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Improved determination of flavour compounds in butter by solid-phase (micro)extraction and comprehensive two-dimensional gas chromatography

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Abstract

The practicability and potential of comprehensive two-dimensional gas chromatography (GC × GC) coupled to both conventional flame ionisation (FID) and time-of-flight mass spectrometric (TOF-MS) detection, were compared with those of conventional one-dimensional (1D) GC, with the determination of flavour compounds in butter as an application. For polar flavour compounds, which were collected from the aqueous fraction of butter by means of solid-phase extraction (SPE), it was found that GC × GC dramatically improves the overall separation. Consequently, quantification and preliminary identification based on the use of ordered structures, can be performed more reliably. The improvement effected by replacing 1D-GC by GC × GC is considerable also in the case of TOF-MS detection, as illustrated by the high match factors generally obtained during identification. GC × GC was also used successfully for the characterisation of volatile flavour compounds in the headspace of butter collected by solid-phase microextraction (SPME) and to study the effect of heat treatment on the composition of butter samples in more detail.

Keywords: SPE; SPME; Comprehensive two-dimensional gas chromatography; GC × GC; Flavour compounds; Butter extracts

1. Introduction

Several years ago, we studied the trace-level determination of flavour compounds in butter by means of gas chromatography–mass spectrometry (GC–MS) [1]. The study dealt with the volatile flavours present in the aqueous fraction of butter, and pre-treatment was by means of solid-phase extraction (SPE). Five well-known test analytes were used which represented various classes of compounds, some of which may be found in butter: diacetyl (ketones), furaneol (furanones), maltol (pyranones), sotolon (furanones) and vanillin (benzaldehydes). Generally speaking, the results were quite encouraging: the analytical performance characteristics were fully satisfactory for all target analytes except diacetyl (baseline subtraction and selected ion monitoring required). The effect of heat treatment on sample composition could be demonstrated convincingly, some 20 further compounds could be identified (although there were also a number of distinct failures) and quantification at the 0.1–10 mg/kg level did not cause serious problems.

Today, re-reading of the quoted paper rapidly shows that – next to the problems regarding failed quantification and/or identification already mentioned – the unresolved baseline envelope clearly present in the chromatograms of at least some of the test samples strongly suggests that a more powerful separation technique should be used: comprehensive two-dimensional gas chromatography (GC × GC) with either non-selective flame ionisation (FID) or, if required, selective time-of-flight mass spectrometric (TOF-MS) detection [2–6]. In order to enable a straightforward comparison of the two methods of analysis, conventional (i.e. one-dimensional, 1D) GC and GC × GC, the same general set-up was used as in the earlier study, and the same target analytes and experimental parameters (heat treatment and storage effects) were used. As an extension, the headspace of the butter samples was analysed (by means of solid-phase microextraction, SPME) next to the aqueous fraction.

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2. Experimental

2.1. Analytes and samples

Methyl acetate (J.T. Baker, Deventer, The Netherlands) was freshly distilled and HPLC-grade water was prepared in a Mili-Q (Millipore, Bedford, MA, USA) filtration system. Helium, used as carrier gas (99.999% purity) was supplied by HoekLoos (Schiedam, The Netherlands). Vanillin and diacetyl were from Fluka (Zwijndrecht, The Netherlands), maltol and furaneol from Acros (Geel, Belgium), and sotolon from Aldrich (Brussels, Belgium). Standard solutions of all flavours were prepared at a concentration of 0.1–20 mg/ml by weighing and dissolution in methyl acetate or HPLC-grade water. They were kept in the dark at 4 °C for a period of maximally 4 months.

Two different types of fresh butter, 'grasboter' and 'gezouten roomboter' (Melkunie, Breda, The Netherlands), were purchased from a local supermarket.

2.2. Preparation of butter extracts and SPE procedure

Preparation of butter extracts and SPE-based sample treatment were performed according to the procedure optimized in the earlier study [1]. Briefly, the SPE cartridge (SDB-1; PS–DVB copolymer) was conditioned with 2 ml of methanol and 2 ml of HPLC-grade water. Next, the water phase of the butter sample was loaded on the SPE cartridge via vacuum suction. After washing with 1 ml of water and drying for 15 min at room temperature, the trapped analytes were desorbed with 1 ml of methyl acetate. After drying by adding anhydrous sodium sulphate, 1 μl of the SPE extract was injected for either GC × GC–FID, GC–MS or GC × GC–TOF-MS analysis.

