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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.

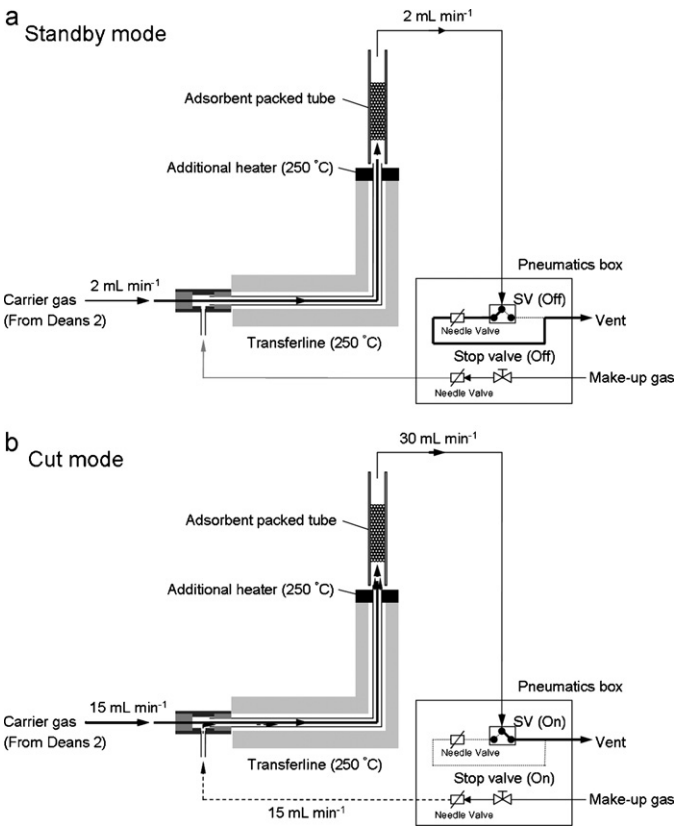

Fig. 1. A diagram of a single PFC module. (a) Standby mode; (b) cut mode.

