



Quantitative analysis of fragrance in selectable one dimensional or two dimensional gas chromatography–mass spectrometry with simultaneous detection of multiple detectors in single injection



Hui Peng Tan, Tow Shi Wan, Christina Liew Shu Min, Murray Osborne, Khim Hui Ng*

Firmenich Asia Pte Ltd, 10 Tuas West Road, 638377 Singapore

ARTICLE INFO

Article history:

Received 27 November 2013
Received in revised form 24 January 2014
Accepted 27 January 2014
Available online 1 February 2014

Keywords:

Perfume
Selectable $^1D/2D$ GC–MS/FID/ODP system
Multidimensional gas chromatography–mass spectrometry
Stir-bar sorptive extraction
Thermal desorption
Dual-linked injectors

ABSTRACT

A selectable one-dimensional (1D) or two-dimensional (2D) gas chromatography–mass spectrometry (GC–MS) system coupled with flame ionization detector (FID) and olfactory detection port (ODP) was employed in this study to analyze perfume oil and fragrance in shower gel. A split/splitless (SSL) injector and a programmable temperature vaporization (PTV) injector are connected via a 2-way splitter of capillary flow technology (CFT) in this selectable $^1D/2D$ GC–MS/FID/ODP system to facilitate liquid sample injections and thermal desorption (TD) for stir bar sorptive extraction (SBSE) technique, respectively. The dual-linked injectors set-up enable the use of two different injector ports (one at a time) in single sequence run without having to relocate the 1D capillary column from one inlet to another. Target analytes were separated in 1D GC–MS/FID/ODP and followed by further separation of co-elution mixture from 1D in 2D GC–MS/FID/ODP in single injection without any instrumental reconfiguration. A $^1D/2D$ quantitative analysis method was developed and validated for its repeatability – t_R ; calculated linear retention indices (LRI); response ratio in both MS and FID signal, limit of detection (LOD), limit of quantitation (LOQ), as well as linearity over a concentration range. The method was successfully applied in quantitative analysis of perfume solution at different concentration level ($RSD \leq 0.01\%$, $n = 5$) and shower gel spiked with perfume at different dosages ($RSD \leq 0.04\%$, $n = 5$) with good recovery (96–103% for SSL injection; 94–107% for stir bar sorptive extraction–thermal desorption (SBSE–TD)).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

GC–MS is a widely used technique for the analysis of complex volatiles – particularly in the fragrance and flavour industry. However, although GC–MS is a valuable tool for analysis, there are instances when analysts face difficulties in trying to resolve the separation of two or more compounds that elute at the same time – co-elution, especially in complex mixtures such as essential oils [1,2]. The essential oil has been an important component in contributing to a perfume formula but also increases the challenge in the analysis. In order to improve the separation, resolution and identification process during analysis, the sample may be injected into 2D comprehensive GC (GC \times GC) for further analysis, or conventional heart-cutting 2D GC technique may be used (GC–GC). These techniques are termed multidimensional GC–MS [1,3,4]. The 2D comprehensive GC is mainly applied in the analysis for total

profiling, whereas the latter approach is more focusing on the target analysis of compounds of interest in a sample.

Fundamentals of 2D comprehensive GC and its applications have been studied and widely reported in recent years [5–8]. In this study, we have taken the approach of heart-cutting 2D GC–MS technique for the separation of co-elution compounds found in the 1D analysis. In fragrance analysis, co-elution has not only imposed complexity in identification but also caused perplexity in olfactive detection of individual raw material in fragrance. Typically a conventional heart-cutting configuration is made up of two different GC for independent oven programming of two capillary columns of different polarity. First GC is usually coupled with a monitor detector such as FID and thus determination of heart-cut region in 2D GC–MS analysis has to be done without mass spectral information. A confirmation detector such as mass spectrometer detector (MSD) is coupled with second GC for providing identification of resolved co-eluted peaks heart-cut from first GC. However, this conventional heart-cutting configuration is unable to perform routine 1D confirmation analysis of unknown sample without mass spectral information.