2.3. SPME procedure

The SPME fibres and the manual holder were purchased from Supelco (Bellefonte, PA, USA). Four types of SPME fibre were used: polydimethylsiloxane (PDMS) of 100 μm thickness; Carboxen/PDMS of 75 μm thickness; Stable Flex Carbowax–divinylbenzene (Carbowax/DVB) of 70 μm thickness and Stable Flex divinylbenzene–carboxen–polydimethylsiloxane (DVB/Carboxen/PDMS) of 50/30 μm thickness. Fibres were conditioned prior to use according to the manufacturer's instructions: PDMS was inserted into the GC injector at 250 °C for 1 h; Carboxen/PDMS at 280 °C for 30 min; Carbowax/DVB at 270 °C for 1 h, and DVB/Carboxen/PDMS at 270 °C for 4 h.

For each headspace (HS)-SPME analysis, approximately 8 g of butter sample placed in a 14 ml clean glass vial was smelted at 40 °C or heated at 170 °C for 5 min. The glass vials were sealed with silicone septa and were kept at 40 °C. The SPME needle pierced the septum and the fibre was extended through the needle to bring the stationary phase in contact with the headspace of the sample. The fibre was withdrawn into the needle after the sampling time, which was varied from 1 to 90 min. Finally, the SPME needle was removed from the vial and inserted for 0.5–3 min in the injection port of the gas chromatograph. The extracted compounds were thermally desorbed at 200–270 °C and transferred directly to the (first-dimension) GC column.

2.4. GC–MS and GC × GC systems

For GC–MS, the gas chromatograph was a Hewlett-Packard HP 6890 (Agilent Technologies, Palo Alto, CA, USA) instrument with a split/splitless injector, and a HP-5972 mass-selective detector. A 30 m × 0.25 mm I.D., 0.25 μm BP21 (polyethylene glycol, TPA-treated) column (SGE Europe, Milton Keynes, UK) was used. Conditions were as follows: injector temperature, 250 °C; GC column temperature, 40 °C (2 min), at 5 °C/min to a final temperature of 230 °C (5 min); transfer-line temperature, 280 °C, ion-source temperature, 200 °C; carrier gas, He at 110 kPa. Analyses were performed in the electron ionisation (EI) mode at 70 eV. The mass range was *m/z* 40–350.

The GC × GC–TOF-MS system consisted of a HP 6890 (Agilent Technologies) gas chromatograph equipped with an Optic 2 programmable injector with a multicapillary liner (ATAS, Veldhoven, The Netherlands) and a Pegasus II time-of-flight mass spectrometer (LECO, St. Joseph, MI, USA). TOF-MS was operated at a storage rate of 50 Hz, using a mass range of *m/z* 40–400 and a multi-channel plate voltage of −1800 V.

For GC × GC–FID, a HP 6890 (Agilent Technologies) gas chromatograph equipped with a split/splitless injector and a FID system capable of producing a digital signal at a rate of 200 Hz was used.

For both GC × GC systems, a 30 m × 0.25 mm I.D., 0.25 μm BP21 (polyethylene glycol, TPA-treated) column (SGE Europe) was used as the first-dimension column. The second-dimension column was a 1 m × 0.1 mm I.D., 0.1 μm BPX-35 column (SGE Europe). The columns were connected with a press-fit connector (Varian universal quick seal; Varian–Chrompack, Middelburg, The Netherlands). The carrier gas, helium, was used at a constant flow of 1.3 ml/min. The temperature of the two GC columns, which were housed in the same oven, was programmed from 40 °C (2 min hold) to 240 °C (3 min hold) at 5 °C/min.

Thermal modulation was performed with a laboratory-made CO_2-cooled dual-jet modulator [7]. Cooling was effected through the Joule–Thompson effect of expanding liquid CO_2 (technical grade; HoekLoos). Briefly, two short sections of the second-dimension column are directly and alternately cooled in order to trap and focus each subsequent fraction which is, next, remobilized by the heat from the surrounding oven air. The modulation time was 3 s; the modulator temperature was kept about 100 °C below the oven temperature.

Table 1
SPME optimization[a]

Parameter	Range tested	Optimum condition
SPME fibre	Four fibres (see Section 3.1)	Combined use of Carboxen/PDMS and Carbowax/DVB
Extraction temperature	25–60 °C	40 °C
Extraction time	1–90 min	20 min for Carboxen/PDMS
	1–90 min	60 min for Carbowax/DVB
Salt addition	0–50%	30% (w/w) NaCl
Desorption temperature	200–270 °C	250 °C
Desorption time	0.5–3 min	1 min

[a] Optimization based on peak height of the analytes.

