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CRITICAL REVIEW

Solid-phase microextraction coupled to comprehensive multidimensional gas chromatography for food analysis

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Abstract

Solid-phase microextraction and comprehensive multidimensional gas chromatography represent two milestone innovations that occurred in the field of separation science in the 1990s. They have a common root in their introduction and have found a perfect coupling in their evolution and applications. This review will focus on food analysis, where the paradigm has changed significantly over time, moving from a targeted analysis, focusing on a limited number of analytes at the time, to a more holistic approach for assessing quality in a larger sense. Indeed, not only some major markers or contaminants are considered, but a large variety of compounds and their possible interaction, giving rise to the field of foodomics. In order to obtain such detailed information and to answer more sophisticated questions related to food quality and authenticity, the use of SPME-GC × GC–MS has become essential for the comprehensive analysis of volatile and semi-volatile analytes. This article provides a critical review of the various applications of SPME-GC × GC in food analysis, emphasizing the crucial role this coupling plays in this field. Additionally, this review dwells on the importance of appropriate data treatment to fully harness the results obtained to draw accurate and meaningful conclusions.

Keywords Solid-phase microextraction · SPME · Multidimensional comprehensive gas chromatography · GC × GC · Food

Introduction

Solid-phase microextraction (SPME) and comprehensive multidimensional gas chromatography (GC × GC) represent some of the most revolutionary innovations in separation science that have occurred since the introduction of the capillary column by M.J.E. Golay in 1958 [1]. The first SPME and GC × GC papers were introduced just 1 year apart: SPME in 1990 by Arthur and Pawliszyn [2] and GC × GC 1991 by Liu and Phillips [3]. Although they can seem unrelated at first glance, a tight relationship exists between the two. Indeed, Janusz Pawliszyn was the first Ph.D. student of Philipps, and he was part of the initial works [4, 5] that opened the door to the invention of both techniques. Besides these common roots, the coupling of the two techniques extends their potential, making them a very good match for multiple applications. Nevertheless, this review focuses on their application in food analysis, a multifaceted and dynamic field, the evolution of which will be shortly summarized before critically discussing the main applications since 2002 when the first coupling of SPME and GC × GC for food analysis was presented by Adahchour et al., for the profiling of garlic volatiles [6]. Since then, the number of papers has been constantly growing, as shown in Fig. 1, with a significant increment from 2014. The main goal of the few earlier papers was highlighting the potential rather than fully taking advantage of the coupling of SPME and GC × GC [7]. Only in 2008 the first works exploiting the full potential in providing the chromatographic fingerprint of food samples were published [8–10]. Although two of them still limited the data mining to univariate [8] and visual [10] approaches, the work of Cordero et al. [9] represented a cornerstone using the two-dimensional (2D) plot as a fingerprint. In this milestone paper, the authors investigated three approaches to extract information from the 2D chromatogram: group-type,

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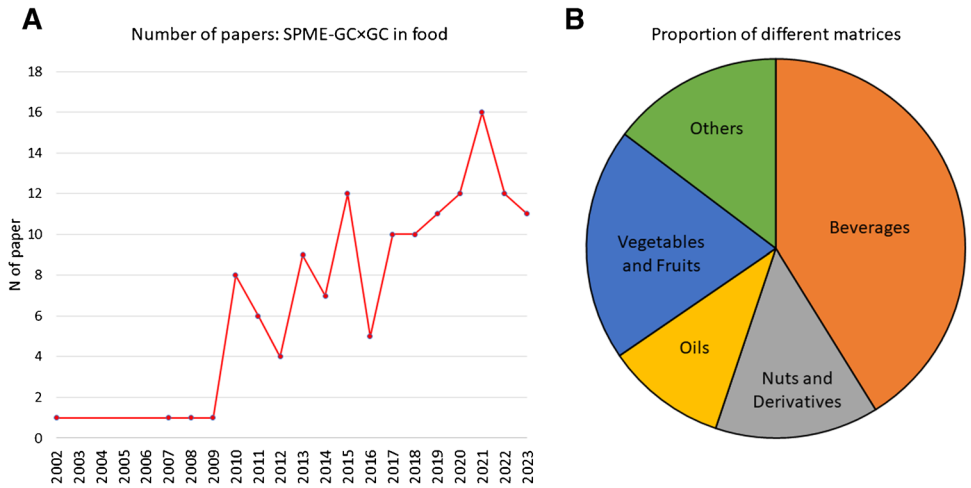

Fig. 1 **A** Evolution of the number of papers published in Scopus searching for the following keywords: "SPME," "GC × GC," "food" over the period 2002–July 2023. **B** Applications using SPME-GC × GC divided by food category

fingerprint-type characterizations, and template matching approaches. The first approach relied on the selectivity of the mass spectrometer detector coupled with the GC × GC system to visualize group-wise the compound's classes and compare them among samples. The fingerprint-type characterization was based on a peer-wise differential image produced by a specific software [11]. Finally, the template matching approach creates a reference template (including 1D and 2D retention times and the MS spectrum information); then, this was applied to all the samples under investigation, creating an aligned table for further chemometrics elaboration [12].

The research group of Cordero keeps leading the use of advanced data mining in food analysis to decrypt the chromatographic fingerprints generated by SPME-GC × GC. Worth mentioning are the new approaches involving artificial intelligence algorithms that have been recently published [12, 13]. In one of these publications, the authors proposed using computer vision for the graphical comparison of multiple fingerprint chromatograms. This allows the comparison of untargeted results, making use of virtually all information available. Another publication by the same group made use of chemometric models (principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA)) to correlate markers and chemical patterns to quality parameters of hazelnuts. These results were further exploited to support an artificial intelligence (AI) decision-making tool to classify samples based on origin and shelf life, with the potential of detecting spoilage and rancidity [12].

Despite the ability of more sophisticated chemometric approaches to decrypt the vast amount of information concealed in the chromatographic fingerprints, which has been proven for about 10 years, their use remains somewhat limited in the vast literature involving SPME-GC × GC.

Concerning SPME coatings and modes of application (*i.e.*, HS or direct immersion (DI)) in relation to GC × GC food-based applications, the innovation is rather scarce. Mainly HS and traditional commercially available coatings are used, with a large predominancy of the triphasic fiber, *i.e.*, divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), followed by CAR/PDMS and PDMS/DVB. The intense efforts of the last years in developing new fiber with antifouling coatings [14] to be used in DI-SPME analysis for complex matrices have not yet been exploited for applications coupled with GC × GC. Nevertheless, exciting applications using HS-SPME-GC × GC have been developed over the years, providing a comprehensive overview of the examined samples. In this review, we will discuss the unique advantages offered by SPME-GC × GC in food analysis, focusing on its holistic analysis capacity of the technique for food fingerprint analysis. We will explore its applications in areas such as quality control, food safety assessment, authentication, and flavor profiling, shedding light on its versatility and broad scope of application. It should be noted that chemometrics plays a central role in the appropriate exploitation of the large amount of data obtained in these cases. However, the fundamentals of data mining are out of the scope of this review, and they can be found elsewhere [15–17]. The same applies to the fundamentals of SPME [18–20] and GC × GC [21, 22], for which the reader is directed to the specific literature for a more detailed description of the technique.

As aforementioned, before entering the discussion on the applications of HS-SPME-GC × GC in food analysis, a brief overview of the evolution of the paradigms in this field is presented hereafter to frame its specificities and highlight how the coupling of SPME with GC × GC can play a crucial role in further developments.

Food analysis: from wet chemistry to a holistic approach

The origin of food chemistry is rooted in agricultural chemistry, making it difficult to establish an initial date. Nevertheless, some traces of this new scientific field appeared at the end of the eighteenth century, when the first food-related components (*i.e.*, lactose, glycerol, citric acid, stearic acid, and oleic acid) were discovered and the primitive methods for the elemental food characterization (C, N, and H) were established. A number of historical reviews nicely described the first steps and the evolution of food chemistry in more detail [23–26].

Since these first steps, food chemistry moved towards determining the major constituents through titration, gravimetric, and precipitation methods during the nineteenth century. It further underwent a significant development during the twentieth century, retro-feeding from instrumental analytical advancements, starting from the introduction of the basic pH meter in 1934, the ultraviolet (UV) spectrophotometer in 1941 [24, 27], the infrared (IR) spectrophotometer in 1944 [28], to the introduction of liquid chromatography (LC) in 1941 [29], gas chromatographic (GC) in 1951 and 1952 [30–34], and their coupling to the mass spectrometer (MS) in 1959 (although invented in 1919 by Thomson) [35].

This evolution of the analytical instrumentation has allowed a paradigm change in the interpretation of food chemistry. This has fuelled the evolution from basic questions related to the elemental composition of major constituents (mainly based on wet chemistry and reductionist approaches), towards the investigation of minor and trace components (instrumental chemistry). More recently, the food chemistry field has been moving towards interactionism (an integrated and interactive approach) and -omics sciences. This change of paradigm follows the consumers' awareness that, granted the safety of food, asks for additional quality parameters (e.g., bio-active compounds, sustainable products). In this regard, the term "foodomics" has been defined in 2009 as "a discipline that studies the food and nutrition domains through the application and integration of advanced -omics technologies to improve consumers' well-being, health, and confidence" [36].

From an analytical viewpoint, food analysis has started looking at the results obtained with highly informative instruments such as information-rich fingerprints, for which new tools (*i.e.*, chemometrics [16, 17]) are necessary to extract the useful information. Moreover, using artificial intelligence strategies can contribute to interpreting and exploiting the obtained results.

On the data treatment side, it is necessary to distinguish between the definition of profiling and fingerprinting [37, 38]. The former aims to provide detailed qualitative and quantitative characterization of the samples (either targeted or untargeted), while the latter seeks to capture the information disregarding the complete and detailed characterization. Initially, which of the two approaches were followed determined the analytical workflow and the instrumental system employed, for instance, GC–MS for the former and NIR for the latter. However, this changed when the concept of chromatographic fingerprint emerged [39]. The chromatographic fingerprint provides a unique situation where the output data can be used for both approaches, targeted and untargeted (mainly valid for comprehensive techniques such as GC × GC) [16, 40].

Considering this framework and paradigm evolution of the field of food analysis, the use of HS-SPME-GC × GC is presented and discussed in the following section for different applications. We hope to inspire further research and development in this rapidly evolving field, ultimately contributing to the improvement of food safety, quality control, and consumer satisfaction.

Applications in food analysis

The application of SPME in combination with GC × GC for food analysis has been increasing since its first introduction (Fig. 1). The analysis of the volatile fraction has significantly increased over the last years for certain products of high value, such as oils or infusions (tea, coffee), for which their organoleptic characteristics are of high interest. Thus, the applications of this technique for the determination of the volatile profile of these samples are predominant in the literature. Moreover, as the interest is focused on the volatile compounds, headspace (HS)-SPME appears as a predominant option for sample pretreatment due to its simplicity for overcoming interference and contamination from the sample matrix. In this review article, we focus on the main food categories, accentuating the interest in advanced omics techniques that make the best use of the large amount of information that can be obtained with comprehensive techniques such as SPME in combination with GC × GC. The discussion herein reported is not intended to be an exhaustive description of all the applications published in the field, but rather a critical discussion on the most significant ones. For a complete overview, the readers are directed towards Table 1.

