



# Development of a selective and sensitive voltammetric sensor for propylparaben based on a nanosized molecularly imprinted polymer–carbon paste electrode



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## ABSTRACT

The design and construction of a selective voltammetric sensor for propylparaben (PP) in cosmetics by using a molecularly imprinted polymer (MIP) as recognition element was introduced. The MIP was synthesized by using PP as template and methacrylic acid as functional monomer and then incorporated in the carbon paste electrode as PP sensor. The molecularly imprinted polymer–carbon paste electrode (MIP–CPE) showed very high recognition ability in comparison to non-imprinted polymer–carbon paste electrode (NIP–CPE). It was shown that electrode washing after PP extraction, led to enhanced selectivity, without noticeably decreasing the sensitivity. Some parameters affecting sensor response were optimized, and a calibration curve was then plotted using differential pulse voltammetric (DPV) technique. A dynamic linear range of 1 nM to 100 nM was obtained. The detection limit of the sensor was calculated to be equal to 0.32 nM. The imprinted electrode also displayed good selectivity for PP and selectivity coefficients were 2.29 and 1.66 for methylparaben (MP) and ethylparaben (EP) respectively. Structural analogs, such as phenol and p-hydroxybenzoic acid had almost no response. This sensor was used successfully for propylparaben determination in cosmetic sample.

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## 1. Introduction

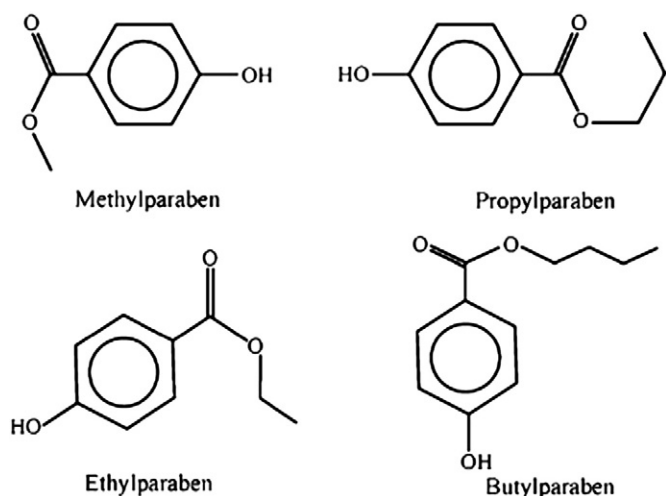
Parabens are a group of synthetic compounds used worldwide as preservative and antimicrobial agents in different products because of their broad antimicrobial spectra, good stability and non-volatility [1–4]. They are a group of homologous p-hydroxybenzoates (Scheme 1), normally including methylparaben (MP), ethylparaben (EP), propylparaben (PP) and butylparaben (BP) [5]. One or more kinds of parabens are found in all types of cosmetic products. Recent reports indicate that exposure to parabens modulates or disrupts the endocrine system and thus may have harmful consequences on animal and human health [6]. Therefore, The European Community with The Council Directive 76/768/EC have restricted paraben contents up to concentration of 0.4% (w/w) for a single ester or 0.8% (w/w) for ester mixtures, expressed as p-hydroxybenzoic acid content [7]. Taking the sample complexity into account, highly fast, simple and selective

methods are required for analyzing parabens. A number of methods including gas chromatography [8–10] high performance liquid chromatography (HPLC) and capillary electrophoresis [1,3,11–19], micellar electrokinetic chromatography [20] and mass spectrometry [21–24] or ultra performance liquid chromatography [25] have been used for the determination of parabens in different matrices. Nevertheless, only a few electroanalytical methods have been reported for the determination of parabens [26]. Electrochemical methods may offer certain advantages, such as requiring easier sample preparation, being less time-consuming and offering detection limit and dynamic range comparable to other analytical methods [27,28]. Molecular imprinting is a promising technique for the preparation of polymers which possess specific recognition sites. By means of a synthetic organic polymer matrix, the imprints of the template molecule are created in the polymer. After the template is eluted from the rigid polymer network, recognition sites complementary to the template molecule in shape and size can be obtained. A molecular imprinted polymer (MIP) has unique advantages over natural biological receptors in terms of physical and chemical stability, ease of preparation, low cost and application in harsh environmental conditions [29]. These materials are somewhat similar to biological specific receptors with respect to their high selectivity for the target molecule and their recognition mechanism [30]. Based on these favorable properties, the MIP has been successfully used in many fields, such as chromatographic separation [31,32], chiral separation [33], immunoassays [34,35], solid-phase extraction [36,37],

*Abbreviations:* PP, Propylparaben; MIP, molecularly imprinted polymer; MP, methylparaben; EP, ethylparaben; BP, butylparaben; MIP–CPE, molecularly imprinted polymer–carbon paste electrode; NIP–CPE, Non-imprinted polymer–carbon paste electrode; CPE, carbon paste electrode; CV, cyclic voltammetric; DPV, differential pulse voltammetric; HPLC, high performance liquid chromatography; SEM, scanning electron microscope; MAA, Methacrylic acid; EGDMA, Ethylene glycol dimethacrylate; AIBN, 2,2-azobisisobutyronitrile; IR, Infrared.

