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Comprehensive two-dimensional gas chromatography coupled to a rapid-scanning quadrupole mass spectrometer: principles and applications

Mohamed Adahchour*, Menno Brandt, Hans-Ulrich Baier[1], René J.J. Vreuls, A. Max Batenburg[2], Udo A. Th. Brinkman

Department of Analytical Chemistry and Applied Spectroscopy, Vrije Universiteit, de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Abstract

The principles, practicability and potential of comprehensive two-dimensional (2D) gas chromatography coupled to a rapid-scanning quadrupole mass spectrometer (GC × GC–qMS) for the analysis of complex flavour mixtures in food, allergens in fragrances and polychlorinated biphenyls (PCBs) were studied. With a scan speed of 10,000 amu/s, monitoring over a mass range of up to 200 atomic mass unit (amu) can be achieved at an acquisition frequency of 33 Hz. Extending this mass range and/or increasing the data acquisition frequency results in a loss of spectral quality. Optimal parameter settings allow, next to unambiguous identification/confirmation of target compounds on the basis of high-quality mass spectra, fully satisfactory quantification (three to four modulations per peak) with linear calibration plots and detection limits in the low-pg level. The potential of time-scheduled data acquisition to increase the effective mass range within one GC × GC run was also explored. The analyses, with baseline separation of the flavours, allergens and PCB target compounds, took less than 30 min.

Keywords: Gas chromatography comprehensive two-dimensional; Detection, GC; Quadrupole mass spectrometer; Flavours; Allergens; Polychlorinated biphenyls

1. Introduction

Comprehensive two-dimensional (2D) gas chromatography (GC × GC) is gaining wide interest and increased acceptance due to its ability to separate and identify analytes in complex samples [1–3]. Impressive results have been obtained in terms of separation efficiency and, also, compound classification based on the presence of ordered structures in GC × GC chromatograms [4,5]. For GC × GC, next to column selection and modulation, detection is also an important consideration. The very fast separation in the short and narrow two-dimension column results in peak widths of, typically, 80–600 ms at the baseline, and in some cases widths as low as 45 ms have been reported [6]. In order to ensure a proper monitoring of these narrow peaks, fast detectors, with a small internal volume and a short detector rise time and a high data acquisition rate, are required. Until recently, the flame ionisation detector (FID) with its high acquisition rate of 50–200 Hz dominated the detection field in GC × GC. Today, micro electron-capture detectors (μECD) with, typically, a 50 Hz sampling rate, are recognised as valuable alternatives, specifically for the many applications dealing with polychlorinated target analytes [4,7].

However, the above detectors do not provide structural information. In conventional GC, mass spectrometry (MS) is nowadays widely used for detection and identification purposes in development as well as in routine laboratories. The main mass analysers are the ion-trap, the sector, the quadrupole (qMS) and the time-of-flight mass spectrometers (ToF MS). There are large mutual differences as regards acquisition rates, detection limits, resolution and quality of the mass spectra obtained. At present, of the four

* Corresponding author. Tel.: +31 20 444 7525; fax: +31 20 444 7543.
E-mail address: m.adahchour@few.vu.nl (M. Adahchour).
[1] Shimadzu Deutschland, Albert-Hahn Straβe 6-10, 47269 Duisburg, Germany.
[2] Unilever Research Laboratory Vlaardingen, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands.

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types of commercially available mass spectrometers, only a ToF MS can acquire the fifty or more mass spectra per second that are required for the proper monitoring of GC × GC chromatograms and, more importantly, for quantification. Admittedly, the extremely popular benchtop qMS systems are much less expensive and more user-friendly, and several authors have reported their use with GC × GC under appropriate operating conditions [8–12]. However, in these studies it was difficult to perform quantification due to the slow quadrupole duty cycle and the need to scan individual masses in the scan range, which results in slow data acquisition.

In the present investigation, the performance of a modern qMS system for use in GC × GC was studied for both qualitative and quantitative purposes. These modern quadrupole instruments have scan speeds of up to 10,000 amu/s and can also meet the 50 Hz requirement, provided proper mass range settings are selected. The principles of coupling a qMS to a GC × GC system are discussed in terms of data acquisition rate, mass range and mass spectral quality. In addition, three different application areas—flavours in food, allergens in perfumes and PCB analysis—were selected to evaluate these principles, i.e. to study the capabilities of the GC × GC–qMS system for the identification and determination of target compounds in complex samples.