Edible oils

Edible oils can be produced from animals or plants, including seeds, leaves, pulp, and nuts. Despite the source, they consist of about 95% triacylglycerides (TAG) and diverse minor components, such as free fatty acids, glycolipids,

Table 1 HS-SPME- GC×GC applications in food published in 2002–2023 (July). When multiple possibilities are presented, the one in bold is retained for the final application.

	Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
				1D	2D			
Oils	Olive oil	HS	DVB/CAR/PDMS	HP-Innowax (30 m×0.25 mm×0.25 µm)	BPX-50 (1.25 m×0.1 mm×0.1 µm)	ToFMS	2010	*Food Chem* (2010) 121 282–289
	Olive oil	HS	DVB/CAR/PDMS	Rxi-5MS (30 m×0.25 mm×0.5 m)	Supelcowax-10 (1.2 m×0.1 mm×0.1 µm)	qMS	2014	*J Chromatogr A* (2014) 1334 101–111
	Olive oil	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2016	*Anal Chim Acta* (2016) 936 245–258
	Olive oil	HS	DVB/CAR/PDMS	VF-Wax (30 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.5 m×0.15 mm×0.15 µm)	ToFMS	2019	*Food Chem* (2019) 270 403–414
	Olive oil	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (2 m×0.1 mm×0.1 µm)	ToFMS	2019	*Separations* (2019) 6 34
	Olive oil	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	ToFMS	2019	*J Agric Food Chem* (2019) 67 5289–5302
	Olive oil	HS	DVB/CAR/PDMS	HeavyWax (20 m×0.18 mm×0.18 µm)	DB17 (1.8 m×0.18 mm×0.18 µm)	qMS/FID	2021	*J Chromatogr A* (2021) 1650 462,232
	Sesame oils and soybean oils	HS	DVB/PDMS; PDMS; CAR/PDMS; **DVB/CAR/PDMS**	DB-5MS (30 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.4 m×0.15 mm×0.15 µm)	ToFMS	2020	*Food Anal Methods* (2020) 13 1328–1336
	Rapeseed oil	HS	DVB/CAR/PDMS	DB-5 (30 m×0.25 mm×0.1 µm)	Supelcowax-10 (0.75 m×0.1 mm×0.1 µm)	ToFMS	2016	*J Chromatogr A* (2016) 1428 292–304
	Rapeseed oil	HS	DVB/CAR/PDMS	DB-5 (30 m×0.25 mm×0.5 µm)	Supelcowax-10 (0.75 m×0.1 mm×0.1 µm)	ToFMS	2017	*Eur J Lipid Sci Technol* (2017) 119 1,600,328
	Olive oil	HS	DVB/CAR/PDMS	VF-Wax (30 m×0.25 mm×0.25 µm)	Rtx-200MS (1.5 m×0.25 mm×0.25 µm)	ToFMS	2019	*Molecules* (2019) 24 1–17
	Rapeseed and camelina oils	HS	**CAR/PDMS 85 µm**; DVB/CAR/PDMS 50/30 µm; PDMS/DVB 65 µm	30 m×0.25 mm×0.25 µm SLB-5	0.75 m×0.2 mm×0.1 µm Supelcowax-10	ToFMS	2022	*J Food Compos Anal* (2022) 110 104,595
	Rapeseed oil	HS	CAR/PDMS 85 µm	30 m×0.25 mm×0.25 µm SLB-5	0.8 m×0.25 mm×0.25 µm SLB-50	ToFMS	2023	*Anal Bioanal Chem* (2023) 415 2523–2534
	Olive oil	HS	**DVB/CAR/PDMS 50/30 µm**; DVB/PDMS 65 µm; PA 85 µm; PDMS 75 µm	30 m×0.25 mm×0.25 µm SolGel-Wax	1 m×0.1 mm×0.1 µm OV1701	ToFMS	2021	*J AOAC Int* (2021) 104 274–287

Table 1 (continued)

	Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
				1D	2D			
	Olive oil	HS	CAR/PDMS; PDMS/DVB; **DVB/CAR/PDMS**	DB-5 (25 m×0.2 mm×0.33 µm)	Supelcowax-10 (1.2 m×0.1 mm×0.1 µm)	ToFMS	2013	*Food Res Int* (2013) 54 1979–1986
Nuts and derivatives	Chocolate	HS	DVB/CAR/PDMS	HP-5 (30 m×0.25 mm×0.25 µm)	SolGel-Wax (0.80 m×0.1 mm×0.1 µm)	qMS	2014	*Talanta* (2014) 129 303–308
	Chocolate	HS	DVB/CAR/PDMS	HP-5 (30 m×0.25 mm×0.25 µm)	SolGel-Wax (0.80 m×0.1 mm×0.1 µm)	qMS	2019	*Br Anal Chem* (2019) 6 16–26
	Cacao bean	HS	PDMS/DVB	RTX-5MS (20 m×0.25 mm×0.5 µm)	RTX-200MS (2 m×0.18 mm×0.2 µm)	ToFMS	2010	*J Chromatogr A* (2010) 1217 1963–1970
	Cocoa	HS	DVB/CAR/PDMS	HP-5 (30 m×0.25 mm×0.25 µm)	Solgel-Wax (0.80 m×0.1 mm×0.1 µm)	qMS; FID	2016	*Food Res Int* (2016) 90 133–138
	Cocoa	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2017	*J Agric Food Chem* (2017) 65 6329–6341
	Cocoa	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS; FID	2018	*J Chromatogr A* (2018) 1536 122–136
	Cocoa	HS	DVB/CAR/PDMS	HP-5 (30 m×0.25 mm×0.25 µm)	SolGel-Wax (0.80 m×0.1 mm×0.1 µm)	qMS	2018	*Microchem J* (2018) 141 353–361
	Cocoa	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (2 m×0.1 mm×0.1 µm)	ToFMS	2019	*J Chromatogr A* (2019) 1597 132–141
	Cocoa	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (2 m×0.1 mm×0.1 µm)	ToFMS	2020	*Food Chem* (2020) 309 125,561
	Hazelnuts	HS	DVB/CAR/PDMS	CW20 M (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2010	*J Chromatogr A* (2010) 1217 5848–5858
	Hazelnuts	HS	DVB/CAR/PDMS	CW20 M (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2012	*J Chromatogr A* (2012) 1243 81–90
	Hazelnuts	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2013	*Anal Chim Acta* (2013) 798 115–125
	Hazelnuts	HS	DVB/CAR/PDMS	DB-5 (30 m×0.25 mm×0.25 µm)	OV1701 (2 m×0.1 mm×0.1 µm)	ToFMS	2020	*J Chromatogr A* (2020) 1614 460,739
	Hazelnuts	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	ToFMS	2021	*Food Chem* (2021) 340 128,135
	Groundnut	HS	DVB/CAR/PDMS	Rxi-5Sil MS (30 m×0.25 mm×0.25 µm)	Rxi-17Sil (0.97 m×0.25 mm×0.25 µm)	ToFMS	2018	*Int J Food Prop* (2018) 21 929–941
	Hazelnuts	HS	DVB/CAR/PDMS 50/30 µm	20 m×0.18 mm×0.18 µm DB-HeavyWax	1.8 m×0.18 mm×0.18 µm DB-17	qMS/FID	2023	*J Chromatogr A* (2023) 1700 464,041
	Chocolate	HS	DVB/CAR/PDMS 50/30 µm	20 m×0.18 mm×0.18 µm SLB-5MS	5 m×0.32 mm×0.25 µm SLB-35MS	SCD/FID	2023	*Molecules* (2023) 28 3038

Table 1 (continued)

	Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
				1D	2D			
	Hazelnuts and Coffee	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×0.25 µm SE52 30 m×0.25 mm×0.25 µm SE52 30 m×0.25 mm×0.25 µm CW20 M	1 m×0.1 mm×0.1 µm OV1701 1 m×0.1 mm×0.1 µm OV17 1 m×0.1 mm×0.1 µm OV1701	qMS	2008	*J Agric Food Chem* (2008) 56 7655–7666
	Cacao	HS	PDMS/DVB 65 µm	20 m×0.25 mm×0.5 µm RTX-5MS	2 m×0.18 mm×0.2 µm RTX-200MS	ToFMS	2009	*J Sep Sci* (2009) 32 2289–2295
	Hazelnuts	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2018	*Anal Bioanal Chem* (2018) 410 3491–3506
vegetables and fruits	Berries	HS	DVB/CAR/PDMS	Equity 1 (30 m×0.25 mm×0.25 µm)	Solgel-Wax (1.6 m×0.10 mm×0.10 µm)	ToFMS	2015	*Talanta* (2015) 134 460–467
	Apple/Pear	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	BPX-5 (2 m×0.15 mm×0.25 µm)	qMS	2010	*J Chromatogr A* (2010) 1217 565–574
	Avocado	DI	PDMS/DVB/PDMS	Rxi-5MS (30 m×0.25 mm×0.25 µm)	Supelcowax BP 20 (10 m×0.1 mm×0.1 µm)	ToFMS	2017	*Talanta* (2017) 167 754–760
	Berries	HS	DVB/CAR/PDMS	Equity-1 (30 m×0.25 mm×0.25 µm)	SolGel-Wax (2 m×0.1 mm×0.1 µm)	ToFMS	2014	*Food Chem* (2014) 152 88–93
	Berries	HS	PDMS/DVB; CAR/PDMS; PDMS; **DVB/CAR/PDMS**	Equity-1 (30 m×0.25 mm×0.25 µm)	SolGel-Wax (2 m×0.1 mm×0.1 µm)	ToFMS	2017	*Food Chem* (2017) 221 1041–1056
	Cucumber fermented	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	Rtx-17 (1 m×0.1 mm×0.1 µm)	ToFMS	2015	*Int J Food Microbiol* (2015) 215 40–48
	Fruit (soursop)	HS	PDMS; **CAR/PDMS**; DVB/CAR/PDMS; PA	DB-5 (30 m×0.25 mm×0.25 µm)	BPX50 (0.69 m×0.1 mm×0.1 µm)	ToFMS	2011	*Food Chem* (2011) 125 1481–1489
	Fruits	HS	DVB/CAR/PDMS	Mega CW (25 m×0.15 mm×0.15 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2017	*Food Chem* (2017) 219 13–22
	Grapes	HS	2 PIL; PDMS; PA	Rtx-5SilMS (30 m×0.25 mm×0.25 µm)	BP-20 (1 m×0.1 mm×0.1 µm)	qMS	2018	*Talanta* (2018) 188 522–530
	Orange juice	HS	DVB/CAR/PDMS	SolGel-Wax (30 m×0.25 mm×0.25 µm)	Rxi-5Sil MS (0.8 m×0.1 mm×0.8 µm)	ToFMS	2015	*Food Res Int* (2015) 75 281–288
	Orange juice	HS	DVB/CAR/PDMS	HP-Innowax (30 m×0.25 mm×0.25 µm)	BPX1 (1 m×0.1 mm×0.1 µm)	qMS	2020	*Talanta* (2020) 217 121,038

Table 1 (continued)

Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
			1D	2D			
Pineapple	HS	DVB/CAR/PDMS	**HP-5 (30 m × 0.25 mm × 0.25 µm)** HP-5 (30 m × 0.25 mm × 0.25 µm) **SPWax (25 m × 0.20 mm × 0.2 µm)**	**SPWax (1 m × 0.1 mm × 0.1 µm)** HP-50 (1 m × 0.1 mm × 0.1 µm) **HP-5 (1 m × 0.1 mm × 0.1 µm)**	FID	2011	*J Sep Sci* (2011) 34 1547–1554
Pineapple	HS	PDMS/DVB	ZB-Wax (30 m × 0.25 mm × 0.5 µm)	BPX5 (2 m × 0.15 mm × 0.25 µm)	qMS	2015	*Anal Bioanal Chem* (2015) 407 2591–2608
Strawberry	HS	PDMS/DVB	BPX5 (30 m × 0.25 mm × 0.25 µm)	BP20 (1 m × 0.1 mm × 0.1 µm)	ToFMS	2013	*Food Chem* (2013) 141 1997–2005
Truffle	HS	DVB/CAR/PDMS	SLB-5 ms (30 m × 0.25 mm × 0.25 µm)	Supelcowax-10 (1.1 m × 0.1 mm × 0.1 µm)	qMS/FID	2015	*LWT* (2015) 60 905–913
Apples	HS/DI	PDMS; PA; CW; PDMS/DVB; CAR/PDMS; **DVB/CAR/PDMS**; Carbopack Z/PDMS	Rxi-5SilMS (30 m × 0.25 mm × 0.25 µm)	Supelcowax (1.15 m × 0.1 mm × 0.1 µm) **DB-17 (1.15 m × 0.1 mm × 0.1 µm)**	ToFMS	2012	*J Chromatogr A* (2012) 1251 208–218
Watermelon juice	HS	DVB/CAR/PDMS	DB-Wax (30 m × 0.25 mm × 0.25 µm)	DB-17 (2.22 m × 0.18 mm × 0.18 µm)	O/qMS	2021	*LWT* (2021) 137 110,478
Grape	HS	DVB/CAR/PDMS	DB-Wax (30 m × 0.25 mm × 0.25 µm)	Mega-17 MS (1.7 m × 0.1 mm × 0.1 µm)	ToFMS	2019	*J Org Chem* (2019) 15 1945–1961
Pears	HS	DVB/CAR/PDMS	Rxi-5MS (30 m × 0.25 mm × 0.25 µm)	Rxi-17Sil MS (2 m × 0.25 mm × 0.25 µm)	ToFMS	2019	*Molecules* (2019) 24 1–10
Cucumber pickles	HS	na	na	na	ToFMS	2022	*J Food Sci* (2022) 87 1475–1488
Tomato	HS	na	30 m × 0.25 mm × 0.25 µm BPX5	2 m × 0.1 mm × 0.1 µm BPX50	ToFMS	2022	*Cells* (2022) 11 3051
Tomato	HS	DVB/CAR/PDMS 50/30 µm	30 m × 0.25 mm × 0.25 µm BPX5	2 m × 0.1 mm × 0.1 µm BPX50	ToFMS	2023	*Cells* (2023) 12 1271
Bell pepper	HS	na	na	na	ToFMS	2023	*Chem A Eur J* (2023) 29
Bell pepper	HS	DVB/CAR/PDMS 50/30 µm	30 m × 0.25 mm × 0.1 µm Optima-5MS	2 m × 0.1 mm × 0.1 µm MEGA-WAX FAST	ToFMS	2023	*Pytochemistry* (2023) 205 113,488
Bell pepper	HS	DVB/CAR/PDMS 50/30 µm	30 m × 0.25 mm × 0.1 µm Optima-5MS	2 m × 0.1 mm × 0.1 µm MEGA-WAX FAST	ToFMS	2022	*J Agric Food Chem* (2022) 70 6719–6725

Table 1 (continued)

	Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
				1D	2D			
	Garlic	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.32 mm×0.25 µm HP1	1.5 m×0.1 mm×0.1 µm BPX50	FID	2002	*Chromatographia* (2002) 55 361–367
Beverages	Tea	HS	DVB/CAR/PDMS	DB-5MS (30 m×0.25 mm×0.25 µm)	DB-17HT (1.9 m×0.1 mm×0.1 µm)	ToFMS	2018	*Food Res Int* (2018) 108 74–82
	Coffee/ Juniper	HS	DVB/CAR/PDMS	SE52 (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2010	*J Chromatogr Sci* (2010) 48 251–261
	Tea	HS	PDMS; PDMS/DVB; ***PDMS/CAR***; DVB/CAR/PDMS; CAR/PDMS; PA; PEG	**HP-5 (30 m×0.25 mm×0.5 µm)** DB-WAXETR (30 m×0.25 mm×0.25 µm)	**Stabilwax (0.6 m×0.15 mm×0.15 µm)** Rxi-5 ms (0.6 m×0.15 mm×0.15 µm)	FID	2017	*Anal Bioanal Chem* (2017) 409 4127–4138
	Tea	HS	DVB/CAR/PDMS	SE52 (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2017	*Food Chem* (2017) 225 276–287
	Tea	HS	PDMS/DVB	Rxi-5Sil MS (30 m×0.25 mm×0.25 µm)	Stabilwax (0.8 m×0.25 mm×0.25 µm)	ToFMS	2018	*J Chromatogr A* (2018) 1536 137–150
	Tea	HS	CAR/PDMS	Rxi-5Sil MS (30 m×0.25 mm×0.25 µm)	Rxi-17 (1.69 m×0.15 mm×0.15 µm)	ToFMS	2020	*Food Res Int* (2020) 137 109,656
	Tea	HS	CAR/PDMS	HP-Innowax (60 m×0.25 mm×0.25 µm)	BPX-1 (2 m×0.1 mm×0.1 µm)	qMS	2021	*Food Chem* (2021) 339 128,136
	Tea	HS	CAR/PDMS	Rtx-5 (30 m×0.2 mm×0.25 µm)	Rtx-200 (1.79 m×0.15 mm×0.15 µm)	ToFMS	2020	*J AOAC Int* (2020) 103 2
	Beer	HS	CAR/PDMS	Stabilwax (30 m×0.25 mm×0.25 µm)	Rtx-200 (1 m×0.15 mm×0.15 µm)	ToFMS	2017	*J Chromatogr A* (2017) 1507 45–52
	Cider	HS/DI	PDMS; CAR/PDMS; DVB/CAR/PDMS	DB-Wax (30 m×0.25 mm×0.5 µm)	DB-5MS (2 m×0.25 mm×0.25 µm)	ToFMS	2012	*Food Chem* (2012) 131 1561–1568
	Fermented beverages	HS	DVB/CAR/PDMS	VF-Wax (30 m×0.25 mm×0.25 µm)	Rxi-17SilMS (1.5 m×0.15 mm×0.15 µm)	ToFMS	2020	*Metabolomics* (2020) 16 102
	Plum brandy	HS	PDMS; DVB/PDMS; PA; CAR/PDMS	**DB-FFAP (30 m×0.25 mm×0.25 µm)** HP-5 (30 m×0.25 mm×0.25 µm)	BPX-50 (1.5 m×0.1 mm×0.1 µm)	ToFMS	2017	*J Food Sci Technol* (2017) 54 4284–4301
	Liquor (Baijiu)	HS	CAR/PDMS	DB-Wax (30 m×0.25 mm×0.25 µm)	DB-5 (2 m×0.15 mm×0.15 µm)	SCD	2019	*Food Chem* (2019) 297 124,959
	Liquor (Baijiu)	HS	DVB/CAR/PDMS	DB-FFAP (60 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.5 m×0.25 mm×0.25 µm)	ToFMS	2020	*J Agric Food Chem* (2020) 68 1666–1677
	Liquor (Baijiu)	HS	DVB/CAR/PDMS	DB-FFAP (60 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.5 m×0.25 mm×0.25 µm)	ToFMS	2020	*Food Res Int* (2020) 131 109,043

Table 1 (continued)

	Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
				1D	2D			
	Liquor (Baijiu)	HS	DVB/CAR/PDMS	DB-FFAP (60 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.5 m×0.25 mm×0.25 µm)	ToFMS	2020	*Food Chem* (2020) 331 127,335
	Liquor (Baijiu)	HS	DVB/CAR/PDMS	SLB-5 (30 m×0.25 mm×0.5 µm) Supelcowax-10 (30 m×0.25 mm×0.5 µm)	Supelcowax-10 (0.2 m×0.18 mm×0.2 µm) Rtx-5 (0.9 m×0.18 mm×0.2 µm)	ToFMS	2021	*J Chromatogr A* (2021) 1636 461,774
	Spirit banana	HS	DVB/CAR/PDMS	HP-FFAP (30 m×0.25 mm×0.25 µm)	Rxi-5Sil MS (1 m×0.18 mm×0.18 µm)	FID	2015	*J Chromatogr A* (2015) 1388 227–235
	Beer	HS	DVB/CAR/PDMS	VF-Wax (30 m×0.25 mm×0.25 µm)	Rtx-200-MS (1.5 m×0.25 mm×0.25 µm)	ToFMS	2021	*Food Microbiol* (2021) 100 103,838
	Liquor (Baijiu)	HS	DVB/CAR/PDMS	DB-FFAP (60 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.5 m×0.25 mm×0.25 µm)	ToFMS	2021	*Molecules* (2021) 26 6910
	Liquor	HS	DVB/CAR/PDMS	HP-5MS (25 m×0.25 mm×0.25 µm)	Supelcowax-10 (1 m×0.1 mm×0.1 µm)	ToFMS	2018	*Chem Cent J* (2018) 12 1–10
	Beverage (huangjiu)	HS	DVB/CAR/PDMS	TG-5MS (30 m×0.25 mm×0.25 µm) **HP-Innowax (30 m×0.25 mm×0.25 µm)**	Rtx-17 (2 m×0.1 mm×0.1 µm) **Rtx-5MS (1.9 m×0.1 mm×0.1 µm)**	ToFMS	2019	*J Food Process Preserv* (2019) 43 14,159
	Beer	HS	DVB/CAR/PDMS; ***PDMS/DVB***; PDMS; PA	Equity-5 (30 m×0.32 mm×0.25 µm)	DB-FFAP (0.79 m×0.25 mm×0.25 µm)	ToFMS	2015	*J Sep Sci* (2015) 38 2140–2148
	Liquor	HS	DVB/CAR/PDMS	DB-5MS (30 m×0.25 mm×0.25 µm)	DB-17HT (1.64 m×0.1 mm×0.1 µm)	ToFMS	2015	*Sci Reports* (2015) 5 1–6
	Wine	HS	DVB/CAR/PDMS	HP-5 (30 m×0.32 mm×0.25 µm)	DB-FFAP (0.79 m×0.25 mm×0.25 µm)	ToFMS	2010	*J Chromatogr A* (2010) 1217 3441–3445
	Wine	HS	PA	ZB-Wax (30 m×0.25 mm×0.5 µm)	BPX-5 (2 m×0.15 mm×0.25 µm)	qMS	2010	*Anal Chim Acta* (2010) 672 114–123
	Wine	HS	CAR/PDMS 75 µm	VF-1 (30 m×0.25 mm×0.1 µm)	SolGel-Wax (1.5 m×0.25 mm×0.25 µm)	ToFMS	2011	*Food Chem* (2011) 129 188–199
	Wine	HS	DVB/CAR/PDMS	VF-5MS (30 m×0.25 mm×0.25 µm)	VF-17MS (1.65 m×0.1 mm×0.2 µm)	ToFMS	2011	*J Chromatogr A* (2011) 1218 504–517
	Wine	HS	DVB/CAR/PDMS	HP-5 (30 m×0.32 mm×0.25 µm)	DB-FFAP (0.79 m×0.25 mm×0.25 µm)	ToFMS	2011	*J Agric Food Chem* (2011) 59 3186–3204
	Wine	HS	DVB/CAR/PDMS	VF-5MS (30 m×0.25 mm×0.25 µm)	VF-17MS (1.44 m×0.1 mm×0.2 µm)	ToFMS	2011	*J Agric Food Chem* (2011) 59 3273–3284