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Scheme 1. Chemical structures of parabens.

pharmaceutical analysis [38,39], and recognition of elements in chemical or biological sensors [40–43]. In this sense the construction of the first MIP sensor for the determination of the total amount of parabens in cosmetics has been reported by Fang et al. [44]. The development of a MIP sensor based on dual-templates (MP and PP) has been published as a second report for paraben detection [45]. It is reported that the affinity between MIP's receptors and template molecules has significant effect on the sensor's sensitivity and this affinity is inversely proportional to MIP's particle size [46]. Therefore the synthesis of micro- or nanosized MIP's particles is desirable to improve the sensitivity of the sensor. In the present work, a single template MIP with PP as template was synthesized and then incorporated in the carbon paste electrode (CPE) as propylparaben sensor. The proposed sensor that was constructed from nanosized MIP's particles improves the sensitivity of the electrode for low level monitoring of the PP. Furthermore, the selectivity of the PP sensor with respect to other parabens (MP and EP) was investigated. This sensor was used successfully for PP determination in cosmetic sample.

## 2. Experimental

### 2.1. Apparatus and chemicals

Electrochemical data were obtained with a three-electrode system using the Autolab electrochemical system (Eco-Chemie, Utrecht, The Netherlands) equipped with GPES and FRA 4.9 software. The unmodified carbon paste and modified CP electrodes (MIP–CPE or NIP–CPE) were used as the working electrode. A platinum wire and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. Infrared (IR) spectra (KBr) were recorded on ABB BOMEM, MB series. The surface morphology of modified electrodes was characterized with a scanning electron microscope (SEM) (Philips XL 30). Methacrylic acid (MAA), obtained from Sigma–Aldrich (Munich, Germany), was purified by passing it through a short column of neutral alumina, followed by distillation under reduced pressure. Ethylene glycol dimethacrylate (EGDMA), obtained from Fluka (Buchs, Switzerland), was distilled under reduced pressure in the presence of a hydroquinone inhibitor and stored at 4 °C until use. Parabens and 2, 2-azobisisobutyronitrile (AIBN) were supplied by Sigma–Aldrich (Munich, Germany) and used as received. Graphite fine powder extra pure was purchased from Fluka (Buchs, Switzerland). All other chemicals were of analytical grade and were purchased from Merck Company (Darmstadt, Germany).

### 2.2. Preparation of the molecularly imprinted polymer (MIP)

The MIP having PP recognition sites was designed and prepared by a thermal precipitation polymerization technique. General procedure to prepare imprinted polymer was as follows: the template molecule (0.1 mmol) was mixed with the selected functional monomer (methacrylic acid 0.4 mmol) in a 15.0 mL screw-capped glass vial followed by the addition of 10.0 mL of solvent mixture (66.5% V/V of acetonitrile in dimethyl sulfoxide) as polymerization solvent. The cross-linker EGDMA (2 mmol) and the initiator AIBN (0.1 mmol) were then added to the above solution. To remove dissolved oxygen, the solution was purged with high purity nitrogen (99.999%) for 5 min. Finally, the test tube was sealed under the nitrogen atmosphere and was then placed in a water bath at 60 °C for 24 h with occasional stirring. The resultant polymeric particles (<50 nm) were collected and the template molecule was extracted from the polymers with 50% (v/v) methanol/acetic acid mixture. The complete removal of template from MIP was tested using spectrophotometric technique. The reference non-imprinted polymers (NIPs) were prepared using the same procedure in the absence of template molecule.

### 2.3. Characterization of MIP

The resulting imprinted nanoparticles obtained from polymerization of the PP and methacrylic acid, with EGDMA as a cross-linking monomer, via precipitation polymerization method, were characterized by IR spectroscopy and scanning electron microscopy. In the IR spectra (Fig. s1), the absorptions due to carbonyl group ( $1733\text{ cm}^{-1}$ ), C–O stretch ( $1000\text{--}1100\text{ cm}^{-1}$ ), C–H stretch ( $2993\text{ cm}^{-1}$ ),  $\text{CH}_3$  and  $\text{CH}_2$  bends ( $1383$  and  $1452\text{ cm}^{-1}$ , respectively) were observed. It is interesting to note that the IR spectrum of unleached sample shows a peak in  $1000\text{--}1100\text{ cm}^{-1}$ . The absence of this peak in leached sample indicates the breaking of ester C=O stretch group due to breaking of hydrogen bonds and removal of template from polymeric structure. The morphology of the MIP produced by the precipitation method was assessed by scanning electron microscopy, and the SEM patterns are shown in Fig. s2. As seen, the precipitation polymerization resulted in colloidal nanoparticles (<50 nm) which are slightly irregular in shape. In this type of polymerization, it has been suggested that the morphology of the individual particles can be improved by varying the stirring speed of polymerization solution during the synthesis of the polymer [47].

### 2.4. Preparation of the sensors

The bare carbon paste electrode (CPE) was prepared by thoroughly mixing analytical grade graphite and n-eicosane, in a 65:35 (w/w %) ratio. The PP modified CPE was prepared by mixing different percentages of graphite powder, n-eicosane, and PP-MIP (or NIP) and each mixture was mixed in a mortar for at least 10 min to become homogeneous. Then each paste was packed into one end of a Teflon holder in which electrical contact was made with a copper rod that runs through the center of the electrode body. The electrode surface was polished using a butter paper to produce reproducible working surface. Electrochemical behavior of PP-MIP at the surface of each electrode was studied using cyclic voltammetric (CV) technique. Best results were obtained at 62.5:25:12.5 (w/w %) ratio of graphite powder, n-eicosane, and MIP (or NIP). This optimized electrode composition was then used for the voltammetric determination of parabens.

### 2.5. General method for electrochemical measurements

The electrochemical measurement of PP and its selected competitors was carried out according to the following sequential procedure:

Extraction step: each prepared electrode was inserted into the solutions containing the known or unknown concentrations of PP in

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