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Selectable one-dimensional or two-dimensional gas chromatography–olfactometry/mass spectrometry with preparative fraction collection for analysis of ultra-trace amounts of odor compounds

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ABSTRACT

A novel selectable one-dimensional (^{1}D) or two-dimensional (^{2}D) gas chromatography–olfactometry/mass spectrometry with preparative fraction collection (selectable $^{1}D/^{2}D$ GC–O/MS with PFC) system was developed. The main advantages of this system are the simple and fast selection of ^{1}D GC–O/MS or ^{2}D GC–O/MS or ^{1}D GC-PFC or ^{2}D GC-PFC operation with a mouse click (without any instrumental set-up change), and total transfer of enriched compounds with thermal desorption (TD) on the same system for identification with ^{2}D GC–O/MS analysis. Recovery of PFC enrichment with 20 injection cycles of 15 model compounds at 500 pg each (e.g. alcohol, aldehyde, ester, lactone, and phenol) was very good with recoveries in the range of 98–116%. The feasibility and benefit of the proposed system was demonstrated with an identification of off-flavor compounds (e.g. 2,4,6-trichloroanisole (TCA), 2-isobutyl-3-methoxypyrazine (IBMP), and geosmin) in spiked wine at odor perception threshold level (5–50 ng L^{-1}). After parallel stir bar sorptive extraction (SBSE) for 20 aliquots of a sample and subsequent PFC enrichment for the odor-active fractions from the 20 stir bars, three off-flavor compounds were clearly resolved and detected with TD–^{2}D GC–O/MS in scan mode. The good efficiency of SBSE-PFC enrichment in the range of 71–78% shows that all analytical steps, e.g. SBSE, TD, $^{1}D/^{2}D$ GC–O/MS, and PFC, are quantitative and identification of off-flavor compounds at ng L^{-1} level in wine is possible.

1. Introduction

GC–Olfactometry (GC–O) is a valuable method for the selection of odor components from a complex mixture [1]. In particular, GC–O in combination with MS (GC–O/MS) allows not only evaluation of the odor compounds, but also identification with mass spectral information. However, many key odor compounds can occur at very low concentrations. Therefore, the identification of odor compounds remains a hard task even with GC–O/MS because some compounds co-elute with other analytes or sample matrix, which leads to difficulties when correlating the detected aroma with the correct compound. Heart-cutting two-dimensional (^{2}D) GC–MS with simultaneous olfactometry can significantly improve the identification capability as well as the resolution of complex regions [2–4]. In 2010, we proposed a novel selectable ^{1}D or ^{2}D GC–MS with simultaneous olfactometry ($^{1}D/^{2}D$ GC–O/MS) for simple and fast operation of both ^{1}D GC–O/MS and ^{2}D GC–O/MS using a single GC–MS system [5]. In certain cases, ^{2}D GC–O/MS is not able to produce high quality mass spectra for the olfactory detected compounds (no peaks on the second dimensional total ion chromatogram (TIC) at the corresponding retention times), particularly when analyzing highly complex aromas. In this case, it is essential to have an enrichment step before final MS detection. In the late 80s through early 90s, Nitz et al. proposed a modular-type multidimensional (MD) GC system for analysis of odor compounds at low level [2]. For example, they reported ^{2}D preparative GC [6] in combination with thermal desorption (TD)–GC–O/MS for analysis of passion fruits [7]. After ^{2}D GC separation and preparative enrichment with an adsorbent trap, the trapped compounds are thermally desorbed and subsequently analyzed by GC–O/MS. A modular-type GC construction could be adopted for different instrumentation, however, one always has to re-configure these MDGC modules. In order to revitalize this concept without any instrumental set-up change, we combined a single preparative fraction collection (PFC) module with the $^{1}D/^{2}D$ GC–O/MS system. After fraction collection and enrichment of an olfactory detected compound over dozens of injections, the trapped and enriched compounds are thermally desorbed into the same system without any instrumental

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set-up change. Finally, the desorbed compounds are analyzed by ^{2}D GC–O/MS for identification.

In this study, a combined system consisting of TD, ^{1}D/^{2}D GC–O/MS, and PFC for odor analysis is described. The feasibility and benefits of the system is demonstrated with analysis of ultra-trace amounts of odor compounds in a complex sample such as wine. Also, stir bar sorptive extraction (SBSE)–TD is combined with the proposed system to enable a miniaturized and solvent-free extraction.

2. Experimental

2.1. Reagents and materials

Hexanal, nonanal, 1-hexanol, 3-hexenol, linalool, citronellol, geraniol, *p*-cymen-8-ol, phenethyl alcohol, guaiacol, ethyl hexanoate, ethyl octanoate, phenethyl acetate, beta-damascenone, gamma-nonalactone, and limonene were kindly obtained from Dr. Katsumi Umano of Takata Koryo Co., Ltd. (Hyogo, Japan). The standard solutions of 2-isobutyl-3-methoxypyrazine (IBMP), 2,4,6-trichloroanisole (TCA) and geosmin at 100 μg mL^{-1} in methanol were purchased from Sigma Aldrich Japan (Tokyo, Japan) as the stock standard solutions. Sodium chloride (NaCl) of analytical grade (Kanto Kagaku, Japan) was previously heated at 350 °C for 2 h.

Bottles of white wine (Sauvignon blanc and Chardonnay) were obtained from local stores in Tokyo, Japan.