Table 1 (continued)

Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
			1D	2D			
Wine	HS	DVB/CAR/PDMS	DB-5 (30 m×0.25 mm×0.25 µm) DB-Wax (30 m×0.25 mm×0.25 µm) **DB-Wax (30 m×0.25 mm×0.25 µm)**	DB-Wax (1 m×0.1 mm×0.1 µm) DB1ms (1.7 m×0.1 mm×0.1 µm) **DB17ms (1.7 m×0.1 mm×0.1 µm)**	ToFMS	2012	*J Chromatogr A* (2012) 1226 124–139
Wine	HS	DVB/CAR/PDMS	Innowax (20 m×0.18 mm×0.2 µm)	HP-5 (5 m×0.35 mm×0.23 µm)	ToFMS	2021	*Food Sci Nutr* (2021) 9 6492–6500
Wine	HS	DVB/CAR/PDMS	DB-5 (30 m×0.25 mm×0.25 µm)	DB-225 (1 m×0.1 mm×0.1 µm)	ToFMS	2013	*Food Chem* (2013) 140 57–67
Wine	HS	DVB/CAR/PDMS	DB-Wax (30 m×mm×0.25 µm)	DB-17 ms (1.7 m×0.18 mm×0.18 µm)	ToFMS	2013	*Food Chem* (2013) 141 3897–3905
Wine	HS	PDMS; PDMS/DVB; CAR/PDMS; **DVB/CAR/PDMS**	DB-5 MS (30 m×0.25 mm×0.25 µm)	Supelcowax-10 (1.2 m×0.1 mm×0.1 µm)	ToFMS	2013	*J Chromatogr A* (2013) 1313 185–193
Wine	HS	DVB/CAR/PDMS; PDMS; CAR/PDMS	SLB-5 ms (30 m×0.25 mm×0.25 µm)	Supelcowax-10 (1.2 m×0.1 mm×0.1 µm)	ToFMS/FID	2014	*Food Chem* (2014) 142 262–268
Wine	HS	DVB/CAR/PDMS	DB-5 (30 m×0.25 mm×0.25 µm)	DB-Wax (1.2 m×0.1 mm×0.1 µm)	ToFMS	2014	*Int J Food Sci Technol* (2014) 49 787–796
Wine	HS	DVB/CAR/PDMS	Carbowax (30 m×0.25 mm×0.25 µm)	DB-17 ms (1.7 m×0.18 mm×0.18 µm)	ToFMS	2014	*Food Chem* (2014) 164 427–437
Wine	HS	DVB/CAR/PDMS	Carbowax (30 m×0.25 mm×0.25 µm)	DB-17 ms (1.7 m×0.18 mm×0.18 µm)	ToFMS	2014	*Food Res Int* (2014) 59 85–99
Wine	HS	Not specified	VF-Wax MS (30 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.5 m×0.15 mm×0.15 µm)	ToFMS	2016	*Metabolomics* (2016) 12 1–25
Wine	HS	DVB/CAR/PDMS	VF-Wax MS (30 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.5 m×0.15 mm×0.15 µm)	ToFMS	2019	*Food Chem* (2019) 277 753–765
Wine	HS	DVB/CAR/PDMS	DB-Wax (30 m×0.25 mm×0.25 µm)	DB-17 ms (1.7 m×0.18 mm×0.18 µm)	ToFMS	2018	*Food Chem* (2018) 243 103–117
Wine sparkling	HS	PDMS; PDMS; PA; CAR/PDMS; **PDMS/DVB**; DVB/CAR/PDMS	DB-5 (60 m×0.25 mm×0.25 µm)	DB-17 ms (1.7 m×0.18 mm×0.18 µm)	ToFMS	2015	*Food Chem* (2015) 183 291–304
Sparkling wine	HS	DVB/CAR/PDMS	VF-Wax (30 m×0.25 mm×0.25 µm)	Rtx-200MS (1.5 m×0.25 mm×0.25 µm)	ToFMS	2016	*Food Chem* (2016) 208 68–80
Wine	HS	DVB/CAR/PDMS	DB-Wax (30 m×0.25 mm×0.25 µm)	DB-17 ms (1.7 m×0.18 mm×0.18 µm)	ToFMS	2020	*Food Chem* (2020) 308 125,552

Table 1 (continued)

	Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
				1D	2D			
	Coffee	HS	CAR/PDMS 85 µm	30 m×0.25 mm×0.25 µm DB-5	1.5 m×0.18 mm×0.18 µm HP-Innowax	ToFMS	2023	*J Agric Food Chem* (2023) 71 4337–4345
	Vermouth	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×0.25 µm DB-5	5 m×0.25 mm×0.2 µm SLB-IL60	qMS; QqQMS	2023	*Anal Bioanal Chem* (2023) 415 2561–2573
	Wine	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×0.25 µm VF-WAXMS	1.5 m×0.15 mm×0.15 µm Rxi-17SilMS	ToFMS	2022	*Agronomy* (2022) 12 2512
	Coffee	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×0.25 µm GB-WAX Ultra Inert	1.7 m×0.1 mm×0.1 µm MEGA-17 MS FAST	ToFMS	2023	*Anal Lett* (2023) 10 1080
	Wine	HS	na	30 m×0.32 mm×0.25 µm HP-5	0.79 m×0.25 mm×0.25 µm DB-FFAP	ToFMS	2021	*Appl Sci* (2021) 11 6294
	Wine	HS	na	30 m×0.25 mm×0.25 µm DB-Wax	1.7 m×0.18 mm×0.18 µm DB-17MS	ToFMS	2022	*Food Chemistry* (2022) 370 131,004
	Whisky	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×1.4 µm Rxi-624SilMS	2 m×0.25 mm×0.5 µm Stabilwax	ToFMS	2022	*IEEE Sens J* (2022) 22 7
	Wine	HS	PDMS	30 m×0.25 mm×0.25 µm SLB-5MS	1.5 m×0.25 mm×0.25 µm SLB-35MS	qMS	2023	*Int J Food Microbiol* (2023) 389 110,107
	Wine	HS	DVB/CAR/PDMS 50/30 µm	10 m×0.25 mm×0.25 µm Supelcowax-10	2 m×0.1 mm×0.1 µm SLB-35MS	ToFMS	2022	*J Chromatogr A* (2022) 1662 462,735
Others	Bread gluten-free	HS	CAR/PDMS	ZB-5 (30 m×0.25 mm×0.25 µm)	SupelcoWax (0.8 m×0.1 mm×0.1 µm)	ToFMS	2015	*LWT* (2015) 63 706–713
	Honey	HS	PDMS; PDMS/DVB; DVB/CAR/PDMS	HP-5 (30 m×0.25 mm×0.25 µm)	Supelcowax-10 (1 m×0.1 mm×0.1 µm)	FID	2013	*Food Chem* (2013) 141 1828–1833
	Rice	HS	PDMS	**HP-5 (30 m×0.25 mm×0.25 µm)** Solgel-Wax (30 m×0.25 mm×0.25 µm) EtTBS-βCD (30 m×0.25 mm×0.25 µm)	**BP-20 (1 m×0.1 mm×0.1 µm)** BP-1 (1 m×0.1 mm×0.1 µm) BP-20 (1 m×0.1 mm×0.1 µm)	ToFMS	2015	*J Food Nutr Res* (2015) 3 114–120
	Spice	HS	PDMS; CAR/PDMS; **DVB/CAR/PDMS**	Innowax (15 m×0.25 mm×0.25 µm)	DB-1 (1.1 m×0.1 mm×0.1 µm)	FID	2013	*Food Chem* (2013) 141 4324–4332
	Dry milk	HS	**DVB/CAR/PDMS**; PDMS; PA; PEG	SolGel-Wax (30 m×0.25 mm×0.25 µm)	OV1701 (1 m×0.1 mm×0.1 µm)	qMS	2013	*J Chromatogr A* (2013) 1318 1–11
	Milk	HS	DVB/CAR/PDMS	DB-5MS (30 m×0.25 mm×0.25 µm)	DB-17HT (2 m×0.1 mm×0.15 µm)	ToFMS	2015	*Int J Food Prop* (2015) 18 2193–2212
	Carp	HS	PDMS/DVB	DB-5 MS (30 m×0.25 mm×0.25 µm)	DB-17HT (1.64 m×0.1 mm×0.1 µm)	ToFMS	2020	*Int J Food Prop* (2020) 23 777–796

Table 1 (continued)