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

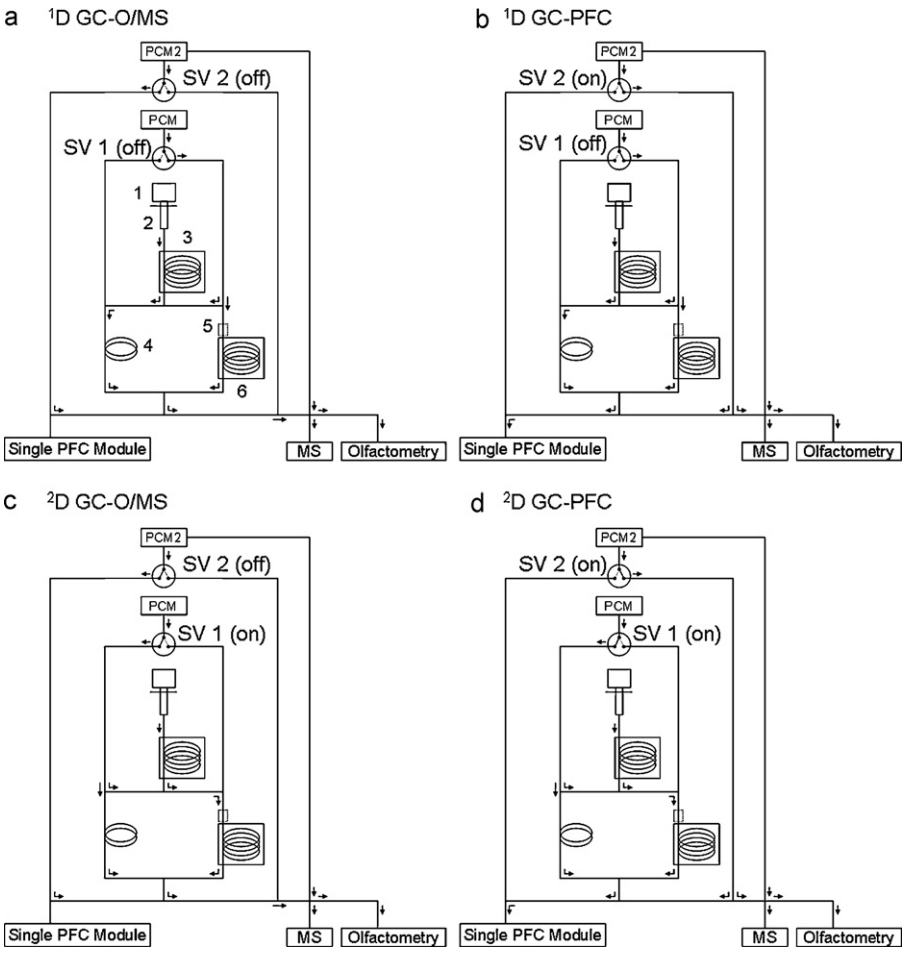

Fig. 2. Schematic flow diagrams for the selectable ^{1}D/^{2}D GC–O/MS with a single PFC module. (a) ^{1}D GC–O/MS; (b) ^{1}D GC-PFC; (c) ^{2}D GC–O/NS; (d) ^{2}D GC-PFC. 1: Thermal desorber; 2: PTV inlet; 3: LTM-GC1; 4: Restrictor; 5: Cryotrap (Option); 6: LTM-GC2; SV: Solenoid valve.

GC–O/MS system previously described [5]. Fig. 2 shows schematic flow diagrams for the selectable ^{1}D/^{2}D GC–MS with a single PFC module. The system consists of, in addition to components of the selectable ^{1}D or ^{2}D GC–MS, the second deans switch (Deans 2), PCM 2 and the single PFC module. Both outlets of ^{1}D and ^{2}D column were merged and then connected to the Deans 2 instead of a splitter to a MS and a olfactory detection port. The outlet flow is switched to the splitter or the single PFC module by Deans 2 which was controlled by PCM 2. The system can provide not only ^{1}D or ^{2}D GC–O/MS analysis, but also PFC on both ^{1}D or ^{2}D GC separation.

The calculation was done step by step from downstream as described for the selectable ^{1}D or ^{2}D GC–O/MS [5]. For a transfer capillary from the Deans 2 to the single PFC device, a 1 m length of 0.32 mm i.d. deactivated fused silica capillary was used to allow a higher carrier gas flow of 15 mL min^{-1} which prevented adsorption and diffusion of target compounds at the connection of the adsorbent trap in the cut mode. Also make-up gas (15 mL min^{-1}) was supplied for the same purpose. The calculation software for the selectable ^{1}D/^{2}D GC–O/MS with PFC (^{1}D/^{2}D sync. software) is available from Gerstel.

Separations were performed on a 30 m, 0.25 mm i.d., 0.25 μm film thickness DB-Wax column (Agilent) as the ^{1}D column and a 10 m, 0.18 mm i.d., 0.40 μm film thickness DB-5 column (Agilent) as the ^{2}D column. The column temperature for the DB-Wax was programmed from 40 °C (held for 2 min) to 240 °C (held) at 10 °C min^{-1}. The column temperature for the DB-5 was 40 °C (held for GC run time) or programmed from 40 °C at 5 °C min^{-1} to 150 °C, and at 20 °C min^{-1} to 280 °C (held). The host GC oven was kept at a constant temperature of 250 °C. A split ratio of 1:2 was set to the MS and the ODP 2 sniffing port. The MS was operated in scan mode and selected ion monitoring (SIM) mode using electron ionization (electron-accelerating voltage: 70 V). Scan range was set from *m*/*z* 29 to 300 and scan speed was set to 2.68 Hz. For SIM, 9 ions were monitored (*m*/*z* 124, 151 and 94 for IBMP, *m*/*z* 112, 125 and 182 for geosmin, *m*/*z* 195, 197 and 210 for TCA: the underlined number is the *m*/*z* of the ions used for determination). The data acquisition speed was 3 Hz for each ion. The sniffing port temperature was set to 250 °C. Pressure was 411 kPa, 338 kPa, 71 kPa and 26 kPa for the inlet, PCM, PCM 2 and AUX of PCM, respectively.

