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Evaluation of pervaporation process of kiwifruit juice by SPME-GC/Ion Trap Mass Spectrometry☆

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ABSTRACT

The processing of kiwifruit for obtaining products with a higher sensory quality, to be used in the food industry, is associated with the use of techniques which can limit the physical and chemical losses of aroma compounds. Pervaporation (PV) represents an alternative to the techniques based on distillation/evaporation or partial condensation to concentrate the aroma compounds preserving the molecule integrity (mild operational conditions used), having a high selectivity towards the organic volatile compounds, and respecting also the environment. The most representative volatile compounds of the kiwifruit aroma was chosen for evaluating the pervaporation process. SPME-GC/ion trap mass spectrometry method was exploited to determine the amounts of these compounds. The approach was based on chemical ionization acquisition with isobutane as reagent gas and 1-heptanol and (Z)-3-hexen-yl acetate as internal standards. In these conditions, the calibration curves were satisfactory as demonstrated by the R^2 values of the straight lines (0.9937–0.9999). A kiwifruit fresh juice was processed by pervaporation through the composite commercial membrane (GFT1070) and the one self-prepared, made of styrene butadiene co-styrene (SBS), at three different feed temperatures. Marked effects for both membranes were observed in the total and partial fluxes of aroma compounds as the temperature was increased. The studied aroma compounds were differently affected by the temperature changes during PV process, with the result of a change in concentration in the permeate of the aroma compounds recovered.

1. Introduction

Kiwifruit can be considered highly nutritional due to its high level of vitamin C and strong antioxidant capacity thanks to its containing a number of phytonutrients including carotenoids, lutein, phenolics, flavonoids and chlorophyll.

Based on these characteristics, kiwifruit offers specific health benefits and has a great potential for industrial exploitation [1]. Nowadays, the kiwifruit derivatives available in the market are mainly represented by semi-processed products used by the food industry as ingredients or components for ice-cream, yogurt, cakes and juice blending.

The industrial goal for processing kiwifruit is to obtain uniform quality of the fruit since kiwifruit is a difficult fruit to process due to possible changes in flavor, loss of the green colour, development of brown pigments, formation of hazes and tendency of precipitates to form in liquid products [2]. In a previous article, Cassano et al. reported the use of an integrated membrane process, as potential alternative to traditional processes based on extraction or distillation, which offers juice clarity, and efficient separation and recovery of the aroma of kiwifruit fruit juice [3]. In the study by Cassano, pervaporation (PV) runs for aroma removal were carried out before and after each membrane unit operation. For the majority of the volatile compounds detected, the enrichment factor in the permeate of the fresh juice was higher than the clarified and concentrated juice. This result suggests the use of PV for the removal and enrichment of aroma directly from the fresh juice, before any concentration process.

The extraction of volatile compounds from natural matrices by PV represents an alternative to the conventional separation techniques, such as, steam distillation, liquid solvent extraction and vacuum distillation. These processes have disadvantages in terms of energy consumption, deterioration of the aroma compounds due to high temperatures and oxidation which might adversely affect the quality of the product.

Several studies have dealt with the aroma recovery by pervaporation but the number of publications which focus on the recovery using the raw fruit juice as the feed is still limited [3–9]. In this paper, our attention focuses on the kiwifruit volatile compound recovery from fresh juice by pervaporation comparing different membranes and operational conditions. In particular, a novel material such styrene–butadiene–co-styrene (SBS) has been tested to prepare PV membranes for exploring its

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potentiality also in the aroma recovery by PV. Up to now this material has been used mainly for VOC recovery by PV [10].

The composition of the volatile fraction of kiwifruit was extensively studied [11–15], with more than 80 individual compounds identified. Several analytical techniques were used to analyze volatile compounds of kiwifruit aroma: simultaneous distillation/extraction (25), vacuum distillation/extraction [11,12,14], dynamic headspace [13] and solid phase microextraction (SPME) [15]. The last one was widely applied to the detection of flavour volatile in a variety of food matrices. SPME is a solvent free method of extracting analytes which utilizes a very easy setup and needs no additional instrumentation other than a simple gas chromatograph.

In this study, the setting of assay of nine selected volatile compounds of kiwifruit by SPME-GC-Ion Trap Mass Spectrometry has been developed for evaluating the PV process.

2. Materials and methods

2.1. Materials

The kiwifruits of cv. Hayward were supplied by a local supermarket in Cosenza (Italy). The Fresh kiwifruit were manually washed and then pulped using a multiple shaker–liquidizer. The fresh kiwifruit juice was then poured into the feed reservoir of the PV unit.

Nine target compounds were analyzed (methyl butanoate, ethyl butanoate, (E)-2-hexenal, 3-hexen-1-ol, (E)-2-hexen-1-ol, 1-hexanol, 1-octen-3-ol, methyl benzoate, ethyl benzoate) and two internal standards were used (1-heptanol, (Z)-3-hexen-yl acetate). These standards were purchased from Sigma–Aldrich (Milan, Italy) while diethyl ether from Carlo Erba (Milan, Italy).