Sample matrix	DI/HS	Coatings (chosen one in bold and italic)	GC×GC column configuration		Detector	Year	Ref
			1D	2D			
Honey	HS	DVB/CAR/PDMS	DB-5MS (30 m×0.25 mm×0.25 µm)	SupelcoWax-10 (1.25 m×0.1 mm×0.1 µm)	ToFMS	2010	*Food Chem* (2010) 118 171–176
foods	HS	**DVB/CAR/PDMS**; PDMS/DVB; PDMS	HP-5MS (30 m×0.25 mm×0.25 µm)	DB-17MS (1.1 m×0.18×0.18 µm)	ToFMS	2021	*Food Res Int* (2021) 142 110,213
Soup	HS	DVB/CAR/PDMS	Rxi-5Sil MS (30 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (0.95 m×0.25 mm×0.25 µm)	ToFMS	2018	*Food Sci Nutr* (2018) 6 2028–2035
Vinegar	HS	CAR/PDMS	TG-5MS (30 m×0.25 mm×0.25 µm) **HP-Innowax (30 m×0.25 mm×0.25 µm)**	Rtx-17 (2 m×0.1 mm×0.1 µm) **Rtx-5MS (1.9 m×0.1 mm×0.1 µm)**	ToFMS	2017	*J Chromatogr A* (2017) 1487 218–226
Cereals (sorghum)	HS	**DVB/CAR/PDMS**; PDMS/DVB; PDMS; CAR/PDMS	DB-FAP (60 m×0.25 mm×0.25 µm)	Rxi-17Sil MS (1.5 m×0.25 mm×0.25 µm)	ToFMS	2021	*Molecules* (2021) 26 4796
Zaoyu (fermented fish)	HS	DVB/CAR/PDMS	Rxi-5MS (30 m×0.25 mm×0.25 µm)	Rtx-200 (1.79 m×0.18 mm×0.2 µm)	ToFMS	2021	*J Food Process Preserv* (2021) 45 1–27
Black pepper	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×0.25 µm DB-5MS	1.8 m×0.25 mm×0.25 µm DB-5MS	ToFMS	2022	*J Biomol Struct Dyn* (2022) 14 6398–6404
Beef	HS	CAR/PDMS 85 µm	30 m×0.25 mm×0.25 µm HP-INNOWAX	2 m×0.15 mm×0.15 µm Rxi-5SilMS	ToFMS	2022	*Eur Food Res Technol* (2022) 248 1733–1747
Pepper	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×0.25 µm DB-Wax	1.85 m×0.18 mm×0.18 µm DB-17	O/qMS	2022	*Food Chem* (2022) 385 132,659
Bean paste	HS	CAR/PDMS 75 µm	30 m×0.25 mm×0.25 µm DB-Wax	1.2 m×0.18 mm×0.18 µm DB-17MS	qMS	2023	*Food Chem X* (2023) 17 100,556
Corn snack	HS	DVB/CAR/PDMS 50/30 µm	25 m×0.2 mm×0.33 µm DB-5MS	1 m×0.1 mm×0.1 µm Supelcowax-10	ToFMS	2021	*Int J Food Sci Technol* (2021) 56 6463–6473
Pork	HS	CAR/PDMS 85 µm	36.4 m×0.25 mm×0.25 µm DB-Wax	1.3 m×0.18 mm×0.18 µm DB-17MS	qMS	2022	*LWT* (2022) 169 113,970
Beef condiment	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×0.25 µm DB-Wax	1.85 m×0.18 mm×0.18 µm DB-17	O/qMS	2021	*LWT* (2021) 147 111,559
Honey	HS	DVB/CAR/PDMS 50/30 µm	30 m×0.25 mm×0.25 µm DB-5MS 30 m×0.25 mm×0.25 µm HP-Innowax	1.25 m×0.1 mm×0.1 µm Supelcowax 10 1.25 m×0.1 mm×0.1 µm BPX50	ToFMS	2007	*J Sep Sci* (2007) 30 534–546

phospholipids, and tocopherols. The specific qualitative and quantitative composition of each class determines the nutritional value and the cost of the final product. Nevertheless, they are susceptible to degradation and oxidation during processing and storage, diminishing their nutritional and economic value, but also impacting consumer`s health. Moreover, the higher the value of the oil, the higher the risk of fraud. Therefore, comprehensive authenticity and quality analytical methods are needed to ensure consumer safety and fair trade.

One of the most valuable and studied edible oils is olive oil. There are three levels of quality of olive oil: extra virgin (EVO), virgin (VO), and lampante (LO). The EVO is the highest quality, while the second one presents some sensorial defects with respect to the EVO. The LO, on the other hand, is not suitable for direct consumption and it is refined, mixed with VO, and commercialized as "olive oil." Although some chemical tests like total acidity, UV absorption (at specific wavelengths), and peroxide value are regularly applied, the classification between EVO and VO largely relies on sensory evaluation, which, although highly standardized, is not highly reproducible around the world. Therefore, there have been several efforts to develop more objective analytical approaches to support the sensory evaluation, which certainly is related to the chemical compounds released by the samples, mainly to the volatile compounds. Therefore, the use of GC to develop an analytical technique for this application seems the most coherent choice. In particular, in this kind of application, HS-SPME-GC × GC has been successfully implemented, improving the quality classification and providing at the same time further valuable information on geographical origin, processing, and storage, among others.

Regarding the SPME, different fiber coatings have been compared for their capacity to cover the most comprehensive profile of the volatilome of olive oil. Although coatings such as PDMS, PDMS/DVB, CW/DVB, and DVB/CAR/PDMS have been tested, as well as different probe formats (SPME, stir bar (SBSE), and monolithic materials) [41], SPME with DVB/CAR/PDMS fiber coating is by far the most employed tool for volatile analytes in this type of samples. It is noteworthy the investigation of alternative sampling techniques in the analysis of EVO, namely, vacuum-assisted SPME (Vac-SPME) [42] and multicumulative trapping SPME (MCT-SPME) [43–45]. The first accelerates the kinetics of extraction, especially of semi-volatiles, by promoting the release of the volatiles by a lower pressure instead of the classical increase in temperature. In contrast, the second reduces the displacement effect by depleting the amounts of the most volatile analytes, increasing the recovery of less volatile compounds in repeated extractions. All the extracted analytes are cumulated in a cryo-trap before being released together into the GC. Both approaches have shown promising results for the determination of olive oil quality classes and geographical origin, and their implementation in combination with GC × GC analysis is ongoing and promising in increasing even more the level of information that can be captured in a single analysis.

For the GC × GC separation of the extracted analytes, the hyphenation with mass spectrometry is predominant due to the good sensitivity and the compound identification ability (Fig. 2). The use of a normal column set (apolar × polar) showed a better distribution of the compounds over the 2D chromatographic space than a reverse column set (polar × apolar) (Fig. 2). However, the polar second dimension in the normal configuration causes some broadening of volatiles and highly polar compounds, hindering their identification [46].

The implementation of HS-SPME-GC × GC to discern between different olive oil cultivars was implemented by Vaz-Freire et al. in 2009 by comparing the 2D chromatograms obtained for samples from Portugal in an untargeted analysis [47]. A second, targeted step, was implemented to identify the compounds of a selected region of the chromatograms. Ten years later, an improved version of this two-step untargeted-targeted analysis was implemented to discriminate five different Croatian cultivars [48]. In this case, an untargeted analysis was implemented for the selection of the discriminant features, followed by a targeted analysis of the identified features. The approach of using an initial untargeted analysis to define the fingerprint of olive oil samples was also applied to differentiate the quality classes (EVO, VO, LO) by Purcaro et al. [46]. In this case, the volatile analytes extracted by HS-SPME (DVB/CAR/PDMS fiber) were analyzed using both column phases configurations in GC × GC–MS [46]. The results obtained in each configuration were used to cross-validate the results. To make full use of the large data sets generated, the chromatograms were properly aligned, and a comprehensive template matching was implemented to compare the fingerprint in the most holistic approach. An unsupervised principal component analysis (PCA) was then implemented and refined by sensorial properties. EVO and non-EVO samples were discriminated by partial least square discriminant analysis (PLS-DA) on the identified features.

This two-step approach has been further formalized by Magagna et al. who named it "untargeted and targeted" (UT) fingerprinting and summarized the template matching fingerprint workflow in three steps: (I) targeted analysis based on MS and linear retention index (LRI) identification, (II) untargeted analysis based on feature determination, and (III) pairwise image comparison of the chromatograms [49]. The authors extended this concept to the identification of ripening markers for olive oil. In 2019, Stilo et al. further developed the UT fingerprinting approach to correct chromatographic misalignment and

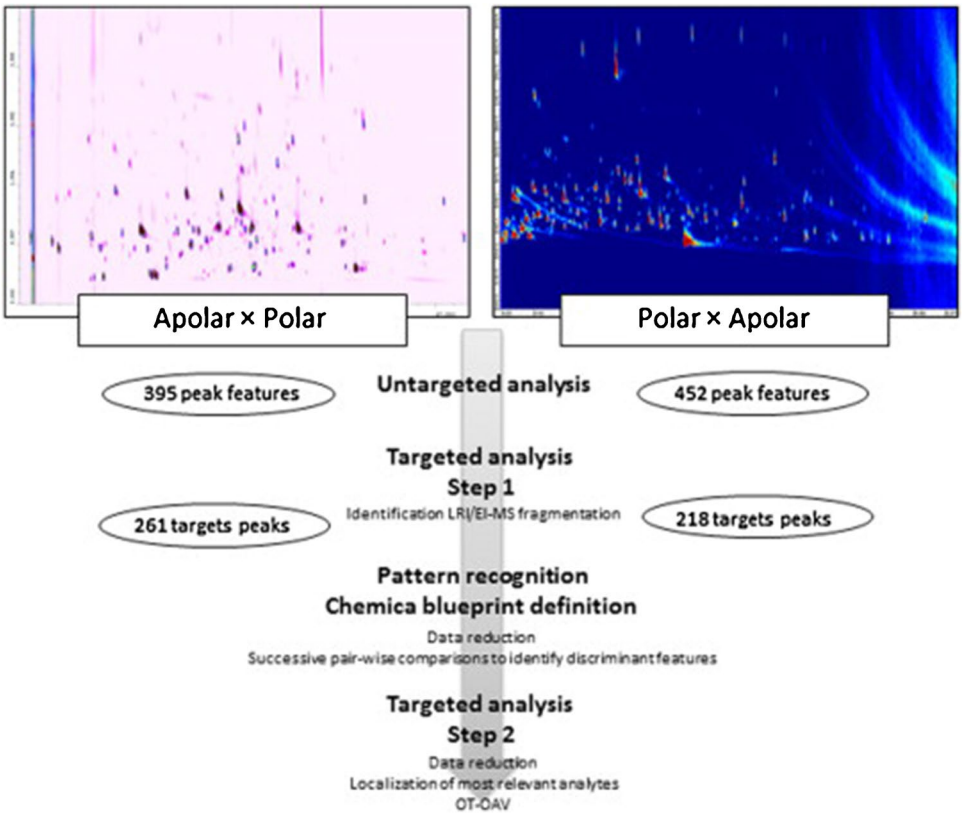

Fig. 2 Comparison of the volatile profile obtained using HS-SPME and an apolar × polar or a polar × apolar column set and scheme of the iterative chemometrics approach used to validate the quality markers of olive oil. Reproduce with permission from [46]

MS fluctuations, enabling long-term studies and compensating for inter-batch differences [50]. Moreover, the same group improved the quality and reliability of the results obtained with this approach by implementing tandem ionization for time-of-flight (TOF) MS at 12 eV and 70 eV. This showed promising results in the identification of new quality markers [51].

Although olive oil has largely driven the advances in edible oil analysis, these developed strategies have been extended to other oils also considered of high value. Indeed, similar applications can be found for fraud detection and process-induced changes in multiple other samples, such as sesame, peanut, soybean, sunflower, and rapeseed oils (Table 1). No more in-depth discussion is herein reported as they refer to similar analytical procedures, just applied to a different sample.

The authors believe that the main limitation of these approaches in the ability to extrapolate robust and reproducible markers for quality and geographical origin determination does not lie in the analytical methods, which have evolved significantly over the years, but rather in the limited number of samples involved in each study. Indeed, the classification algorithms need a set of samples able to capture the most extended variability due not only to the geographical origin but also to the year of harvesting, the pedoclimatic conditions, the process conditions, storage, etc. Otherwise, the marker extracted, although significant and often partially overlapping among different studies, will remain a proof-of-concept.