3. Results and discussion

3.1. Evaluation of PFC

We first evaluated PFC recovery of a single injection of the 15 model flavor compounds at 10 ng each including various types of compounds (e.g. alcohol, aldehyde, ester, lactone, and phenol). The average linear retention indices (LRI) for the model compounds on the DB-Wax column, which were obtained from Aroma Office ^{2}D database (Nishikawa keisoku/Gerstel KK, Japan), were in the range of 1090 (hexanal, n = 84) to 2029 (γ-nonalactone, n = 16). One micro-liter of a standard solution containing the model compounds at 10 μg mL^{-1} was directly injected into the TD–^{1}D GC–O/MS with single PFC system. The 15 model compounds were separated and entirely transferred onto the single PFC with Tenax TA trap at ambient temperature. The trapped compounds were analyzed by the

Table 1
Average LRI, PFC recovery of single injection, and PFC recovery of enrichment with 20 injection cycles for 15 model flavor compounds.

Compound	Average LRI (DB-Wax)[a]	PFC recovery (%) of single injection (RSD %, $n = 7$[b])	PFC recovery (%) of enrichment with 20 injection cycles[c]
Hexanal	1090 ($n = 84$)	97 (2.2)	102
Limonene	1199 ($n = 65$)	93 (2.0)	103
Ethyl hexanoate	1237 ($n = 38$)	95 (2.2)	113
1-hexanol	1358 ($n = 76$)	90 (1.8)	106
3-hexenol	1392 ($n = 65$)	87 (1.5)	105
Ethyl octanoate	1435 ($n = 28$)	98 (3.3)	116
Linalool	1547 ($n = 103$)	89 (2.1)	112
Citronellol	1765 ($n = 33$)	88 (2.8)	110
Phenetyl acetate	1816 ($n = 3$)	93 (2.9)	109
β-Damascenone	1828 ($n = 29$)	88 (2.1)	98
Geraniol	1846 ($n = 58$)	85 (3.2)	105
p-cymen-8-ol	1837 ($n = 19$)	88 (2.7)	108
Guaiacol	1851 ($n = 30$)	86 (1.7)	103
Phenetyl alcohol	1917 ($n = 5$)	90 (1.7)	104
γ-Nonalactone	2029 ($n = 16$)	94 (2.0)	106

[a] Average linear retention indices on DB-Wax column (Aroma Office ^{2}D database, Nishikawa Keisoku/Gerstel KK).
[b] PFC recovery of single injection is examined with seven replicate analyses of the 15 model flavor compounds at 10 ng each.
[c] PFC recovery of enrichment is examined with 20 injection cycles of the 15 model flavor compounds at 500 pg each.

same system with thermal desorption of the Tenax TA trap. The PFC recovery was calculated by comparing peak areas with those of a direct injection of a standard solution. Very good recovery in the range of 85–98% was obtained with low relative standard deviation (RSD) of less than 3.2% ($n = 7$). We then evaluated PFC recovery of enrichment with 20 injection cycles of the model compounds at 500 pg each. After the 20 injection cycles of a one micro-liter injection of the standard solution at 500 ng mL^{-1}, the Tenax TA trap was analyzed by the same system. The recovery of PFC enriched compounds was in the range of 98–116%. The high recoveries of PFC enrichment show that the transfer and the trap efficiency of the model compounds at sub-ng level with the proposed system are quantitative and acceptable. The average LRI on the DB-Wax column, the PFC recovery of a single injection, and the PFC recovery of enrichment with 20 injection cycles are summarized in Table 1.

