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Simultaneous multicomponent spectrophotometric monitoring of methyl and propyl parabens using multivariate statistical methods after their preconcentration by robust ionic liquid-based dispersive liquid–liquid microextraction

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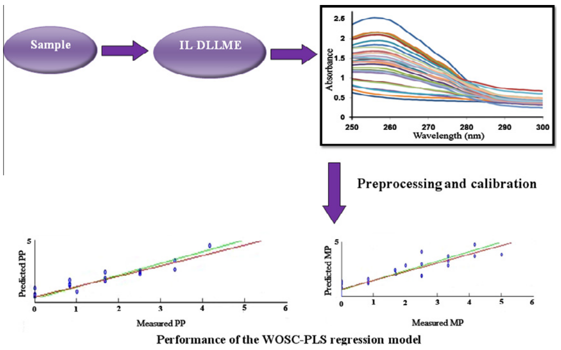
HIGHLIGHTS

- Combination of IL-DLLME/WOSC-PLS/UV–Vis detection methods.
- Simultaneous determination of MP and PP with overlapping spectra in real samples.
- The RMSEP for MP and PP were 0.1046 and 0.1275, respectively.
- This technique is green, inexpensive, precise, fast and affordable.

GRAPHICAL ABSTRACT



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ABSTRACT

A powerful and efficient signal-preprocessing technique that combines local and multiscale properties of the wavelet prism with the global filtering capability of orthogonal signal correction (OSC) is applied for pretreatment of spectroscopic data of parabens as model compounds after their preconcentration by robust ionic liquid-based dispersive liquid–liquid microextraction method (IL-DLLME). In the proposed technique, a mixture of a water-immiscible ionic liquid (as extraction solvent) [Hmim][PF_6] and disperser solvent is injected into an aqueous sample solution containing one of the IL's ions, $NaPF_6$, as extraction solvent and common ion source. After preconcentration, the absorbance of the extracted compounds was measured in the wavelength range of 200–700 nm. The wavelet orthogonal signal correction with partial least squares (WOSC-PLS) method was then applied for simultaneous determination of each individual compound. Effective parameters, such as amount of IL, volume of the disperser solvent and amount of $NaPF_6$, were inspected by central composite design to identify the most important parameters and their interactions. The effect of pH on the sensitivity and selectivity was studied according to the net analyte signal (NAS) for each component. Under optimum conditions, enrichment factors of the studied compounds were 75 for methyl paraben (MP) and 71 for propyl paraben (PP). Limits of detection for MP and PP were 4.2 and 4.8 ng mL^{-1}, respectively. The root mean square errors of prediction for MP and PP were 0.1046 and 0.1275 μg mL^{-1}, respectively. The practical applicability of the developed method was examined using hygienic, cosmetic, pharmaceutical and natural water samples.

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Introduction

Simultaneous spectrophotometric determination of several components in a mixture can be a difficult problem, especially for components that have similar spectral characteristics. The problem of how to distinguish overlapped signals is often faced in analytical experiments. In recent years, rapid-scanning spectrophotometers are now capable of fast generation of large data sets. However, the acquired data have complicated structures, are contaminated by noise and redundancy, and can cause collinearity. One possibility how to solve the above mentioned problems is a wavelet transform, which is presented in this work.

Parabens are a homologous series of hydroxybenzoic acid esterified at the C-4 position, including methyl, ethyl, propyl and butyl, used as preservatives for over seven decades [1]. Methyl paraben (MP) and propyl paraben (PP) are effective antibacterial and antifungal agents, which are commonly used as preservatives in foods, beverages, cosmetics and pharmaceuticals [2]. The parabens meet several criteria of an ideal preservative; they have a broad spectrum of antimicrobial activity, are safe to use (i.e. relatively non-irritating, non-sensitizing and of low toxicity), are stable over a wide pH range, and are sufficiently soluble in water to produce the desired effective concentration in the aqueous phase [3,4]. For many years parabens have been considered among the preservatives with low toxicity. However, some years ago it was declared that some paraben preservatives were estrogenic and so could affect the endocrine system of humans and probably cause breast cancer [5,6]. Due to their wide use and resistance to antimicrobial degradation, parabens are also released into the environment and can affect wildlife. However, little work has been done to quantify their distribution and fate in the environment. Because of these reasons, a fast, inexpensive, sensitive, accurate and green analytical method for paraben determination is highly required.