Over the past few years, newer approach of 2D GC–MS technique has been reported [5,9–12]. New generation of Deans switch

* Corresponding author. Tel.: +65 63472705; fax: +65 68626617.
E-mail addresses: khim.hui.ng@firmenich.com, ngkshshowe@singnet.com.sg (K.H. Ng).

based on CFT and low thermal mass GC (LTM-GC) are integrated into a ^2D GC–MS system which provides many advantages over the conventional ^2D GC–MS system, such as rapid heating and cooling of LTM-GC, independent temperature control, low dead volume of Deans switch, high degree of inertness, as well as electronic pressure control [13–15]. In 2010, K. Sasamoto and N. Ochiai developed a novel selectable $^1\text{D}/^2\text{D}$ GC–MS system using a CFT and dual LTM-GC for simple and fast operation of both ^1D GC–MS and ^2D GC–MS with selective detection using a single GC–MS system [16]. In this selectable configuration, signals from multiple detectors can be collected simultaneously for both the ^1D and ^2D analysis under a constant split ratio. As compared to conventional ^2D GC–MS system, the need of having to run a preliminary analysis to determine a heart-cut region based on FID-signal is no longer required.

Application of the selectable $^1\text{D}/^2\text{D}$ GC–MS system has not been widely reported by far. In this study, a method was developed and validated for the analysis of perfume oil and consumer product by using selectable $^1\text{D}/^2\text{D}$ GC–MS system coupled with FID and ODP. Dual injectors–SSL injector (front inlet) and PTV injector (back inlet), which are linked via a CFT 2-way splitter without make-up gas line, are installed in the selectable $^1\text{D}/^2\text{D}$ GC–MS/FID/ODP system. In the analysis of consumer products for fragrances, it is inevitable that multiple extraction techniques are required for identification of perfume raw materials which are in general volatiles. Some of the techniques involved are liquid extraction, SBSE, headspace-SBSE, and direct thermal desorption (DTD) from samples. In view of various sample types prepared, liquid injection and thermal desorption via SSL and PTV injectors, respectively, are often conducted for consumer product analysis. In a conventional GC–MS configuration, switching the use of one inlet to another involves venting down MS detector to facilitate column relocation. This could be a tedious and time-consuming procedure based on routine analyses of consumer products in the laboratory. The dual-linked injectors set-up enable the use of two different injector ports (one at a time) during a single sequence run without having to disconnect the ^1D capillary column from one inlet to another and thus, reducing the machine downtime significantly. Various parameters which include repeatability, calibration linearity, LOD and LOQ were investigated in this study for $^1\text{D}/^2\text{D}$ analysis via the dual-linked injectors set-up. The validated method was then further illustrated by simultaneous $^1\text{D}/^2\text{D}$ quantitative analysis of perfume oil and spiked shower gel with perfume oil at different dosages.

2. Experimental

2.1. Chemical and reagents

Perfume A is an in-house test mixture which contains the following raw materials in partial: methylparacresol (2.5% w/w), methyl benzoate (4.5% w/w), linalool (24.5% w/w), phenethylol (37.4% w/w), benzyl acetate (14.8% w/w), ethyl phenylacetate (6.3% w/w), indol (1.2% w/w), methyl anthranilate (2.8% w/w), ionone alpha (2.5% w/w) and ionone beta (1.6% w/w). 1,4-dibromobenzene was purchased from Sigma–Aldrich (Buchs, Switzerland) and acetonitrile was provided by Fisher Scientific (Fair Lawn, New Jersey). Terpinene gamma (terpinene G) is an in-house perfume raw material. The chemical name, formula, molecular structure, molecular weight and partition coefficient ($\log P$) of the raw materials are presented in Table 1. Alkane standard solution (C_8 – C_{20}) and (C_{21} – C_{40}) were supplied by Fluka (Buchs, Switzerland). De-ionized water was provided by an USF Elga – Option 7 plus BP system (Buckinghamshire, England). Ethanol (reagent grade) was purchased from Tedia (Ohio, USA). The unperfumed shower gel was an in-house base (Base no: LGL-99-005).