3.2. Analysis of ultra-trace amounts of off-flavor compounds in wine

The most widely recognized off-flavor compound in wine are halogenated anisole derivatives such as 2,4,6-trichloroanisole (TCA), which has corky odor. Also, 2-isobutyl-3-methoxypyrazine (IBMP), which has a bell pepper like odor, and geosmin, which has an earthy/musty odor, are important off-flavor compounds in wine [8]. These off-flavor compounds have very low odor perception threshold levels (e.g. ng L^{-1} level) in wine. Therefore, analytical methods have included powerful extraction and enrichment steps, e.g. solid phase microextraction (SPME) [9,10] and SBSE [8,11], before TD–GC–MS analysis in selected ion monitoring (SIM) mode. In order to describe the feasibility and benefits of the proposed system, the analysis of ultra-trace amounts of off-flavor compounds (e.g. IBMP, TCA and geosmin) in wine was performed by using SBSE–TD–^{1}D/^{2}D GC–O/MS with PFC. For the identification of the target off-flavor compounds, the MS was operated in scan mode.

Spiked sauvignon blanc, which contains three off-flavor compounds at odor perception threshold levels [8] (e.g. IBMP at 25 ng L^{-1}, TCA at 5 ng L^{-1}, and geosmin at 50 ng L^{-1}, respectively), was analyzed with SBSE–TD–^{1}D/^{2}D GC–O/MS (scan mode). The three off-flavor compounds were clearly detected with olfactometry on the 1st dimensional (^{1}D) separation. The retention times of the GC–O signal were 12.45, 16.25, and 16.55 min for IBMP, TCA, and geosmin, respectively. However, these peaks were completely buried in the ^{1}D total ion chromatogram (TIC). Therefore, two regions including the three compounds were transferred onto a second dimension. ^{2}D GC–O/MS was performed just after this run without any instrumental set-up change. Fig. 3 shows both ^{1}D and ^{2}D TIC and olfactometric signals of the spiked sauvignon blanc. The ^{1}D separation was done until 17.00 min, the two heart-cut regions from 12.40 to 12.55 min and from 16.10 to 17.00 min were transferred to the second dimension. After the heart-cutting, back flush was immediately started by setting the inlet pressure to 10 kPa, while the ^{2}D separation was done simultaneously. The ^{2}D separation started at the retention time of 17.50 min after pressure stabilization. The three off-flavor compounds were clearly detected with olfactometry on the ^{2}D separation. However, no detectable peaks were found on the ^{2}D TIC because of lack of detectability in scan mode after a single SBSE. In order to further enrich the target off-flavor compounds for the detection with the scan mode, SBSE was performed for 20 samples in parallel. Then, TD–^{1}D GC-PFC with Tenax TA was performed with the proposed system, to trap and enrich the odor active fractions from the 20 stir bars. After 20 injection cycles, the Tenax TA trap was finally analyzed by TD–^{2}D GC–O/MS using the same system without any instrumental set-up