3. Results and discussion

3.1. SPME

The optimization of the SPME conditions was performed by studying the parameters listed in Table 1. To this end, next to a solution of the five target analytes in water (each at 1 μg/ml), butter samples spiked with the five target analytes (each at 1–5 μg/g) were used. All experiments were performed under stirring to enhance the release of the analytes into the headspace. A short discussion of the experimental findings is given below.

Four commercial fibres were tested, PDMS, Carboxen/PDMS, Carbowax/DVB and 50/30 μm DVB/Carboxen/PDMS Stable Flex. The PDMS fibre was found to mainly extract non-polar (volatile) compounds and to strongly discriminate polar analytes. The three mixed-phase fibres, on the other hand, all showed a satisfactory behaviour; however, with the Stable Flex fibre, analyte responses were somewhat lower (typically, 15–25%) than for the remaining two fibres. Carboxen/PDMS was found to give the best results for lower-molecular-weight analytes, while higher-molecular-weight compounds were trapped more efficiently by Carbowax/DVB. Because of the complementarity of these two medium-polarity fibres, which reduces the discrimination at both the polar and the non-polar end, the combination of Carboxen/PDMS and Carbowax/DVB was used in the further evaluation.

As regards the extraction temperature, for most test analytes plateau conditions were found to be reached at ca. 40 °C; a further increase was not considered prudent because of the possibility of analyte degradation or conversion (see Section 3.3) and/or artefact formation. Analyte extraction was distinctly faster for the Carboxen/PDMS as compared with the Carbowax/DVB fibre: equilibrium was reached in about 20 and 60 min, respectively. Further, the addition

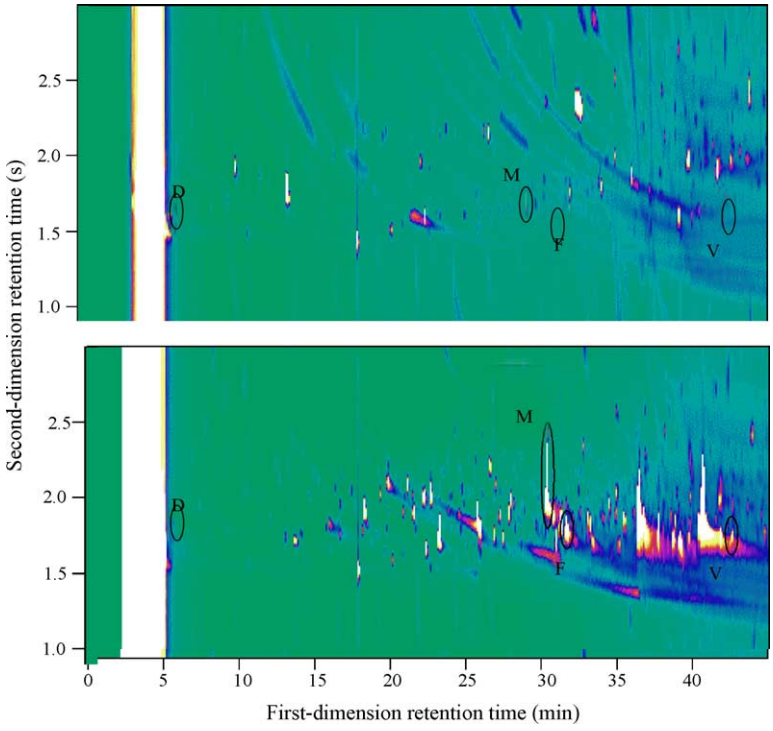

Fig. 1. GC × GC–FID chromatograms of 'gezouten roomboter' sample heated at 40 °C (top) and 170 °C (bottom) and extracted by SPE. D = diacetyl; M = maltol; F = furaneol; S = sotolon and V = vanillin.