2. Experimental

2.1. Analytes and samples

Two standard mixtures were used in the present study. Mixture 1 containing 25 allergen compounds (for compound names, see Table 1), was dissolved in isooctane and standard solutions were prepared over the concentration range 2–50 mg/L. Perfume samples were diluted 1:1000 (v/v) with isooctane prior to injection. Mixture 2 containing 25 flavour compounds (for compound names, see Table 1) found to be responsible for the odour of olive oil samples (see Section 3.4.1), was dissolved in freshly distilled methyl acetate. All 95–99% pure standards were from the Unilever Research Laboratory, which also provided various olive oil extracts in diethyl ether.

High-vacuum degassing (HVD), which is a suitable technique to isolate flavour compounds from fat or oily matrices under mild conditions, was used to isolate the volatile flavours from the extract [13]. The olive oil samples were subjected to HVD at room temperature under high vacuum (1.6×10^{-6} mbar). After 5 h of extraction, the solid material trapped by means of liquid nitrogen (−185 °C) was dissolved in 2 mL of diethyl ether or pentane. In order to avoid losses of volatiles, 1 μL of each final extract was injected in the GC system without any pre-concentration.

Table 1
Retention time data of the flavour and allergen standard compounds

Flavours	Quantification mass (amu)	^1t_R (min)	^2t_R (s)	Allergens	No.	Quantification mass (amu)	^1t_R (min)	^2t_R (s)
2-Methyl-1-butanol	70	6.0	1.39	Benzyl alcohol	1	108	8.5	3.17
Ethyl isobutyrate	116	6.2	0.76	Limonene	2	68	8.7	0.64
Butanoic acid	60	6.7	5.15[a]	Linalool	3	93	9.8	0.92
Hexanal	72	6.7	1.33	Methyl 2-octynoate	4	95	11.1	1.07
Ethyl butyrate	88	6.8	0.88	Citronellol	5	69	11.7	0.93
trans-2-Hexenal	98	7.8	1.79	Citral (neral)	6	69	11.8	1.18
Isovaleric acid	60	7.9	4.82[a]	Geraniol	7	69	12.1	2.45
Ethyl-2-methylbutyrate	102	7.9	0.82	Cinnamic aldehyde	8	131	12.1	1.06
trans-2-Hexenol	82	8.4	2.00	Citral (geranial)	9	69	12.2	1.13
1-Hexanol	69	8.6	1.67	Anisyl alcohol	10	108	12.4	3.26
Pentanoic acid	60	8.8	5.33[a]	Hydroxycitronellal	11	59	12.4	1.83
Heptanal	70	9.0	1.18	Cinnamyl alcohol	12	92	12.7	2.82
trans-2-Heptenal	83	10.5	1.70	Eugenol	13	164	13.6	1.64
1-Octen-3-one	70	11.2	1.24	Coumarine	14	146	14.5	3.72
Octanal	84	11.9	1.09	Isoeugenol	15	164	14.8	1.86
trans-2,4-Heptadienal	81	11.9	2.52	α-Isomethylionone	16	135	15.5	0.81
Hexylacetate	84	12.3	0.85	Lilial	17	189	15.9	0.92
3-Octen-2-one	111	12.9	1.58	Amyl cinnamic aldehyde	18	202	17.5	0.92
trans-2-Octenal	70	13.5	1.58	Amyl cinnamic alcohol	19	133	18.0	1.13
1-Octanol	70	14.4	1.33	Farnesol 1	20	81	18.2	0.74
Nonanal	98	14.9	0.97	Farnesol 2	21	93	18.4	0.77
β-Phenylethyl alcohol	122	15.4	0.85	Hexyl cinnamic aldehyde	22	216	18.7	0.92
Ethyl cyclohexanoate	101	15.9	0.88	Benzyl benzoate	23	105	18.8	1.35
trans-2-Nonenal	83	16.6	1.39	Benzyl salicylate	24	91	20.0	1.26
1-Nonanol	70	17.4	1.12	Benzyl cinnamate	25	131	22.2	1.43

For GC×GC conditions, see Section 2.
[a] Compounds showing wrap-around.