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Simultaneous quantitation of volatile compounds in citrus beverage through stir bar sorptive extraction coupled with thermal desorption-programmed temperature vaporization

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ABSTRACT

Due to disparate concentrations and physicochemical properties of analytes, difficulties in terms of sensitivity and reproducibility are commonly encountered in flavour analysis. In this study, we attempted to improve the performance of stir bar sorptive extraction coupled with thermal desorption and programmed temperature vaporization (SBSE–TD–PTV) based on a model citrus beverage. Through response surface methodology, thermal desorption conditions (i.e. desorption flow, thermal desorption time and cryofocusing temperature) were optimised based on constrained optimisation. Solute discrimination during injection was alleviated by normalising the variability of peak responses of different analytes. In addition, the effects of extraction conditions (i.e. ionic strength, stirring speed, extraction time, temperature and pH) were also investigated using partial factorial design. The obtained method showed high precision and good linearity over the concentration ranged from 0.10 to 20.00 $\mu\text{g L}^{-1}$ with the correlation coefficients higher than 0.991 for most of the selected chemicals, except indole. The limit of detection ranged from 0.03 to 3.89 $\mu\text{g L}^{-1}$. Hence, our results indicated that through the systematic study, SBSE–TD–PTV method became much less solute discriminative and more reliable to quantitate complex analytes.

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1. Introduction

Recent developments in sample preparation have attracted much attention to sorptive extraction techniques, e.g. open-tubular trapping (OTT), solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE) [1,2]. With larger volume of sorbent materials used, the sensitivity of SBSE and sample capacity could be remarkably increased [2–4]. To date, it has been widely applied in environmental analysis [2–10] and biomedical analysis [11–13]. Apart from these extensive applications, SBSE is gaining acceptance in flavour analysis, for example flavour profiling of aroma-active volatiles in wines [14–18], beers [19], fruit juices [20,21] and vinegars [22] as well as elucidation of the changes of volatile metabolites in an intra-oral odour investigation [23]. However, the quantitation of flavour compounds in food samples still remains a challenging task due to their highly diverse physicochemical properties (i.e. volatility and polarity) and disparate concentrations. For

instance, distinctive flavours of citrus beverages are contributed to aroma-active volatile compounds that range from ppm to ppb levels while some potent polar oxygenated compounds are present at low ppt levels [24,25]. Moreover, the various soluble solids (e.g. acids, sugars, and pectins) that are usually found in citrus beverages give rise to matrix effects that would further complicate the extraction process [26]. Hence, this has led to the need to develop a more effective and versatile SBSE method for flavour analysis.

SBSE could be generally viewed as a two-step process—the first step involves partitioning of analytes from aqueous phase into sorbent materials and the second step is to desorb the extracted analytes through thermal desorption or solvent dissolution, with the former being more commonly employed. The thermally desorbed analytes can be transferred into a gas chromatograph through a programmed-temperature-vaporization (PTV) inlet, which could focus the compounds in a cryofocusing trap before transferring them into the column [27]. The combination of SBSE and TD–PTV injection is a sensitive yet complicated technique. To improve the performance of SBSE–TD–PTV method, different approaches were attempted in previous studies with one-variable-at-a-time univariate approach [9,15,17,19]. However, response surface methodology

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would be more appropriate in optimising multiple experimental factors whether extraction conditions only were optimised [19] or both important extraction and GC conditions were treated together in a set of sequential experimental designs [22,28]. In our preliminary experiments, we found that the effects of SBSE extraction conditions and TD–PTV injection parameters were basically unrelated (data not shown). In fact in the process of experimental design, all variables should be interrelated/correlated among themselves. Otherwise, the interpretation on the responses could disregard certain unfavourable conditions/discrimination towards certain group of analytes [22,28]. Thus, these factors should be separately optimised by examining the response of each compound and taking advantage of multi-responses optimisation approach to maximize these responses. Through understanding the influence of TD–PTV factors (i.e. thermal desorption time, flow and cryofocusing temperature) and extraction parameters (i.e. extraction time, temperature stirring speed, electrolyte concentration and pH) on the performance of each compound, which was significantly different in physicochemical properties (e.g. boiling point, solubility, etc.), analyte discrimination could be alleviated.

Therefore, our objective was to develop a SBSE–TD–PTV method for simultaneous determination of a wide range of volatile compounds using model citrus beverage. RSM was applied to understand the interactive parameters in the TD–PTV process, while partial factorial was used to prescreen extraction condition. Furthermore, the optimised method was evaluated and validated through various performance parameters (i.e. linearity, repeatability, precision and limit of detection).

2. Experimental section

2.1. Materials and sample preparation

Milli-Q water was generated from a Millipore water system (Milford, MA, USA). Analytical grade ethanol 96% was obtained from Gadot-Lab, Hezlia, Israel, and methanol from VWR International Ltd., Poole, UK; HPLC grade dichloromethane was purchased from Tedia, Fairfield, OH, USA.