Table 2
GC × GC–TOF-MS vs. 1D-GC–TOF-MS of flavour standards in aqueous fraction of butter samples

Compound	Grasboter				Concentration (ratio)[a]
	40 °C		170 °C		
	1D-GC (s–r–*p*)[b]	GC × GC (s–r–*p*)[b]	1D-GC (s–r–*p*)[b]	GC × GC (s–r–*p*)[b]	
Diacetyl	674–764–4363	895–917–7320	646–748–5633	859–907–6320	0.6
Maltol	911–924–9364	921–942–9646	929–954–9598	932–961–9682	350
Furaneol	745–777–4042	795–827–5243	803–817–7596	865–882–8372	100
Vanillin	697–728–3505	800–820–3837	812–855–3228	894–904–3263	1.2
	Gezouten roomboter				
	40 °C		170 °C		
	1D-GC (s–r–*p*)[b]	GC × GC (s–r–*p*)[b]	1D-GC (s–r–*p*)[b]	GC × GC (s–r–*p*)[b]	
Diacetyl	683–788–3191	853–898–7191	653–727–2849	907–958–7506	0.7
Maltol	798–873–8822	924–951–9534	928–953–9548	933–959–9597	330
Furaneol	749–783–2585	811–836–7585	786–801–5096	838–863–7792	90
Vanillin	635–654–1570	805–833–4242	752–768–3202	900–909–3182	1.1

[a] Concentration ratio in aqueous phase of butter heated at 170 °C/40 °C.
[b] s–r–*p*, similarity–reverse–probability.

of 30 wt.% of sodium chloride typically created a two-fold enhanced analyte response. Finally, the optimum desorption temperature and time were essentially the same for the two fibres, with 250 °C and 1 min, respectively, used in all further work.

3.2. Applications

3.2.1. Aqueous phase of butter

In order to analyse polar flavour compounds, the aqueous phases – where, generally speaking, these compounds are present – of the two butter samples were analysed. As an illustration of the practicability of the procedure, Fig. 1 shows the GC × GC chromatograms of the aqueous phases of a 'gezouten roomboter' sample heated at 40 and 170 °C and extracted by SPE. As expected, rather different profiles were obtained, with more complexity for the higher sampling temperature. As is clear from Fig. 1, not only do the polar analytes show up more intensely at 170 °C, but many more (newly formed) polar compounds are present. As will be discussed below, the majority of these compounds are lactones, furanes and heterocyclic pyrroles and pyridines. They are retained not very strongly in the second dimension and show up as a band between 1.5 and 2.5 s in the chromatogram.

All target analytes except sotolon, which was not present in any sample, were identified in all butter samples; they are indicated in Fig. 1. As regards diacetyl—its peak being visible in both chromatograms even with FID–GC × GC–TOF-MS of the SPE extracts led to the identification of diacetyl as well as the other three target analytes with high match factors. In all but one case, the similarity and reverse values were higher than 800 (Table 2). Especially for diacetyl and vanillin, the improvement effected by replacing 1D-GC by GC × GC is considerable. The relatively low values sometimes found with the former technique demonstrate that even the powerful deconvolution capabilities of TOF-MS do not always suffice to create the required resolution [8,9]. As for the occasionally low probability values, with vanillin as the clearest example, it is well-known that probability is a measure of the uniqueness of a spectrum compared with all other spectra in the library. That is, the low value for vanillin merely indicates that the mass spectrum of this analyte has no special characteristics. The data of Table 2 also show that, as in the earlier study, heat treatment was found to effect a dramatic increase of the maltol and furaneol concentrations, while vanillin remained at essentially the same level. However, the superior performance of the GC × GC system enabled us to modify two other earlier statements: (i) furaneol was found to be also present in the samples heated at 40 °C, although at low levels, and (ii) diacetyl certainly does not disappear completely when increasing the temperature from 40 to 170 °C.

As a further illustration of the usefulness of the GC × GC approach, several classes of unknown compounds were detected and identified in the two butter samples, both with and without heat treatment. These included aldehydes, 2-enals, ketones, alcohols, fatty acids and lactones. Furan

Table 3
Classes of analytes found by GC × GC–TOF-MS in the aqueous phase of butter samples with similarity >800 and reverse >900[a]

Compound classes	Grasboter		Gezouten roomboter	
	40 °C	170 °C	40 °C	170 °C
Aldehydes	4 (–)	3 (–)	1 (1)	1 (–)
2-Enals	4 (–)	2 (–)	1 (–)	1 (–)
Alcohols	3 (1)	3 (–)	3 (–)	– (–)
Ketones	3 (–)	5 (–)	– (–)	1 (–)
Fatty acids	12 (10)	16 (6)	11 (10)	7 (7)
Alkanes	4 (1)	5 (1)	– (–)	2 (1)
Lactones	7 (–)	13 (7)	7 (2)	12 (7)
Furans	4 (–)	17 (11)	5 (–)	14 (13)
Pyridines	– (–)	1 (–)	– (–)	4 (3)
Pyrroles	– (–)	3 (1)	– (–)	3 (1)

[a] Values in brackets are numbers of analytes found by 1D-GC–TOF-MS.