Nuts and derivatives

Like edible oils, some nuts and derived products are of high value, both nutritionally and economically. Hazelnuts are among the most studied products using HS-SPME-GC × GC. They are used in multiple products, requiring strict quality controls to ensure their safety and organoleptic properties, including the presence of mycotoxins, and rancid/rotten off-flavor defects. These controls are required at different stages of production because the common drying and roasting procedures may create undesirable changes to the final product. Moreover, similarly to olive oil, the geographical origin of the hazelnuts is a valuable attribute for the specific aroma profiles. Therefore, origin fraud detection is also a valuable control in this case. There has been a series of publications by Cordero and co-workers dedicated to the characterization of hazelnuts' volatile profile [9, 52–54]. Initially, the aim was to discriminate varieties and origins between thermally treated hazelnuts from Italy, Chile, and Turkey [52]. The samples were all analyzed by HS-SPME-GC × GC–MS. The obtained chromatograms were processed to create a consensus template based on tiles, as proposed for other samples [9]. This template was then applied to all

chromatograms to compare the fingerprint of the different samples. Although this approach was useful to some extent for the differentiation of the samples, it presented the risk of underusing the information contained in the 2D chromatogram. Indeed, by arbitrarily defining the tiling of the chromatogram, some features may be only partially accounted (a peak may split between two or more tiles) and some others may be accounted together (two or more peaks falling within the same tile). Therefore, matching peaks based on retention times and MS fragmentation patterns was used to define the consensus template used for comparison between samples. This approach showed better discrimination power than the previous approach, and it was further implemented to identify the main features with processing and sensorial relevance. Moreover, thanks to this comprehensive template matching methodology, markers of geographical origin, variety, processing (drying and roasting), and storage stability could be determined [53, 54].

Aside from this exhaustive comparison of the 2D chromatograms through the comprehensive template matching, the UT fingerprinting approach — originally applied to olive oils — has also been applied to hazelnuts. It has been used to identify rotted hazelnuts from their volatilome and to correlate the latter to the primary metabolome of these samples. More recently, Squara et al. compiled quantitative results obtained for the volatilome of a large number of hazelnut samples ($n = 207$). Then, these results constituted the basis for a robust artificial intelligence for quality decision-making, extending the technique's applicability [12]. The putative contribution of the most potent odorants to the overall aroma profile at different storage times was finally visualized using a spider diagram (Fig. 3).

Another largely studied product, also due to its high value, is the cocoa bean and its main derivative, chocolate. In order to obtain the nibs used to produce chocolate, the beans go through several processes, including fermentation, drying, and roasting. Then, the obtained nibs are mechanically processed to obtain the cocoa mass and butter, which will be further modified to produce chocolate. The optimization of every step is crucial to guarantee the final quality of the product. Moreover, the origin, transport, and storage of beans or intermediates will impact the aroma, or cause spoilage. Humston et al. successfully proposed the use of HS-SPME-GC×GC–MS to detect markers of mold proliferation to prevent spoilage from an early stage of production [55].

On the other hand, the lengthy processing from cocoa beans to chocolate and other products, on top of the four varieties and multiple origins, drastically impacts the final sensory quality. Unriddling how these different parameters affect the final volatile profile of cocoa products has drawn the attention of various researchers [55–61]. For instance, Oliveira et al. used HS-SPME with a DVB/CAR/PDMS fiber coupled to GC×GC–MS to differentiate chocolate products produced with cocoa beans of different geographical origins (Brasil and Ivory Coast) [56]. They applied multiway principal component analysis (PCA) on the main discriminant features selected according to Fisher's ratio. Apart from discriminating by origin, the obtained results showed that hydrocarbon profile differed within the same origin depending on the harvesting period. Furthermore, Oliveira and collaborators extended the study to samples of different stages

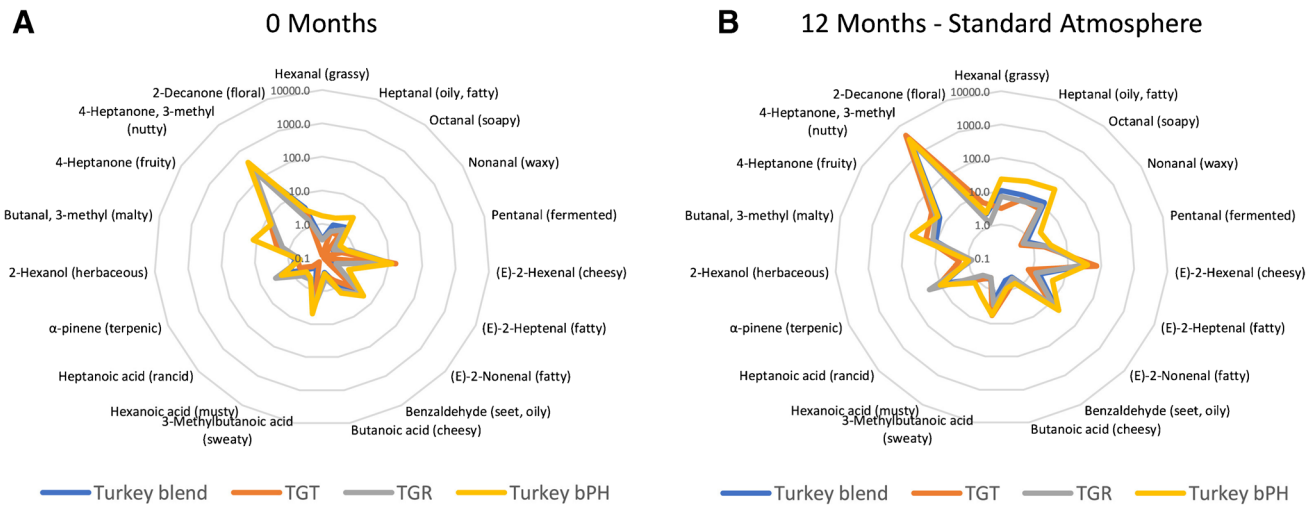

Fig. 3 Spider diagrams reporting the odor active value in log10 scale for odorants related to the hazelnut aroma blueprint, spoilage, and rancidity at 0 and 12 months. Storage condition with standard atmosphere. Cultivar/geographical blends are the Tonda Gentile Trilobata (TGT), Tonda Gentile Romana (TGR), Turkey blend, and Turkey undergone bad post-harvest conditions (bPH). Reproduce with permission from [12]

of chocolate production, namely cocoa nibs and chocolate liquor [58]. The method differentiates the stages of production, allowing the identification of compounds that characterize each step of the process. The great capability of HS-SPME-GC × GC for the determination of the processing markers was further exploited to highlight the evolution of the main odorant compounds during chocolate production by applying the UT fingerprinting approach.

This high discriminating power of the technique for the different process steps has also proven useful for monitoring the formation and contamination by undesirable compounds that can cause off-flavors of finished products. Particularly, an undesirable smokey flavor may be produced during the drying step. By applying the formerly described UT fingerprinting workflow, the compounds responsible for the undesired smoky flavor were unambiguously determined in beans and chocolate liquor [57, 59]. Then, the identified compounds could be monitored by a simpler HS–SPME–GC–MS method targeting these compounds.

Interestingly, when applying the template matching strategy within the UT fingerprinting workflow, the developed methods proved to be translatable to different GC × GC platforms [62]. Namely, a thermally modulated GC × GC–MS method was successfully transferred to a flow modulated GC × GC–MS/FID, preserving a high accuracy for the classification of cocoa samples [60]. The possibility of transferring templates of markers defined under a certain system to a different one is certainly a promising advancement for the enablement of routine applications of GC × GC methods for quality control. Another interesting outcome of the application of UT fingerprinting to cocoa products is the data fusion of the chromatograms obtained by tandem ionization MS at 70 eV and 12 eV. In this case, Cordero et al. proved the usefulness of a richer database by comparing the discriminant features obtained with each MS acquisition mode and the fused data of both modes [61].

It is noteworthy the more extended development in data treatment for this kind of samples than for oil ones. This is likely due to the need for further information to draw useful conclusions for the intended applications. However, the final goal remains similar to any other food sample, geographical origin, and quality markers determination.

Vegetables and fruits

Although there may be lower interest in determining the geographical origin or very specific quality markers for vegetables and fruits, determining the metabolites that define a specific product or identifying contaminants, such as pesticide residues, can benefit from the combination of the relatively simple SPME extraction with the holistic analytical capacity of GC × GC. These types of samples present a particularly complex matrix due to their fibrous and fatty composition that can hinder the recovery of the compounds of interest. Therefore, when dealing with this food category, the main applications in the literature have explored the use of novel and alternative fiber coatings to minimize the fouling effect, and targeted approaches. The use of advanced data handling is here minimized due to a need for further optimization of the analytical method and limited relevance of more holistic questions requiring sophisticated algorithms.

The interesting results that SPME-GC × GC can generate for the determination of the metabolites of fruits and vegetables were fully exploited by Pawliszyn and collaborators in 2012 [63]. In this exhaustive work, multiple commercially available fibers were compared for their extraction efficiency when used in HS and direct immersion (DI) SPME for the determination of the metabolome of apple samples. The homogenized samples were diluted in water containing NaCl and submitted to a mild temperature extraction at 30 °C for 60 min. The extraction performance of the coatings was evaluated based on the coverage of the 2D space (Fig. 4). The largest coverage of analytes was obtained for combined fibers, i.e., DVB/CAR/PDMS, PDMS/DVB, and CAR/PDMS. Although the microporous structure of the latter improved the extraction of the most volatile analytes, the chromatogram presented a higher tailing of these compounds due to their slow desorption into the GC system. Therefore, the DVB/CAR/PDMS fiber presented the best result for the characterization of the apple samples. After further optimizing the extraction procedure, the SPME-GC × GC-TOFMS method was implemented to generate a complete database of 399 apple metabolites.

The large coverage of analytes of DVB/CAR/PDMS SPME fibers has been largely exploited to perform straightforward characterizations of multiple products (Table 1). In some cases, this complete but rather simple application has been extended to -omics studies [63–68]. Nevertheless, exploring the use of alternative SPME coatings remains interesting to overcome the complexity of the matrix of this type of sample. For instance, fatty matrices like avocados can be challenging in terms of reproducibility and sensitivity, even damaging the fiber. Overcoated fibers, i.e., PDMS/DVB/PDMS, were developed to overcome this situation. De Grazia et al. applied this type of SPME fibers to improve the determination of targeted compounds in avocados [69]. Moreover, other researchers have also used the antifouling properties of PDMS to improve the extraction of triazole in grape pulp by DI-SPME [70]. Different cleaning procedures have been proposed depending on the sample matrix. Methanol/water was preferred in the latter case, while water/acetone was required for the fattier matrix of avocados. GC × GC proved a reliable analytical technique to monitor the contamination by matrix compounds and artifact formation that could hinder the determination of target analytes.