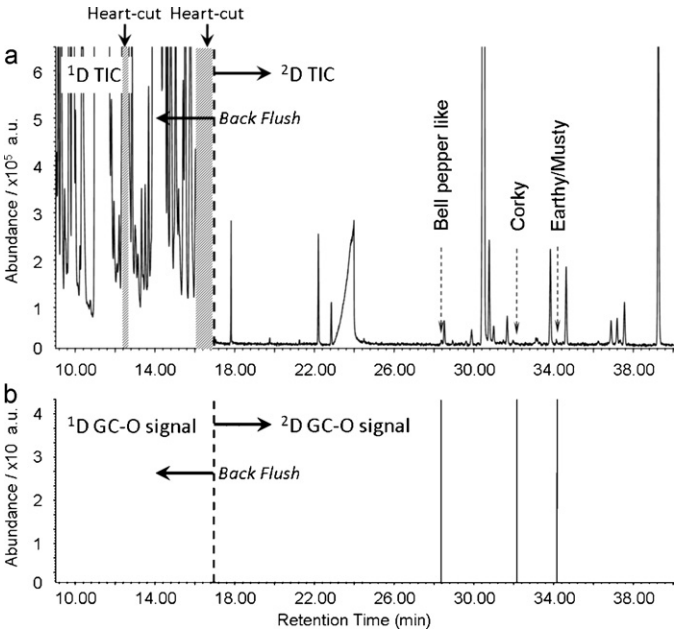

Fig. 3. ^{1}D/^{2}D total ion chromatogram (TIC) and olfactometric signals obtained by SBSE–TD–selectable ^{1}D/^{2}D GC–O/MS for spiked wine at 5–50 ng L^{-1} level. (a) ^{1}D/^{2}D TIC; (b) ^{1}D/^{2}D olfactometric signals.

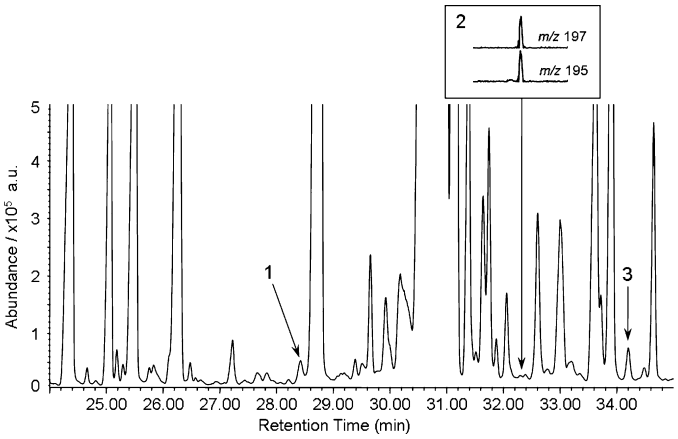

Fig. 4. $^{1}D/^{2}D$ total ion chromatogram (TIC) and mass chromatograms (m/z 195, 197) of SBSE-PFC enrichment with 20 injection cycles for spiked wine (zoom in ^{2}D GC–MS analysis). IBMP at 25 ng L^{-1}; (2) TCA 5 ng L^{-1}; (3) Geosmin 50 ng L^{-1}.

change. Fig. 4 shows ^{2}D TIC of the PFC enrichment with 20 injection cycles. After the PFC enrichment and ^{2}D separation, the peaks of IBMP and geosmin, which were corresponding to their olfactometric signals, could be found on the ^{2}D TIC. Although the peak of TCA was almost buried in the ^{2}D TIC, specific mass chromatograms (e.g. m/z 195 and 197) were clearly found at the corresponding time to the olfactometric signal of TCA. Fig. 5 shows a comparison of ^{2}D mass chromatograms (m/z 112 and 125) of geosmin between the single SBSE (a) and the PFC enrichment with 20 injection cycles (b). The mass spectra of all target compounds were compared with those of a Wiley library using an Agilent ChemStation (Fig. 6). For IBMP at 25 ng L^{-1}, probability based matching (PBM) of 72 was obtained. For TCA at 5 ng L^{-1} and Geosmin at 50 ng L^{-1}, PBM of 94 and 93 were obtained, respectively. After the identification, quantification of the three off-flavor compounds in sauvignon blanc was performed with single SBSE–TD–$^{1}D/^{2}D$ GC–O/MS in the SIM mode using a 4 point standard addition calibration method. Very good linearity with a correlation coefficient (r^2) of more than 0.9990 was obtained for all compounds. Only IBMP was detected with non-spiked sauvignon blanc and determined at an ultra-trace level of 13 ng L^{-1} (RSD = 4.4%, n = 6).