2.2. Instrumentation

Stir bars coated with 24 μL PDMS (Twister) were obtained from Gerstel (Gerstel, Mülheim an der Ruhr, Germany). For stir bar sorptive extraction (SBSE), 10 mL headspace vials with screw cap containing PTFE-coated silicon septa (Gerstel) were used. SBSE was performed with a multiple position magnetic stirrer (20 positions) from Global change (Tokyo, Japan). The thermal desorption (TD)–^{1}D/^{2}D GC–O/MS analysis was performed with a TDU thermal-desorption unit equipped with a MPS 2 auto-sampler and a CIS 4 programmed temperature vaporization (PTV) inlet (Gerstel), dual Low Thermal Mass (LTM)-GC system (Agilent Technologies, CA, USA) installed on an Agilent 7890 gas chromatograph (host GC) with a 5975C mass-selective detector. The LTM-GC system consists of dual wide format column modules (5 in.; 1 in. = 2.54 cm), LTM-heated transfer lines, cooling fan, temperature controller, power supply, and a specially constructed GC door. The GC was equipped with a ODP2 olfactory detection port (Gerstel), a proto-type of a single preparative fraction collection (PFC) module (Gerstel), two Agilent CFT Deans switches and two 3-way splitters (with make-up gas line), which were controlled with two pressure control modules (PCM). PCM has two pressure control capabilities. One is called PCM (main) and the other is called Auxiliary (AUX).

2.3. Sample preparation

Prior to use, the stir bars were conditioned for 30 min at 300 °C in a flow of helium. For SBSE, 10 mL of wine samples were transferred to 10 mL headspace vials. Then, 20% NaCl was dissolved in the sample. A stir bar was added and the vial was sealed with a screw cap. SBSE was performed at room temperature (24 °C) for 60 min while stirring at 1500 rpm. After extraction, the stir bar was removed with forceps, dipped briefly in Milli-Q water, dried with a lint-free tissue, and placed in a glass thermal desorption liner. The glass liner was placed in the thermal desorption unit. No further sample preparation was necessary.

Reconditioning of stir bars was done after use by soaking in Milli-Q purified water and acetonitrile for 24 h each; stir bars were then removed from the solvent and dried on a clean surface at room temperature for 1 h. Finally, the stir bars were thermally conditioned for 30 min at 300 °C in a flow of helium. Typically, more than 30 extractions could be performed with the same stir bar.

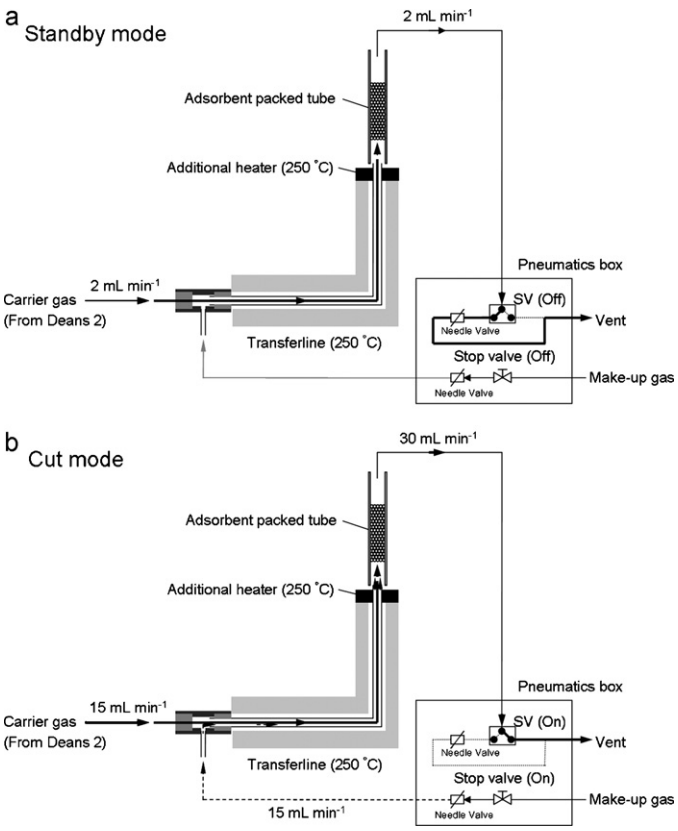

Fig. 1. A diagram of a single PFC module. (a) Standby mode; (b) cut mode.

2.4. Thermal desorption

The stir bar was thermally desorbed by programming the TDU from 30 °C (held for 0.5 min) to 200 °C (held for 3 min) at 720 °C min^{-1} with 50 mL min^{-1} desorption flow. Desorbed compounds were focused at 10 °C on a Tenax TA packed liner in the PTV inlet for subsequent ^{1}D/^{2}D GC–O/MS analysis. After desorption, the PTV inlet was programmed from 10 °C to 240 °C (held for GC run time) at 720 °C min^{-1} to inject trapped compounds onto the analytical column. The injection was performed in the splitless mode with a 2 min splitless time.

2.5. Single preparative fraction collection module

Fig. 1 shows a diagram of a single PFC module (a: standby mode; b: cut mode). The single PFC module consists of a heated transfer line, an additional heater, an adsorbent packed tube (e.g. Tenax TA tube), and a PFC pneumatic box. The transfer line temperature was 250 °C and the additional heater was preset at 250 °C. In the standby mode, carrier gas of low flow at 2 mL min^{-1} is supplied from the second Deans switch (Deans 2). In the cut mode, carrier gas of high flow at 15 mL min^{-1} and make-up gas at 15 mL min^{-1} (total 30 mL min^{-1}) are supplied to the adsorbent packed tube.

2.6. Selectable ^{1}D/^{2}D GC–Olfactometry/MS with preparative fraction collection

Selectable ^{1}D or ^{2}D GC–O/MS with preparative fraction collection (PFC) system was designed based on the selectable ^{1}D/^{2}D