Custom fibers were also developed to improve the target extraction and analysis of pesticides. Indeed, the use

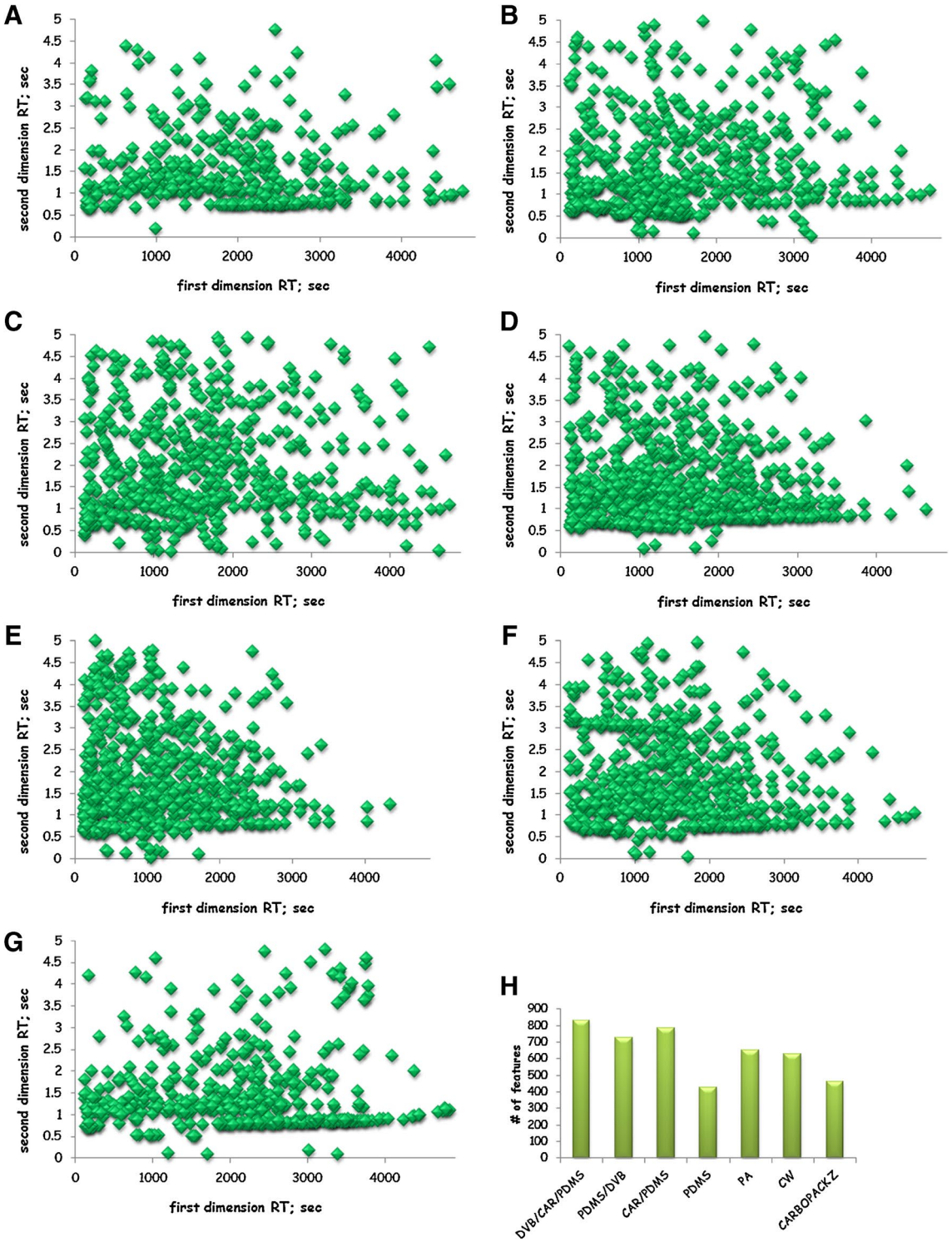

Fig. 4 Comparison of the HS-SPME-GC×GC peak apex plots obtained by using **A** PDMS, **B** PA, **C** CW, **D** DVB/CAR/PDMS, **E** CAR/PDMS, **F** PDMS/DVB, and **G** carbopack Z/PDMS coatings in real apple matrix. **H** Comparison between coatings in terms of number of extracted metabolite features. The peak finding algorithm was operated above *S/N* threshold of 50 and ChromaTOF peak tables were manually filtered to exclude blank peaks and "unknowns" for which library similarity match factor was lower than 800. Reproduce with permission from [63]

of polymeric ionic liquids (PIL) as SPME fiber coatings showed very promising results for the determination of organophosphorus pesticides in grapes, achieving comparable limits of detections to the traditional polyacrylate (PA) SPME fibers and a good repeatability [71]. Moreover, the particularly high polarity of the PIL coating provided broad coverage of compounds that could be identified thanks to GC × GC-TOFMS, extending the potential of PIL coatings for untargeted applications that could provide complementary information to the most used SPME fibers.

Other studies focused on the exploitation of the chromatographic fingerprints obtained by SPME-GC × GC–MS. For instance, image processing techniques combined with multivariate statistical analysis were applied to predict geographical origin and ripening level [66–68]. The large amount of information contained in the comprehensive experiments of fingerprinting was also useful to determine the authenticity of orange juice by applying chemometrics for the data treatment [64]. Furthermore, Johanningsmeier et al. presented an interesting application of SPME-GC × GC–MS for the investigation of the changes in the volatile profile caused by *Lactobacillus buchneri* in fermented cucumbers [65]. The UT fingerprinting methodology contributed to the elucidation of biological changes in the spoilage of the samples never reported before.

Beverages

Similar to other food products, the organoleptic perception of a beverage is directly related to its volatilome. Therefore, there have been multiple studies exploiting the great capabilities of SPME-GC × GC for the determination of key compounds that define the aroma of a certain product. For instance, tea aroma has been largely studied by various authors (Table 1) [72–77]. The sampling conditions of the HS were studied by Magagna et al. who compared different HS modes and paid particular attention to the effect of water on sampling [72]. They compared the volatile profile obtained by HS sorptive extraction (HSSE), dynamic HS (DHS), and HS-SPME with a DVB/CAR/PDMS fiber. Not surprisingly, the absolute extraction amount with SPME was lower than that with the other tested techniques; however, it provided complementary information. Further in the exploration of sampling techniques in this field, Ntlholkwe et al. evaluated the performance of six SPME coatings [73]. The authors found the most comprehensive extraction for PDMS/DVB and DVB/CAR/PDMS. Although the latter showed superior coverage of volatiles, it overloaded the modulator and hindered the exploitation of the results. Zhu and collaborators further optimized the SPME extraction using a DVB/CAR/PDMS fiber and adapted the GC × GC method to avoid extensive tailing, obtaining a comprehensive volatile profile for tea samples [74]. This method was then applied for the identification of the key compounds responsible for the chestnut aroma in certain teas by comparing the volatilome obtained for tea samples against chestnut ones. Other studies used CAR/PDMS fibers to define key odorants of tea, such as the ones responsible for the orchid-like aroma, although giving less importance to the sampling optimization [75–77].

Aside from tea, another interesting non-alcoholic beverage that presents a complex volatilome is coffee. However, the number of publications making use of the advantages of SPME-GC × GC for these samples remains limited [78, 79]. One article applied the UT fingerprinting method to coffee samples; however, the authors focused on presenting the methodology (already detailed above) rather than on the results obtained for the volatilome of the coffee samples [80]. More recently, Eggermont et al. applied different SPME sampling techniques for the discrimination of coffee packaging. The authors applied less conventional SPME techniques, such as a high-capacity probe-like tool (HiSorb®) and multicumulative trapping (MCT) [81, 82]. These techniques showed improved recoveries for untargeted and targeted analysis that could unriddle the impact of the packaging on the coffee quality.

HS-SPME-GC × GC has also been extensively used for the characterization of the alcoholic beverages. In particular, the characterization of their volatilome and the relationship with origin and processing parameters have been studied to optimize their production. Among these, wine is probably one of the most largely studied samples. The "bouquet" of a wine defines its quality and directly affects the attraction of consumers. The large variety of compounds that define the "bouquet" are related to the grape origins, variety, and ripening, and also to the multiple processing steps, including fermentation, maturation, maceration, and others. There have been direct applications of SPME-GC × GC for the successful characterization of wines from different geographical origins and varieties [83–88]. Moreover, different stages of the production process, aging and storage, pedoclimatic conditions, and vine management have also been investigated using diverse data mining approaches to exploit the large amount of information obtained by GC × GC [89]. Interestingly, Nicolli et al. combined the results obtained with SPME-GC × GC with olfactometry GC (GC-O) to study the impact of vine management practices [90]. They proved the impact of air circulation and solar exposure of vines on the volatile profile of the finished product. Other applications of this analytical method include the differentiation between products [83–88], such as "Asti Spumante" and "Moscato d'Asti" [91], and the monitoring of their evolution during storage [92, 93], or even the determination of target analysis of contaminants, such as ethyl carbamate [94] and haloanisoles [95].

Another extensively analyzed fermented alcoholic beverage by SPME-GC × GC is Baiju. This Chinese distillate, produced from the sorghum fermentation, has been analyzed by the combination of GC × GC results with other methodologies, such as mono-dimensional GC with multiple detectors and sensory evaluation [96–106]. He et al. applied frequency observation cutoff and a correlation network to define a regional classification and its relationship with sensory attributes, identifying the main characteristic aroma compounds [102]. Moreover, they explored the influence of the GC × GC column setup on the information that could be extracted in this case, showing that the data obtained may be complementary [104]. Figure 5 shows the comparison between the two column sets in terms of space occupancy and profile of compounds separated.

In terms of the sample pretreatment for the characterization of fermented beverages, Zhang and collaborators tested diverse extraction techniques for the sampling of volatiles from wine, beer, and cider samples [107]. They tested vortex-assisted liquid–liquid microextraction, solid-phase extraction (SPE), dynamic HS, multiple stir bar sorptive extraction (mSBSE), and SPME. The authors concluded that although SPME may be the best option in terms of automation for routine applications, the extracted volatile profile differed between the different techniques, suggesting a complementarity of the techniques. An interesting approach towards a better coverage of the volatile profile by a single technique has been proposed by Pawliszyn's group. They suggested the use of a sequential thin-film (TF) SPME extraction to maximize the recovery of polar compounds in beer samples by minimizing the displacement effect [108].

Surprisingly, apart from the aforementioned sample pretreatment investigations involving beer samples, only a limited number of publications have dealt with the characterization of the volatile profile of beers. Nevertheless, SPME-GC × GC-TOFMS was successfully applied to compare the volatilome of beers produced through fermentation with five different and fully characterized yeast strains