A group of 36 common food flavourings was obtained from Firmenich Asia, Singapore (Table 1). Then, these compounds were diluted with ethanol (10 mg mL⁻¹) as flavouring for further analysis. For each SBSE extraction, 10 µL of this flavouring was spiked into 10.00 mL of Milli-Q water.

2.2. SBSE procedure

Stir bars coated with 24 µL of polydimethylsiloxane (PDMS, 10 mm length × 0.5 mm thickness) were purchased from Gerstel GmbH & Co.KG (Mülheim an der Ruhr, Germany). Prior to use, stir bars were conditioned for 1 h at 300 °C in a flow of helium at 80 mL min⁻¹. Reconditioning of stir bars was done after use by soaking in Milli-Q water and a mixture of dichloromethane–methanol (1:1) for 2 h; as described elsewhere [19]. SBSE was performed using a multiple position magnetic stirrer (Variomag Poly15, Thermo Fisher Scientific, MA, USA). Prior to optimisation, the extraction time profile was examined by stirring solutions spiked with the flavouring (10 mg mL⁻¹) at room temperature and 800 rpm for durations between 10 min and 24 h. After extraction, the stir bars were dried with a lint-free tissue and placed in a glass thermal desorption tube.

2.3. Analytical procedure

TD–PTV–GC–MS/FID analysis was performed using a thermal desorption unit (TDU) coupled with an Agilent 7890C gas chromatograph with a 5975C mass-selective detector and a flame

ionization detector with two-way splitter kit (Agilent Technologies, Santa Clara, CA, USA). The Thermal desorption unit (TDU) was mounted on top of a cooled injection system (CIS-4), a programmed-temperature-vaporization (PTV) type universal GC inlet (Gerstel). The entire system was operated under Maestro (Gerstel) integrated with Chemstation (Agilent Technologies).

Initially, the default condition for TD–PTV was set based on the recommendation by Gerstel, where stir bar was thermally desorbed from 40 °C (held for 1 min) to 250 °C (held for 5 min) at 720 °C min⁻¹ with the desorption flow of 60 mL min⁻¹. Using a glass wool liner (ID 2.0 mm), the desorbed compounds were cryofocused inside the CIS-4 at –100 °C. After desorption, CIS-4 was programmed from –100 to 250 °C (held for 5 min) at 12 °C s⁻¹ to transfer the trapped compounds into the analytical column. Splitless transfer of analytes was performed through solvent vent mode, and the effect of splitless time on the peak areas obtained was predetermined by varying opening time of split valve between 1 min and 7 min.

The separations were carried out on a DB-FFAP fused-silica capillary column of dimensions 60 m × 320 µm and 0.25 µm film thickness (Agilent Technologies). The oven temperature was programmed from 40 °C (held for 5 min) to 145 °C at 5 °C min⁻¹, then to 178 °C at 3 °C min⁻¹, and finally to 230 °C (held for 23 min) at 5 °C min⁻¹. Helium was used as the carrier gas at a flow rate of 1.3 mL min⁻¹. The mass spectrometer was operated in the scan mode with electron ionization of 70 eV.

2.4. Optimisation of TD–PTV injection process

As shown in Table 2, three interactive parameters were desorption flow (40–80 mL min⁻¹), thermal desorption time (5–15 min) and cryofocusing temperature in the PTV injection system (–120 to 40 °C). Central composite design (CCD) was applied in this work, where a total of 20 experimental runs were constructed with 6 central points, 8 cubic points and 6 axial points at α value = 1.68 using Design Expert Version 6.0.10 software (Stat-Ease, MN, USA) [29,30].

The experimental data were fitted by a multiple regression equation including up to the second-order polynomial terms and interaction terms [29]. The adequacy of the model was determined by evaluating the coefficient of determination (R^2) and lack-of-fit tests obtained from the analysis of variance (ANOVA), while statistical significances of the model and model terms were determined at 95% confidence level. The terms found to be non-significant ($p > 0.05$) were dropped from the initial model and refitted with the significant ($p < 0.05$) independent variables in order to obtain the final reduced model. However, some insignificant linear terms were retained in the model if a quadratic or interaction term containing these variables was significant. Three dimensional response surface plots were used to visualize the modelled region and to determine the optimal experimental conditions.

Simultaneous optimisation was carried out through an objective function in the Design Expert software. With the overall objective function, individual desirabilities of all the estimated response variables were combined using geometric mean to give an overall desirability D to achieve desirable response goals.

2.5. Partial factorial design for SBSE extraction

A partial factorial experimental design (2⁵⁻¹) was used to evaluate the significance of the extraction conditions, as well as the interactions between them. The factors investigated were ionic strength (sodium chloride concentration), stirring speed (rpm), extraction time (h), temperature (°C) and pH. Extraction was carried out in a temperature controlled water bath. All variables were evaluated at two levels, low (denoted as –1) and high (denoted as +1). The significant factors were indicated

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