2.2. Pervaporation unit and procedure

A description of the pervaporation setup employed in this study is reported in a previous article [3]. The permeate samples were collected every throughout the duration of experiment run (7 h). The permeate was weighed for determining the total fluxes. The data reported are the averages of two experiments.

PV membrane performance was tested at different temperatures and constant pressure.

Pervaporation experiments were carried out using: a) a hydrophobic commercial composite membrane, GFT Pervap 1070 type, made of polydimethylsiloxane (PDMS) with incorporated silicates (thickness of about 20 μm) on a polyacrilonitrile (PAN) support and b) a composite membrane prepared at ITM-CNR in which the active layer made of styrene–butadiene–co-styrene (SBS), thickness of about 40 μm, was coated using a casting knife on a commercial ultrafiltration support of PVDF.

The performance of the pervaporation process is described by calculating two characteristic parameters:

a) the total and partial fluxes (J) at steady state was calculated from the weight (w) of the permeant volatile compounds i, and water (both in kg/m^2 h) by using the following equation:

$$J = \frac{w_i}{A \times t}$$

b) the enrichment factor (β), which gives an indication of the separation selectivity of the component i, is defined according to

$$\beta_i = \frac{w_i^{\text{perm}}}{w_i^{\text{feed}}}$$

where w_i represents the weight fraction of the volatile compounds in the permeate and in the feed phases.

2.3. Analysis of kiwifruit volatile compounds

2.3.1. Preparation of standard solutions

A mother solution (40 mg/l) was prepared by dissolving 0.020 g of each analyte in 500 ml of distilled water:diethyl ether 95:5 mixture. In the same manner a solution containing the internal standards was made. The standard solutions were prepared through serial dilutions. The final six solutions were buffered to pH 3.3 by mixing an appropriate quantity of a 0.2 M aqueous acetic acid solution with a proper volume of a 0.2 M sodium acetate solution and diluting to a 250 mL volume. Since pH is a critical parameter in the extraction of analytes in SPME technique, it was crucial to have the pH of the standard solutions equal to the one of the real sample.

2.3.2. Preparation of samples

Samples were prepared by adding 50 μl of a 20 mg/l solution of internal standards in 2.000 g of each sample.

2.3.3. Experimental procedure

The most suitable SPME fiber and the adsorption and desorption cycles were adopted from a study of Melton et al. [15]. SPME was performed with a 65 μm carbowax/divinylbenzene (DVB) fiber (Supelco, Bellefonte, PA). Equal amounts of samples (2 g) were placed in each septum-closed vial, and the extraction was performed in the headspace volume (~8 mL) at room temperature for 30 min. The adsorbed analytes were thermally desorbed by introducing the fiber into the injector set at 250 °C for 3 min. A blank analysis of the fiber did not display any peak due to the analytes under investigation.

2.3.4. Quantitative analysis

The calibration curves were obtained by covering the concentration range 0.05–5 mg/kg with six steps at 0.05, 0.1, 0.5, 1, 2.5, and 5 mg/kg for each analyte, with 0.5 mg/kg of internal standards (1-heptanol for alcohols and (Z)-3-hexen-yl acetate for esters and (E)-2-hexenal). Each experimental value corresponds to the average of three replicates. The quantitative assay was performed by selecting the area that are characteristic of the ionic species as follows: m/z 103; m/z 117; m/z 99; m/z 83; m/z 83 m/z 85; m/z 69 and m/z 111; m/z 137; m/z 151 for methyl butanoate, ethyl butanoate, (E)-hexenal, 3-hexen-1-ol, (E)-2-hexen-1-ol, 1-hexanol, 1-octen-3-ol, methyl benzoate, ethyl benzoate, respectively; m/z 97 and m/z 83 for the internal standards 1-heptanol and (Z)-3-hexen-yl acetate. The analysis on the feed and on the extracts of volatile compounds (permeates) of the kiwifruit juice, obtained by PV, were carried out three times. The experimental value, used for evaluating the PV performance, corresponds to the average of the three replicates.

2.3.5. Instrumentation

Sample analyses were performed using a Varian (Walnut Creek, CA) Saturn 2000 GC–MS ion trap system in positive chemical ionization modes, with isobutane as reagent gas, coupled to a Varian 3400 gas chromatograph equipped with a Varian 8200 autoinjector.

The ion trap temperature was set at 210 °C with an ionization time of 2 ms, reaction time at 50 ms, and scan rate at 1000 ms. The transfer line temperature was set at 230 °C. The column was a 30 m Chrompack CP-Sil 8 CB low-bleed/MS (0.25 mm i.d., 0.25 μm film thickness). The GC oven temperature was initially held at 40 °C for

Table 1
The activation energies, E_a, (KJ/mol) calculated from Arrehenius plots.

Membranes	Water flux		Volatile compounds		Total flux	
	E_a	R^2	E_a	R^2	E_a	R^2
SBS	35.2	0.9875	66.3	0.9674	35.35	0.9999
GFT1070	35.1	0.9900	42.5	0.9046	35.1	0.9900