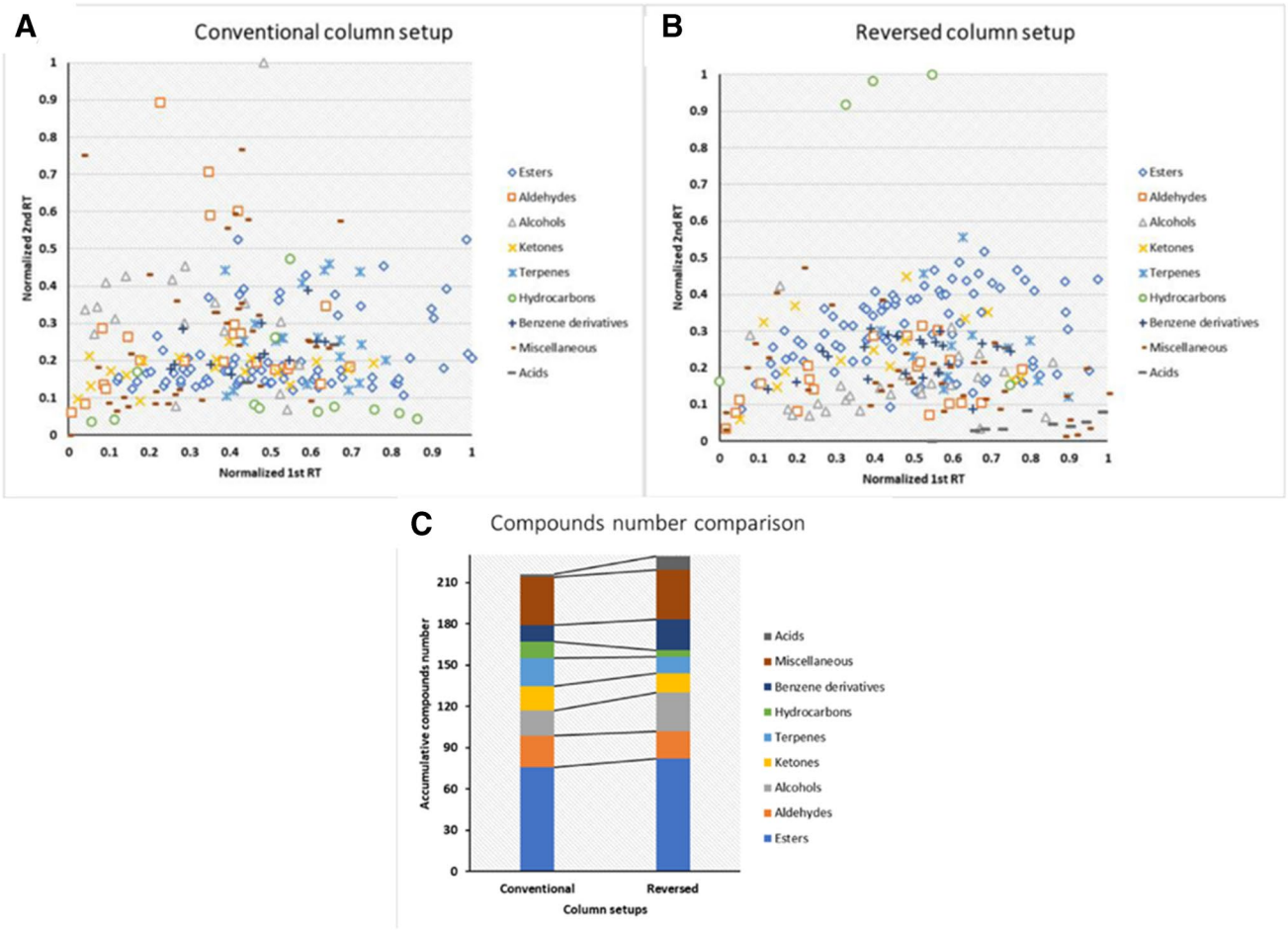

Fig. 5 Comparison of GC × GC separations of Baijiu samples using **A** conventional and **B** reversed column setup. **C** Comparison of the profile of different chemical groups in conventional (216 compounds in total) and reversed (229 compounds in total) column setup. Adapted with permission from [104]

[109]. Other works focused on the optimization of the HS sampling, rather than making full use of the generated data for comprehensive analysis of the samples [110, 111].

Although there are many other alcoholic beverages of high value that could benefit from the volatilome characterization, to the best of our knowledge, the number of publications using SPME-GC × GC in this field remains rather limited. Nevertheless, recent publications showed the interest in the technique for the cross-validation of an electronic nose for the classification of whiskies [112] and the characterization of the volatile profile of vermouth [113]. In the latter case, it is noteworthy the use of a soft ionization source, namely a novel tube plasma ion source, to enhance the identification of the compounds of interest.

Others

Although other food products have also been investigated by means of SPME-GC × GC, they were not exhaustively researched; thus, considering the sparse number of publications in each case, we grouped them together in this section.

An interesting outcome of the SPME-GC × GC analysis of the aroma profile of gluten-free bread was presented by Pacyńsky and collaborators in 2015 [114]. The authors compared the results obtained for wheat and wheat-rye breads against a commercial gluten-free premix. The main difference between the products was found to be the lower amounts of pyrazines and 2-acetyl-1-pyrroline in the gluten-free bread. Thanks to these findings, the authors added precursors of these compounds to improve the aroma profile of the product. They identified the best additives (proline and glucose) to improve consumer acceptance after a sensory evaluation of different alternatives. Some other more recent works also implemented HS-SPME-GC × GC–MS for the study of processing conditions. For instance, multivariate statistical analysis was applied to determine the flavor formation mechanisms in bean paste due to the processing parameters [115], and to study the effect of extrusion conditions in the quality, aroma, and taste desirability of fortified corn snacks [116].

Another less usual application of SPME-GC × GC was presented by Fang et al. They identified potential markers of food contaminated with *Shigella sonnei*, *Escherichia coli*, *Salmonella typhimurium*, *Vibrio parahaemolyticus*, and *Staphylococcus aureus* by multivariate statistical analysis of the results obtained by the analytical technique [117]. The determination of these markers was then applied to three contaminated food samples as proof-of-concept of the great potential of this technique for the early detection of foodborne pathogens.

Cajka et al. presented an exhaustive study on the differentiation of geographical origin of honey samples [118]. The authors evaluated 374 honey samples, collected from different European countries over a 2-year period (2006 and 2007). By means of HS-SPME-GC × GC-TOFMS, a targeted profiling approach consisting of 26 features was applied to the discrimination of the geographical origin of the samples from Corsica by means of PCA and artificial neural networks (ANN). The ANN approach accurately discerned samples from Corsica from the other ones. When the samples from 2006 were used as training data, accuracy was 81.3% for the differentiation of the Corsica's samples from 2007. While an accuracy of 81.9% was obtained when the data sets were inverted. Further investigation proved that training a model with a mixed 2006 and 2007 subset of samples allowed for better classification, extending the application to a full classification on geographical origin for 347 samples [119].

The increased sensitivity and great resolution power of GC × GC have also been used to evaluate possible artifacts due to hydrolysis and thermolysis in the pretreatment for the analysis of honey samples. By testing different times and temperatures of HS-SPME extraction, Rivellino and collaborators could identify different artifacts (e.g., hydroxymethylfurfural, methyl-furone, furfural) that may be formed during the sampling [120].

The comprehensive template matching fingerprint approach was also implemented for the characterization of milk samples. Cordero et al. implemented different sampling techniques, such as SPME, SBSE, HSSE, and DHS, in combination with GC × GC–MS to determine the volatile profile of these samples. The obtained results could be correlated with sensory information obtained by GC-O [121]. Other studies also correlated results obtained with sensory techniques for the characterization of key aroma in condiments [122, 123] and meat products [124, 125]. In some of these cases, the results obtained by HS-SPME-GC × GC–MS contributed to the development of electronic nose devices that can be easily used for on-site analysis [122, 124, 125].

It is also worth mentioning the use of HS-SPME-GC × GC–MS for the determination of the metabolite profile of black pepper to identify the precursors of its characteristic aroma [126]. In combination with the identified precursor genes, this can contribute to the improvement of the bioprocessing of black pepper.

It is clear from this section that the use of SPME-GC × GC can extend to a myriad of sample types. The simplicity of the technique combined to the potential correlation of the volatile profile of food samples to their quality in a broad sense makes this an appealing alternative for characterization and control applications.

Concluding remarks

The great advantage of SPME sampling to overcome matrix interferents while acting as a preconcentration step for the extraction of specific analytes has been largely

exploited in the field of food analysis. The simplicity of the combination of this microsampling technique to GC made SPME-GC one of the most largely used techniques for the analysis of quality markers in food products. With the great advances in comprehensive multidimensional chromatography, in particular in GC × GC, the research capability has evolved from a targeted analysis towards a more holistic approach to cover the largest number of compounds possible. Although the application of an extraction technique characterized by an intrinsic selectivity, such as SPME, seems contradictory with the implementation of untargeted comprehensive analysis, overcoming the matrix effects and artifacts that could hinder the chromatographic run is fundamental to obtain useful results. For this reason, multiple authors made a considerable effort to test various fiber alternatives and even complementary techniques to broaden the compounds' coverage. Nevertheless, a single technique, such as SPME with a combined fiber selectivity, could suffice for a large number of applications. Therefore, it is not surprising that DVB/CAR/PDMS fibers are the primary choice regardless of the sample type. Nonetheless, the research on fundamental aspects of the techniques, *i.e.*, the development of new coatings to overcome possible limitations encountered with some samples, such as oily matrices, as well as investigation of alternatives to the most classical HS- or DI-SPME approaches, such as MCT- or Vac-SPME, is essential. All this without overseeing the basic theory of the technique, which alone can solve many encountered issues, maximizing the outcomes. Similarly, GC × GC–MS is a mature technique but still complicated. It benefits from the support of a large amount of literature and many tools provided by the different vendors to support the users. Nevertheless, the fundamentals of the techniques should be well understood to fully take advantage of its potential to generate information-rich chromatographic fingerprints. Indeed, to obtain valuable information for the following chemometrics approaches, robust and reliable data sets need to be generated, which can only be done by a clear understanding of the fundamentals of the techniques, thus from adequately optimized methods.

Subsequently, to make use of the large amount of data obtained, chemometrics approaches are required. Although different strategies have been reported, the UT fingerprinting seems to prevail, and it has been applied to different food samples. Nevertheless, articles devoted to the data treatment in food analysis seem to be limited in comparison with the number of applications that have been reported. Moreover, among the different applications reported, a very limited number of publications delve into the discussion of the chemometric approaches implemented. In many cases, the large amount of chromatographic data generated remains underused. Although whichever approach is chosen, it should fit the purpose of the study, a more justified choice of the strategy implemented will contribute to the better acceptance of these approaches for routine applications. Indeed, the acceptance of a new method for routine and regulatory applications needs proof of robustness and ease of use that, in our opinion, has not been achieved yet in most of the applications so far explored in food analysis and herein discussed. This statement does not want to undermine the immense, necessary, and valuable work so far done in the field but wants to stimulate scientists towards the continuous development of the field, never forgetting the main requisite of robustness of the final analytical flow. To achieve such robustness and reliability, the three steps of the analytical flow, namely sample preparation, instrumental separation, and data handling, need to be further investigated and fully understood to provide a final protocol not subjected to analyst interpretation and no error-prone, thus to be applied on a routine base.

The large scope of applications of SPME-GC × GC for food analysis becomes evident from the different sample types that have been analyzed. The learnings from more developed field of applications (e.g., oils or nuts) should be extrapolated to be applied to other less developed applications (e.g., vegetables and fruits). This is true not only within food analysis but also referring to other fields, such as clinical application, and not only for the analytical technique but also the chemometric approaches implemented in other fields and with different techniques.

In conclusion, SPME combined with GC × GC for food analysis has proven to be a reliable yet simple technique that can bring new information to improve the value and guarantee the quality of food commodities. Moreover, it can become a cornerstone in the development of other analytical techniques, such as electronic noses, and contribute to the unriddling of the complex relationship of multiple factors that impact food products. Further investigation involving systemic optimization approaches, supported by appropriate design of experiments, and adequate chemometric methodologies to make full use of the chromatographic data generated, should contribute to the further acceptance of the technique for routine application. A special attention must always be taken to the theory behind the techniques used (SPME, GC × GC, and chemometrics) to ensure the robustness and reliability of the outcomes. Hopefully, this review will encourage new research into this field, extending the applicability of SPME-GC × GC for food analysis by implementing strategies that allow to harness the full potential of the method.

Declarations

Conflict of interest The authors declare no competing interests.

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