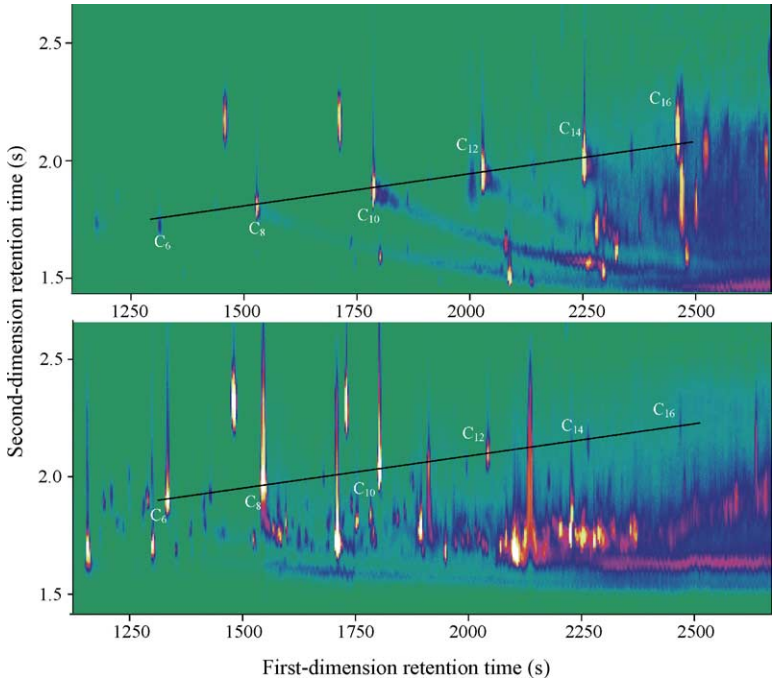

Fig. 2. GC × GC–TOF-MS ion traces *m/z* 99 of aqueous phase of 'grasboter' treated at 40 °C (top) and 170 °C (bottom) and extracted by SPE. C_6–C_{16} indicates the carbon numbers of the δ-lactones.

derivatives and heterocyclic compounds such as pyrroles and pyridines were exclusively found in the heat-treated samples. It is known that these compounds, especially the latter two groups, begin to be formed at temperatures above 150 °C [10]. Table 3 summarizes typical results for the two butter samples, at 40 and 170 °C. Also here, GC × GC is seen to provide much more information than 1D-GC at the high similarity and reverse threshold values selected. The effect is

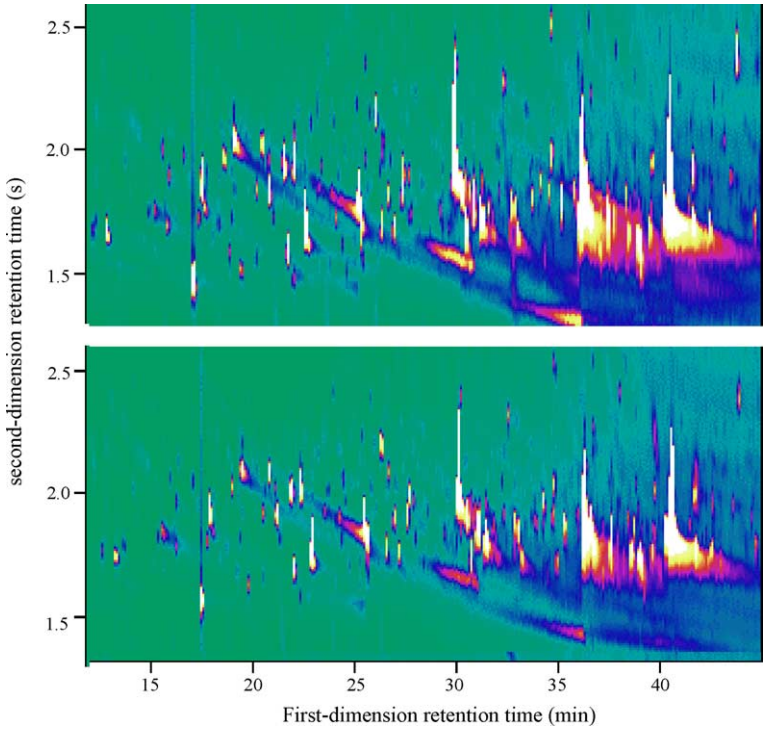

Fig. 3. GC × GC–FID chromatograms of the aqueous phase of 'grasboter' heated at 170 °C and extracted by SPE: (top) 2-month-old, and (bottom) fresh (1-day-old) sample. Storage temperature, 4 °C.

especially pronounced for 'grasboter', and for analyte classes such as the lactones and furans.