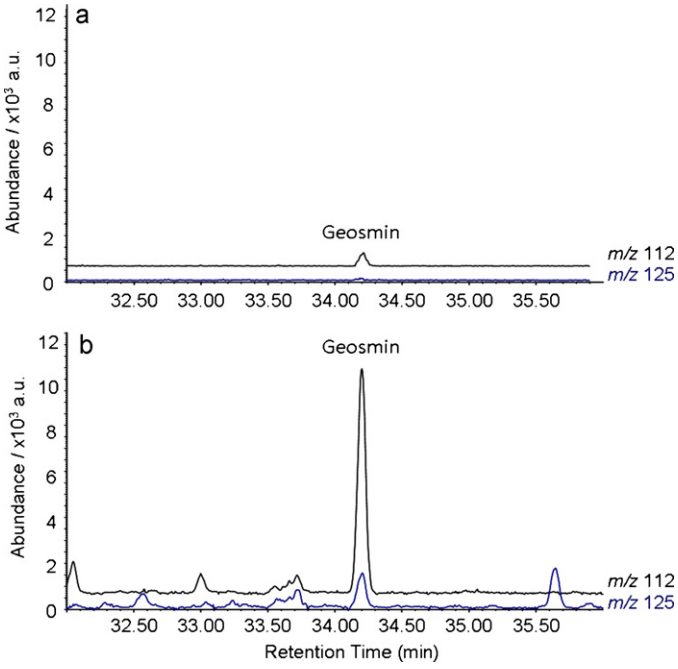

Fig. 5. Comparison of ^{2}D mass chromatograms (m/z 112 and 125) of geosmin between the single SBSE (a) and the PFC enrichment with 20 injection cycles (b) for spiked wine at 50 ng L^{-1} level.

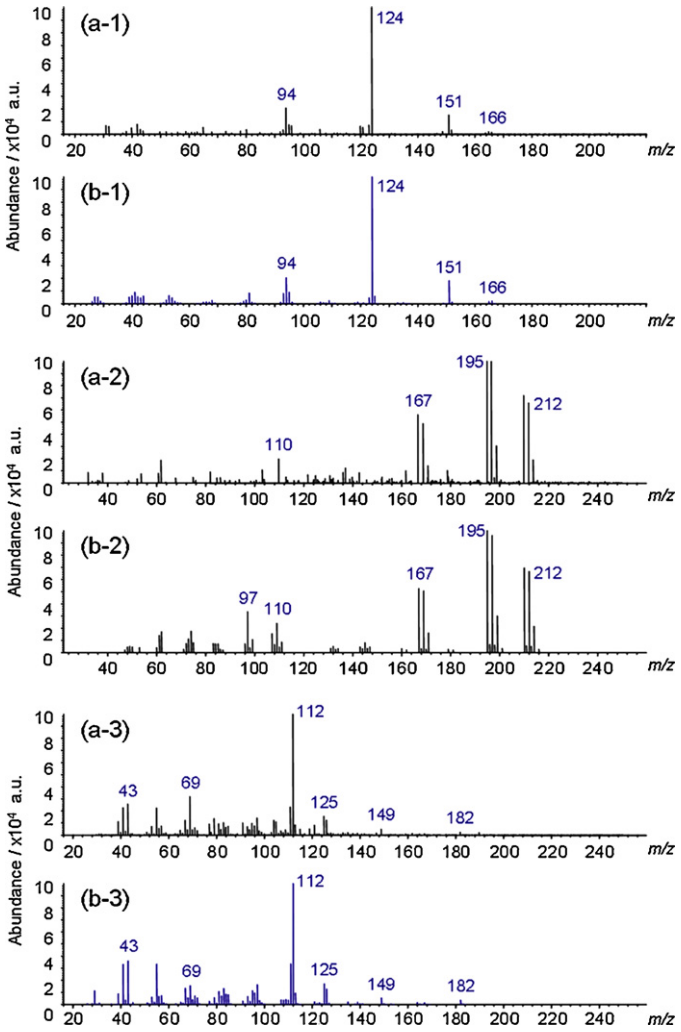

Fig. 6. Measured mass spectra of IBMP (a-1), TCA (a-2), and geosmin (a-3) in spiked wine obtained by SBSE-PFC enrichment with 20 injection cycles and subsequent TD–$^{1}D/^{2}D$ GC–O/MS analysis, and Wiley library mass spectra of IBMP (b-1), TCA (b-2), and geosmin (b-3).