The reported methods for the determination of parabens in foods, cosmetics and pharmaceuticals are based on high-performance liquid chromatography (HPLC) [7–11], capillary zone electrophoresis (CE) [12] and gas chromatography (GC) [13,14]. These are the classic and widely used instruments. But CE has a poor sensitivity and GC–MS analysis is expensive; although HPLC is the most common method used for detecting these compounds, but in the analysis process a lot of organic solvent is needed, which is not environmentally friendly. Therefore, ultraviolet visible (UV–Vis) spectrophotometric techniques are some of the most useful analytical methods, due to their availability, versatility, accuracy, precision, cost-effectiveness, experimental speed and simplicity, and to their wide application range. However, a simultaneous determination of these compounds by using traditional spectrophotometric techniques is difficult, because the absorption spectra usually overlap and superimposed curves are not suitable for quantitative evaluation. Under computer-controlled instrumentation, derivative techniques and multivariate calibration methods play a very important role to solve above problems in the multicomponent analysis of mixtures by ultraviolet (UV)/visible, molecular absorption spectrophotometry [15,16]. The application of quantitative chemometrics, particularly partial least squares (PLS), to multivariate chemical data is becoming more widespread owing to the availability of digital spectroscopic data and commercial software for laboratory computers [17,18].

The spectra are often influenced by instrumental variation and measurement conditions, such as light scattering, background noise and baseline drift. Therefore, the first step of a multivariate calibration is often preprocessing of the input data. Preprocessing methods can be applied in such cases to enhance the relevant information to make resulting models simpler and easier to interpret. Orthogonal signal correction (OSC) is a multivariate preprocessing method that intends to eliminate undesired effects in the data by restricting the filtered variation in the response matrix **(X)**, to be mathematically orthogonal and unrelated to concentration matrix **(Y)**. Wavelet orthogonal signal correction (WOSC) [19] is a signal preprocessing technique aimed at removing undesirable background effects and enhancing the subsequent PLS regression model, by a combination of wavelet prism (WP) transformation of data into a set of frequency-domain spectra and OSC preprocessing on the frequency-domain data to remove signal uncorrelated to the target property, followed by reconstruction of the filtered spectra from the processed frequency components. Many applications of wavelet analysis have been found in analytical chemistry [20–22].

However, some reports have been published on the simultaneous determination of MP and PP using chemometrics methods [23,24]. But in these reported methods, detection limits are sometimes poor and detection of MP and PP in complex sample matrices is not sufficiently sensitive. Therefore, a sample preparation step is commonly needed before analysis. Different sample preparation methods have been adopted and reported in literature for the determination of parabens [3,11,25–30]. Those methods have some serious drawbacks, such as being time-consuming and a complicated procedure, and in some of them must also use large amounts of organic extraction solvent and the sensitivity is poor.

Room-temperature ionic liquids (RTILs) have attracted increasing interest in analytical chemistry and are applied more and more as the extraction solvent, replacing the volatile solvent in the sample preparation, due to their unique chemical and physical properties [31–35]. In the present study, the authors demonstrated a very efficient and toxic solvent-free IL-based DLLME technique that is robust against high salt concentration and applied for preconcentration of some preservatives in hygienic, cosmetic, pharmaceutical and natural water samples. In the proposed technique, a mixture of a water-immiscible ionic liquid (as extraction solvent) and disperser solvent is injected into an aqueous sample solution containing one of the IL's ions. In the present work, [Hmim][PF_6] (a water-immiscible ionic liquid) and $NaPF_6$ were used as extraction solvent and common ion source, respectively. According to the common-ion effect, the solubility of ionic compounds (such as ILs) decreases in the presence of a common ion, even at high ionic strength. Therefore, proposed IL-based DLLME can be applied for aqueous samples containing high concentration of salt (up to 40%, w/v) [36].

In this study, the possibility of the combination of IL-based DLLME and WOSC-PLS for the separation/preconcentration and the simultaneous spectrophotometric determination of multicomponent was considered. This method combines the concepts of OSC and WP with PLS regression for enhancing the ability in extraction of characteristic information and the quality of regression. MP and PP were used as an example for evaluation of the proposed method. The method was applied for simultaneous determination of these compounds in hygienic, cosmetic pharmaceutical and natural water samples.

Experimental

Instrumentation and software

A Perkin Elmer (Lambda 25, www.perkinelmer.com) spectrophotometer with 10 mm quartz cells was used for UV–Vis spectra acquisition. A Universal 320R refrigerated centrifuge equipped with an angle rotor (6-place, 9000 rpm, Cat. No. 1620A) was from Hettich (Kirchlengern, Germany). A Metrohm digital pH meter