisted extraction

Ultrasonic assisted extraction (UAE) is recognized as an efficient extraction technique that dramatically reduces working times, increasing yields and often the quality of the extract [18]. Ultrasonic energy can enhance the extraction efficiency through induced cavitations that produce microenvironments with high pressures and high temperatures, so speeding up the removal of analytes from the matrices [19,20].

Recently, two works from the same laboratory using UAE in small columns [21,22] have been reported. In these two works, glass columns containing polyethylene frits placed at the end of the columns, the environmental solid samples and moderate acetonitrile were immersed in an ultrasonic water bath and two consecutive extraction steps of 15 min were carried out. Then the columns were placed in a vacuum manifold and the extracts were collected into graduated tubes. The main difference between two works was that the extracts obtained after UAE procedure in the former work were directly determined, while the extracts obtained after UAE procedure in the later work undergone a clean-up step before determination.

The main advantages of UAE are that:

- A wide range of solvents or solutions can be used.
- The solvents used for extraction can be collected by centrifugation or filtration easily.
- The method can be safely performed under general circumstance.

However, the method still consumes relatively long time and large volume of solvents.

2.1.2. Supercritical fluid extraction

In the supercritical fluid extraction (SFE), supercritical fluids (usually is $\mathrm{CO_2}$), which can diffuse easily through solid materials and can therefore realize faster extraction because of their low viscosity and relatively high diffusivity [23], are adopted as extraction media to remove various kinds of substances from distinct types of solid matrices since decades ago.