Single SBSE recovery and SBSE-PFC recovery with 20 injection cycles were examined with the spiked chardonnay at the odor perception threshold levels (5–50 ng L^{-1}), which did not contain the target off-flavor compounds. The single SBSE recovery was obtained from the six replicates analysis of the spiked samples. Although the single SBSE recovery for IBMP, which has relatively low log K_{ow} of 2.86 (SRC-KOWWIN software, Syracuse Research, Syracuse, NY, USA), was 44% (RSD = 5.8%, n = 6), the single SBSE recovery for TCA (log K_{ow}: 4.01) and geosmin (log K_{ow}: 3.57) were very good with 99% (RSD = 3.4%, n = 6) and 91% (RSD = 3.4%, n = 6), respectively. The SBSE-PFC recoveries with 20 injection cycles were 35% for IBMP, 78% for TCA, and 65% for geosmin, respectively. Finally, the SBSE-PFC efficiency with 20 injection cycles was estimated from the single SBSE recovery and the SBSE-PFC recovery (SBSE-PFC recovery × 100/single SBSE recovery). The SBSE-PFC efficiency was in the range of 71–78% for all target compounds. The good efficiency of SBSE-PFC enrichment shows that all analytical steps, e.g. sample preparation (SBSE), sample introduction (TD), MDGC separation ($^{1}D/^{2}D$ GC), simultaneous detection (O/MS), and PFC, for the identification of off-flavor compounds

Table 2
Single SBSE recovery, SBSE-PFC recovery, and SBSE-PFC efficiency for off-flavor compounds in spiked wine at odor perception threshold levels[a].

Compound	$\log K_{ow}$[b]	SBSE recovery (%)	SBSE-PFC recovery (%)	SBSE-PFC efficiency (%)[c]
IBMP	2.86	44	35	78
TCA	4.01	99	78	78
Geosmin	3.57	91	65	71

[a] IBMP at 25 ng L^{-1}; TCA at 5 ng L^{-1}; geosmin at 50 ng L^{-1} [8].
[b] $\log K_{ow}$ is calculated with SRC-KOWWIN software (Syracuse Research, Syracuse, NY, USA).
[c] SBSE-PFC efficiency is estimated from the single SBSE recovery and the SBSE-PFC recovery (SBSE-PFC recovery × 100/single SBSE recovery).

at ng L^{-1} level in wine, are quantitative. The single SBSE recovery, SBSE-PFC recovery, and SBSE-PFC efficiency are summarized in Table 2.

4. Conclusion

A new multi-dimensional GC system referred to as the selectable ^{1}D/^{2}D GC–O/MS with PFC was developed for the analysis of ultra-trace amounts of odor compounds. This system can perform ^{1}D GC–O/MS, ^{2}D GC–O/MS, ^{1}D GC-PFC, and ^{2}D GC-PFC analysis without any instrumental set-up change. The thermal desorption inlet equipped on the proposed system can inject the enriched compounds into the same system with splitless mode, and allows identification of odor compounds by ^{2}D GC–O/MS analysis (in scan mode). The performance of the system was demonstrated by identifying three off-flavor compounds (e.g. TCA, IBMP, and geosmin) in spiked wine at 5–50 ng L^{-1} level. The good efficiency of SBSE-PFC enrichment (71–78%) shows that a combined approach consisting of SBSE, TD, ^{1}D/^{2}D GC–O/MS with PFC is practical for identification of odor compounds at ng L^{-1} level in aqueous samples.

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