Another problem encountered in the 1D-GC study, and briefly referred to above, was the failed identification of several compounds having *m/z* 99 and 71 as their major ions (Table 5 of ref. [1]), due to separation and detectability problems. With GC × GC–TOF-MS, these compounds were found to be δ-lactones. The improved separation yielded clean mass spectra and, consequently, very high match factors. As an illustration, Fig. 2 shows the *m/z* 99 ion traces of 'grasboter' heated at 40 and 170 °C. The ordered structures, which cannot be recognized in the much too crowded TIC chromatograms (e.g. FID; cf. Fig. 1, lower frame), are readily observed if the added selectivity of an extracted ion trace is used: even minor peaks can now be confidently identified. The chromatograms also show that the concentrations of the high-volatile δ-lactones increase upon heat treatment, while those of the less volatile ones decrease.

A final aspect of interest is the comparison of the chromatographic profiles of a fresh and a several-months-old butter sample. Fig. 3 shows relevant GC × GC peak patterns for a 'grasboter' sample extract. Next to a comparison with the 'gezouten roomboter' chromatograms of Fig. 1 which demonstrates that, qualitatively, there is much similarity, the more important conclusion is that the two GC × GC patterns of Fig. 3 are essentially the same: no effect of the 2-month storage is observed. This agrees with findings of Peterson and Reineccius [12]: considerable changes are found only at higher storage temperatures of 10–21 °C. Admittedly, a similar conclusion was earlier reported on the basis of 1D-GC traces [1]. However, the extremely complex and, in some parts of the GC × GC plane, very crowded chromatograms of the present figure impressively illustrate how much information is lost when the resolution provided by the second-dimension separation is not available for interpretation of the results.

3.2.2. *Headspace of butter samples*

In order to extend our knowledge of the composition of the butter samples, their headspace was sampled by SPME, using a Carboxen/PDMS as well as a Carbowax/DVB fibre

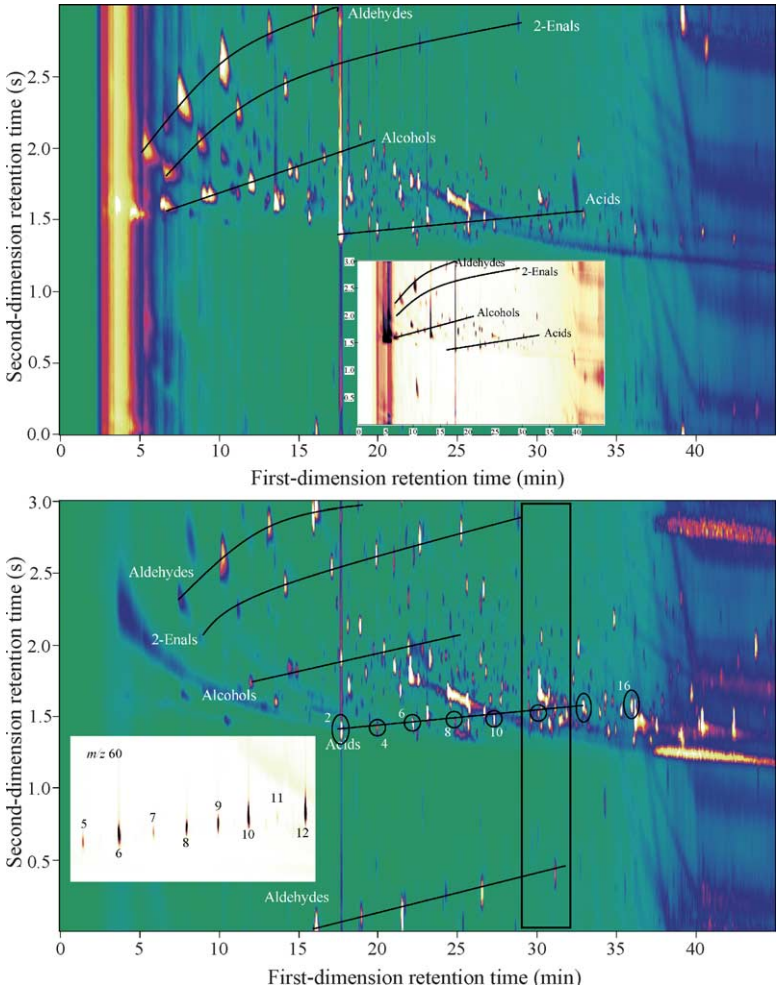

Fig. 4. GC × GC–FID chromatograms of 'grasboter' heated at 170 °C and extracted by Carboxen/PDMS (top) and Carbowax/DVB (bottom) fibres. Insert: profile of same sample but heated at 40 °C. Blow-up of the region marked in the lower chromatogram is shown in Fig. 5. The numbers 2–16 indicate carbon numbers of the circled acids. Insert: part of GC × GC–TOF-MS ion traces *m/z* 60 showing both even- and odd-numbered fatty acids.

