Journal of Chromatography A, xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Short communication

Analysis of volatile compounds responsible for kiwifruit aroma by desiccated headspace gas chromatography–mass spectrometry

Chun-Yun Zhang[a,b], Qiong Zhang[a], Cai-Hong Zhong[a], Ming-Quan Guo[a,b,*]

[a] Key Laboratory of Plant Germplasm Enhancement and Specialty Agriculture, Wuhan Botanical Garden, Chinese Academy of Sciences, Wuhan 430074, China
[b] Sino-African Joint Research Center, Chinese Academy of Sciences, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form 17 February 2016
Accepted 18 February 2016
Available online xxx

Keywords:
Volatile compounds
Organoleptic quality
Desiccated headspace sampling
Kiwifruit
GC–MS

ABSTRACT

A new method for desiccated headspace (DHS) sampling of aqueous sample to GC–MS for the analysis of volatile compounds responsible for kiwifruit aroma in different kiwifruit cultivars has been developed based on the complete hydrate formation between the sample solvent (water) with anhydrous salt (calcium chloride) at an elevated temperature (above the boiling point of the aqueous sample) in a non-contact format, which overcame the water-effect challenge to directly introduce aqueous sample into GC–MS analysis. By means of DHS, the volatile compounds in three different kiwifruit cultivars were analyzed and compared under the optimized operating conditions, mainly time and temperature for headspace equilibration, column temperature program for GC–MS measurement. As a result, 20 peaks of volatile compounds responsible for kiwifruit aroma were detected and remarkable differences were found in the relative contents of three major volatile compounds among the three different kiwifruit cultivars, i.e., acetaldehyde, ethanol and furfural. The DHS sampling technique used in the present method can make the GC–MS analysis of volatile compounds in the aqueous sample within complex matrix possible without contaminating the GC–MS instrument. In terms of the analysis of volatile compounds in kiwifruit, the present method enabled a direct measurement on the filtrate of the aqueous kiwifruit pulp, without intermediate trap phase for the extraction of analytes, which will be more reliable and simpler as compared with any other headspace method in use. Thus, DHS coupled with GC–MS will be a new valuable tool available for the kiwifruit related research and organoleptic quality control.

1. Introduction

Kiwifruit (*Actinidia chinensis*) is one of the most valuable fruit crops that is native to China and now gaining international commercial importance [1]. It is widely appreciated by consumers for its flavor and nutritional qualities, e.g., high levels of vitamin C and health-promoting effects [2,3]. Together with sweetness and acidity, kiwifruit aroma is one of the crucial factors that contribute to the kiwifruit flavor, which is the result of a subtle mixture of volatile compounds [4]. Therefore, techniques that can efficiently and effectively analyze these volatile compounds of kiwifruit will be of great importance for the explanation of the fruit aroma and the breeding of new kiwifruit cultivars with better organoleptic quality.

Recently, more and more consumers have paid more attention to organoleptic quality of kiwifruit, even a growing percentage of consumers are willing to pay a premium for kiwifruit cultivars with higher organoleptic quality. Nowadays, with an increasing demand for kiwifruit around the world, the determination of the organoleptic quality of kiwifruit is becoming highly important. Since the organoleptic quality of kiwifruit is often ascribed to its volatile aroma components, many methods have been developed for the analysis of the aroma compounds in kiwifruit to date. Because of the ability of simultaneously separating and identifying multiple volatile components, GC–MS was commonly used for the analysis of aroma compounds in kiwifruit [5]. However, prior to GC–MS measurement, it is mandatory to isolate the volatile species from the complex sample matrix. Those techniques commonly used for the isolation of volatile compounds, including solvent extraction [6], distillation [7,8], static or dynamic headspace (SH or DH) [9,10] and solid phase micro-extraction (SPME) [11], were typically based on the volatility or solubility of the volatile compounds. In more details, solvent extraction and distillation were aiming at

* Corresponding author at: Key Laboratory of Plant Germplasm Enhancement and Specialty Agriculture, Wuhan Botanical Garden, Chinese Academy of Sciences, Wuhan 430074, China. Fax: +86 27 87518018.
E-mail address: guomq@wbgcas.cn (M.-Q. Guo).

