CHAPTER I

INTRODUCTION

1.1 Introduction

Parabens (alkyl esters of *p*-hydroxybenzoic acid) have been widely used as preservatives for many years in beverages, food, and pharmaceutical products and especially in cosmetic products. These compounds and their salts are used primarily for anti-microbial activities. Parabens become popular preservatives because of their biodegradability and stability in air and in solutions, efficiency in wider pH ranges, non-volatility, and other properties such as low cost, no color, resistance to hydrolysis, and their broad antimicrobial spectrum [1-7]. The antimicrobial activities of the parabens increase when the length of its alkyl chain increases but with decreasing solubility. Moreover, two or more parabens can often be used together to achieve synergistic effects; Methyl and Propyl paraben mixtures are the most commonly used [8, 9]. However, high doses of these compounds are dangerous for the customers they can cause allergic contact dermatitis [5, 10], produce inhibitory effects on mitochondrial respiratory capacity, and eliminate the human reproductive potential as well as promote breast cancer [6, 11, 12]. Therefore, the use of parabens has been limited by the European Economic Community (EEC); i.e. the maximum concentration allowed in cosmetics is 0.4% (w/w) for single paraben and up to 0.8 % (w/w) for their mixtures, and the maximum thresholds of paraben concentration in foodstuffs and pharmaceutical products are 0.1% (w/w) and 1% (w/w), respectively [13, 14].

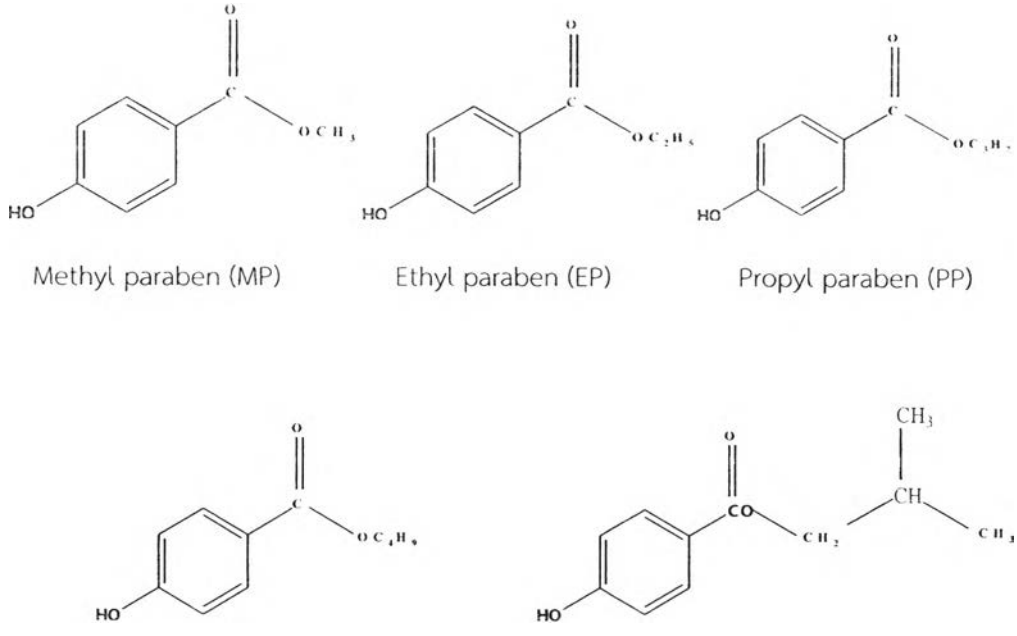

Figure 1.1 Structures of parabens in this work

Various analytical methods have been utilized for the determination of parabens, for instance, UV-spectroscopy coupled with high performance liquid chromatography (HPLC) [15-17], flame ionization detection (FID) in gas chromatography (GC) [18], mass spectrometry (MS) [11, 19]. Electrochemical detection (ECD) is an alternative and very attractive detection method for the determination of parabens because of its low cost, simplicity, fast analysis, portability and high sensitivity. A variety of working electrodes have been established for the detection of parabens, including molecularly imprinted polymers (MIPs) film on glassy carbon electrode [20], boron doped-diamond (BDD) electrode [21] and multi-wall carbon nanotubes (MWNTs) coupled with nafion modified glassy carbon electrode [22]. In this work, screen-printed carbon electrode (SPCE) was chosen as the working electrode due to its inexpensiveness and ease of preparation and modification. However, the use of a bare SPCE may be limited by its inadequate sensitivity. To improve the sensitivity, nanomaterials such as carbon nanotubes (CNTs), carbon nanofibers (CNFs) and carbon nanodots (CNDs), have been employed to modify the working electrodes and increase its surface area [23-25].

Graphene (G) is a monolayer, crystalline allotrope of carbon which is densely packed in a regular sp^2-bonded atom into a two dimensional honeycomb lattices. Graphene has been widely studied in different fields due to its good physical and chemical properties. Recently, graphene has become a popular nanomaterials in electrochemistry because it exhibits many desirable electrochemical properties such as large surface area, high electrical conductivity, and rapid electron transfer. Despite its numerous desirable properties, the uncontrolled agglomeration of graphene due to attractive van der waals forces can occur and result in its inhomogeneity [26-28]. Therefore, polyaniline (PANI) and polyvinylpyrrolidone (PVP) were additionally used to increase the dispersibility of graphene. PANI is an outstanding conducting polymer and it is widely used for electrode modification in electrochemical biosensors because of its excellent electrochemical properties, ease of synthesis and functionalization, high environmental stability, and low toxicity [23, 29]. In addition, It has been reported that using PVP can stabilize high concentration of graphene in any organic solvent [30]. For the fabrication of G/PVP/PANI modified SPCE, electrospraying was chosen because of its simplicity, homogeneity of droplet and inexpensiveness.

Recently, there has been reported that G/PVP/PANI nanocomposite-modified, paper-based biosensor was successfully developed for the determination of cholesterol in a complex biological fluid [31]. In addition, G/PANI nanocomposite modified SPCE was also effectively coupled with ultra-performance liquid chromatography (UPLC) system for the determination of eight sulfonamides (SAs) in shrimp. The sensitivity of eight SAs was higher than the unmodified electrode including BDD electrode [32].

1.2 Objective of the thesis

The aims of this work are to develop an inexpensive and sensitive electrode, G/PVP/PANI nanocomposite-modified SPCE, coupled with HPLC for separation and detection of parabens, and to apply the developed method for simultaneous determination of parabens in real samples, such as soft drink and cosmetic products.

1.3 Scope of the thesis

This research was separated into five parts. The first part is the fabrication and characterization of G/PVP/PANI nanocomposite-modified SPCE. The second part is cyclic voltammetry study to investigate the electrochemical behavior of ferri/ferrocyanide and parabens using the modified electrode. The third part is the separation part carried out by HPLC system for simultaneous determination of five parabens. The fourth part is the analytical performance of the proposed system. Finally, the application of this system for the simultaneous determination of five parabens in a soft drink and a cosmetic product (makeup remover) was investigated.