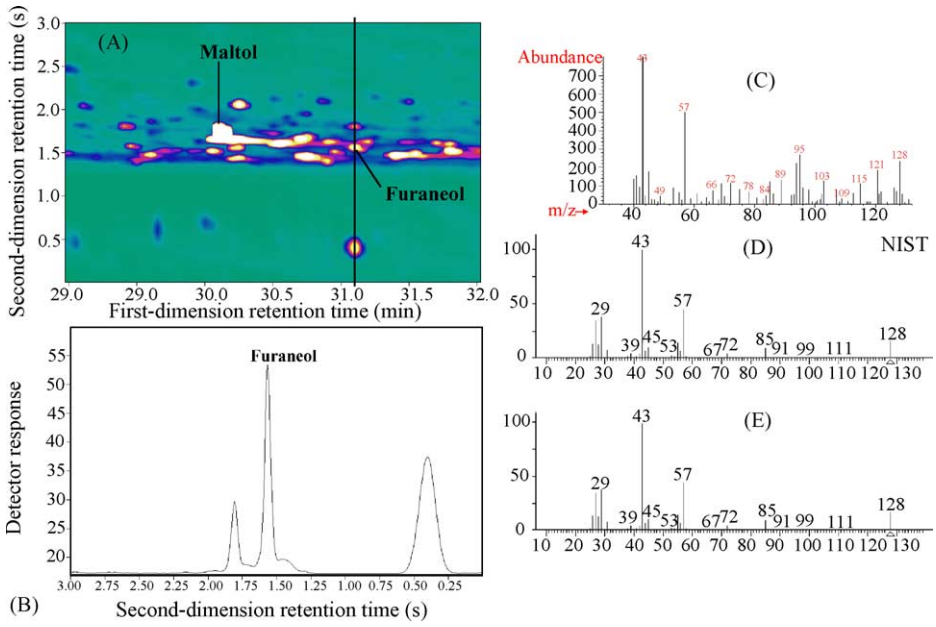

Fig. 5. (A) Blow-up of the marked region in Fig. 4; (B) second-dimension chromatogram across the vertical line in (A); (C) acquired mass spectrum of furaneol after 1D-GC; (D) library (NIST) spectrum of furaneol and (E) acquired mass spectrum of furaneol after GC × GC.

because of the complementarity discussed in Section 3.1. As was expected on the basis of earlier studies [1,12], the profiles observed for butter heated at 170 °C were considerably more complex than for butter heated at 40 °C. Fig. 4 shows the GC × GC–FID chromatograms for 'grasboter' at 170 °C obtained with the two SPME fibres. The higher affinity of the Carboxen/PDMS fibre for more volatile compounds, and of the Carbowax/DVB fibre for the less volatile flavours, is easily visible. The increasing complexity of the headspace at higher temperatures becomes clear upon comparing the top chromatogram (170 °C) and its insert (40 °C): the intensities of most peaks increase and many additional compounds show up. Several classes of compounds present at 40 °C as well as 170 °C, and forming ordered structures in the GC × GC plane, are indicated in Fig. 4: aldehydes, 2-enals, alcohols and fatty acids. As an illustration, some of these fatty acids are circled in Fig. 4 and indicated according to their carbon number. In these samples, the acids found ranged from formic (C_1) up to hexadecanoic (C_{16}) acid, with even carbon numbers being dominant (the odd-numbered fatty acids are not visible due to the limitations of colour shading [9]). Because of this, the odd-numbered fatty acids often remain undetected in 1D-GC [1]. However, they are visible as indicated in the insert of Fig. 4 (bottom) which shows the GC × GC–TOF-MS ion traces *m*/*z* 60. The assignment of the various structures was confirmed by analysing a test mixture containing six classes of polar compounds used in an earlier study on food analysis [11]. Further, comparison of the chromatograms presented in Figs. 1–4 clearly demonstrates the complementarity of the two sampling techniques. SPE gives more detailed results on the polar part of the sample while SPME provides a general profile of its headspace which also contains non-polar analytes.