2.2. Sample preparation

2.2.1. Perfume solution

Perfume A was dissolved in ethanol at a predetermined dosage and spiked with ^1D I.S. (150 mg L^{-1} of 1,4-dibromobenzene in acetonitrile) and ^2D I.S. (terpinene G).

2.2.2. SBSE

Sample preparation via SBSE is straight forward and uses de-ionized water as a solvent. This technique was developed by Sandra et al. and reported in 1999 [17]. Since then many applications and advantages of the technique were widely reported [16,18–26]. In this study, a 10 mm length stir-bar encased in glass and coated with $55\ \mu\text{L}$ of polydimethylsiloxane (PDMS) liquid phase was used [17,27], also known as Twister bar which is commercially available from Gerstel (Müllheim an der Ruhr, Germany) [18,28]. When placed in solution, analyte(s) of interest is extracted into the PDMS layer depending on their $\log P$ [18,28,29] and is selective for non-polar compounds with $\log P$ more than 4.

A bulk of 50.00 g unperfumed shower gel was dosed with Perfume A at a predetermined dosage, and left to macerate for at least 3 h. Sample solution at a predetermined concentration was prepared in bulk by dissolving the perfumed shower gel in 400.0 mL of de-ionized water. 20.00 g of this solution was weighed into a 20 mL vial, whilst adding $100\ \mu\text{L}$ each of the ^1D I.S. (150 mg L^{-1} of 1,4-dibromobenzene in acetonitrile) and the ^2D I.S. ($0.6\ \mu\text{L mL}^{-1}$ of terpinene G in acetonitrile). The vial was then shaken thoroughly to mix well the contents of the solution before adding a Twister bar and placing the vial on multiple position magnetic stirrer (15 positions) from VARIOMAG (Florida, USA) to be stirred at 900 rpm for an hour. Prior to use, the Twister bars were conditioned for 30 min at $280\ ^\circ\text{C}$ in a flow of helium. After extraction, the Twister bar was removed from the solution, rinsed with de-ionized water and blotted dry with a lint-free tissue paper before placing into a glass TD liner (Gerstel, Müllheim an der Ruhr, Germany) for TD.

2.3. Instrumentation

All the experiments were performed by using Agilent 7890A GC with 5975C MSD (Agilent Technologies, USA), a FID (Agilent Technologies, USA) and a dual LTM-GC system (Agilent Technologies, USA). Samples were programmed by using a Gerstel MultiPurpose Sampler-2 (MPS-2) coupled with Gerstel automated GC Inlet Liner Exchange (ALEX) technology (Gerstel, Müllheim an der Ruhr, Germany). The ALEX technology is able to work with a PTV inlet (Gerstel, Müllheim an der Ruhr, Germany) and a SSL inlet (Agilent Technologies, USA). Gerstel PTV inlet consists of Gerstel Thermal Desorption Unit (TDU), Gerstel Cooled Injection System-4 (CIS-4) and Gerstel exclusive cryogen-free Universal Peltier Cooling-2 (UPC-2) (or cryo-static cooling) system. The GC was operated with a micro-fluidic Dean switch (G2855B), two 3-way splitter named 3-way Effluent Splitter (G3183B) (Agilent Technologies, USA), two 2-way splitter named Agilent Un-purged Effluent Splitter (G3181B) (Agilent Technologies, USA), a cryogenic-trap system-2 (CTS-2) (Gerstel, Müllheim an der Ruhr, Germany) and a pressure control module (PCM) which play as a make-up gas line controller. Gerstel Maestro software (Müllheim an der Ruhr, Germany) integrated with Agilent GC–MS Chemstation Enhanced Data Analysis software (Agilent Technologies, USA) were used for the instrument control, data acquisition, as well as data interpretation.

2.4. GC–MS condition

Fig. 1(a) shows a simplified diagram of $^1\text{D}/^2\text{D}$ GC–MS system coupled with multiple detectors. The GC was equipped with SSL inlet, PTV inlet, dual LTM-GC system, two 2-way splitter, two

Download English Version:

<https://daneshyari.com/en/article/1200126>

Download Persian Version:

<https://daneshyari.com/article/1200126>

[Daneshyari.com](https://daneshyari.com)