http://dx.doi.org/10.1016/j.chroma.2016.02.056
0021-9673/

analyzing the whole set of volatiles in the matrix because of their high accessibility of volatile compounds. However, they are time-consuming and easy to introduce other chemical impurities, such as some co-existing non-volatile components and some remaining solvents, which also cause contamination problems in the GC–MS analysis. Headspace based extraction techniques, e.g., SH, DH and SPME, have been proposed as the simpler techniques for extracting volatile components from fruits and vegetables [12–14]. Since SH is based on an in-situ releasing and sampling of the volatiles, different from that of DH and SPME where an intermediate trap phase is involved, it is promising to be developed as an in-situ and simple method for the analysis of volatiles in fruits and vegetables [15]. Generally, SH is employed at an elevated temperature to obtain higher amount and more components in gas phase partition in order to increase sensitivity and adaptability of detection [15]. However, for the aqueous kiwifruit pulp sample, this elevated temperature, especially higher than the boiling point of water, would result in high stream pressure of water vapor introduced to GC and then to MS with high risk of damaging the ion source of MS detector [16], which is not allowed in methodology. Thus, measures that can remove this high stream pressure of water should be taken in the high-temperature SH–GC–MS measurement of aqueous samples. Recently, an application of acetone acetals as water scavengers was reported to remove water and increase the detection sensitivity in SH–GC analysis [17]. However, the by-products of the reaction between the scavenger and water, such as methanol and acetone, could cause impurities when the whole set of volatiles in sample were tackled. Previous works on SH–GC analysis have also shown that adding anhydrous salt can effectively remove the water pressure by the formation of hydrate, and increase the detection sensitivity of volatiles [18,19]. Thus, we believe this technique can also be used in the high-temperature SH–GC–MS measurement of volatile compounds in the aqueous kiwifruit sample to achieve a desiccated headspace (DHS) sampling and make the non-damaging GC–MS measurement possible.

In this work, a desiccated headspace GC–MS (DHS–GC–MS) method has been developed for the analysis of volatile compounds in kiwifruit. The main focuses were on the feasibility and applicability of this new methodology. After the optimization of the headspace equilibration conditions and the column temperature program of GC, the volatile compounds of three different kiwifruit cultivars were identified and compared as cases of studies. Meanwhile, the precision and adaptability of the present method were also evaluated.

2. Experimental section

2.1. Chemicals and materials

Anhydrous calcium chloride used in the experiment is of analytical grade and purchased from commercial sources without further purification. Samples of three different kiwifruit cultivars, i.e., Jintao, Maohua and Jinkui, were collected from Wuhan botanical garden in December, 2015. The samples were stored in room temperature for 5–7 days, and then prepared for the analysis.

2.2. Apparatus and operations conditions

An automated headspace sampler (Agilent 7697A, US) equipped with a sample loop volume of 1 mL, a GC system (Agilent 7890A, US) equipped with HP-5 capillary column, and MS system (Agilent 5975C, US), were used for the analysis of volatile components in different kiwifruit cultivars. The headspace operating conditions were as follows: Equilibration time = 60 min; Equilibration temperature = 160 °C; Pressing time = 0.5 min; Extracting time = 0.2 min; Injecting time = 0.5 min. GC operating conditions were as follows: The carrier gas was helium at a flow rate of 1 mL/min; the column temperature program of GC was initially set at 30 °C for 5 min, and gradually increased to 120 °C at 6 °C/min, then kept there for 10 min before gradually increased to 250 °C at 12 °C/min, and then kept there for 10 min. For GC–MS detection, electron ionization (EI) system was used with ionization energy at 70 eV.

2.3. Procedures for sample preparation

50 g of pulverized fruit tissue was centrifuged and filtered through a membrane filter (0.45 μm). 1 mL of filtrate was measured into a half-open glass tube (2 mL), and then the whole tube was embedded into a headspace vial containing 5 g of anhydrous calcium chloride. After that, the sample vial was sealed with a PTFE/silicone septum and an aluminum cap and equilibrated at 150 °C for a proper time (about 3 h) in the oven to completely remove the water in sample by the formation of hydrate with anhydrous calcium chloride in a non-contact format (shown in Fig. 1). Headspace extraction, followed by GC–MS measurement, was performed on the sample vial after further equilibrating in the oven of headspace sampler at 160 °C for another one hour.

3. Results and discussion

3.1. Principle of the method

When the liquid sample was placed into a closed headspace vial without anhydrous salt, there is a tendency for the volatile species

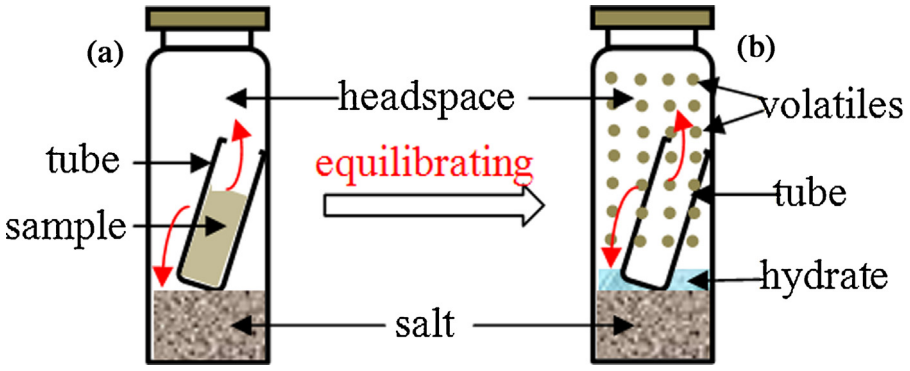

Fig. 1. The schematic of the principle of the method.

Please cite this article in press as: C.-Y. Zhang, et al., Analysis of volatile compounds responsible for kiwifruit aroma by desiccated headspace gas chromatography–mass spectrometry, J. Chromatogr. A (2016), http://dx.doi.org/10.1016/j.chroma.2016.02.056