Next to sample characterisation, with the use of ordered structures as a special tool, the detection and identification of individual analytes also is important. As an example, Fig. 5 shows details of the region marked in Fig. 4. In the crowded area at a second-dimension retention time of 1.5–2.0 s, maltol and furaneol elute in the vicinity of at least some 30 or 40 other sample constituents (Fig. 5A). As the second-dimension chromatogram across the vertical line drawn in Fig. 5A, depicted in Fig. 5B, shows even more vividly than Fig. 5A, the rather broad peak at a ^2t_R of about 0.5 s would largely obscure furaneol, and proper identification would become impossible. The broad peak belongs to the aldehydes band discussed above (cf. Fig. 4). The non-volatile aldehydes elute at high second-dimension retention times and show wrap-around, as also obtained in another GC × GC study [11]. The considerable advantage of using GC × GC instead of 1D-GC is demonstrated in Fig. 5C–E which show the mass spectra recorded in 1D-GC–MS, included in the NIST library, and recorded in GC × GC–TOF-MS.

It will be clear that with major sample constituents such as maltol, proper identification will not be difficult. However, in such cases – with overloading in both dimensions being clearly visible in Fig. 5A – all minor constituents co-eluting with maltol and its pronounced tail, i.e. having t_R = 30.1–30.8 min in 1D-GC, will essentially be lost. Again, GC × GC is needed to solve the resolution problem: the maltol tail is only a minor nuisance now.

3.3. Analytical data

In order to demonstrate the suitability of GC × GC procedures for quantitative analysis, the performance of SPME–GC × GC–FID and SPME–GC–MS was briefly stud-

Table 4
Analytical performance data for five model compounds

Analyte	SPME–GC × GC–FID			SPME–GC–MS		
	LOD (pg)	RSD of peak area (%)[a]	Correlation coefficient[b]	LOD (pg)	RSD of peak area (%)[a]	Correlation coefficient[b]
Diacetyl	7	10	0.995	25	12	0.993
Maltol	5	6	0.998	30	8	0.997
Furaneol	12	5	0.996	50	5	0.990
Sotolon	10	8	0.990	30	6	0.992
Sotolon[c]	10	9	0.991	35	8	0.990
Vanillin	3	5	0.998	25	5	0.998

[a] Determined at 0.5 μg/g of analyte injected ($n = 5$).
[b] Six concentrations in 0.1–20 μg/g range ($n = 2$).
[c] Data for spiked 'grasboter' at 0.1–20 μg/g ($n = 2$).

ied. Relevant results are reported in Table 4. Linearity was fully satisfactory for both techniques in the 0.1–20 μg/g range, with GC × GC giving marginally better results. A similar result was found for the repeatabilities of the entire procedures, determined at the 0.5 μg/g level: RSDs values typically were 5–8 ($n = 5$), but for diacetyl the high 12% of 1D-GC improved to 10% when using GC × GC. One may add that, in GC × GC, for all five test compounds (but also for other analytes studied in the context of the present paper), the RSDs of the first- and second-dimension retention times were fully satisfactory, i.e. less than 0.2% and 2% ($n = 6$), respectively. The limits of detection (with FID detection in GC × GC being compared with full-scan MS detection in 1D-GC) were some five-fold better for the comprehensive approach.

Finally, for sotolon, which is the only test analyte not present in the butter samples, quantification was also performed for spiked 'grasboter' and 'gezouten roomboter' in the 0.1–20 μg/g range. As Table 4 shows, with SPME–GC × GC–FID and SPME–GC–MS analyses the performance data were essentially the same as for the other analyses reported in the same table.

In conclusion, the present set of data demonstrates that GC × GC – although sometimes considered too complicated for that purpose – is perfectly suitable for quantitative analyses.

4. Conclusions

GC × GC coupled to both conventional flame ionisation and time-of-flight mass spectrometric detection, is a powerful separation and identification technique for the analysis of complex mixtures of compounds such as are often found in food samples. With the determination of flavours in butter as an example, the improved performance of GC × GC compared with 1D-GC is demonstrated. The main advantages are a more reliable analysis of target compounds, the rapid recognition of prominent classes of compounds on the basis of ordered structures, and the provisional identification of a much larger number of unknowns. As in earlier studies, the powerful identification and deconvolution potential of TOF-MS is indispensable in these studies.

More specifically, the present results – including the satisfactory analytical performance data – indicate that the proposed approach, with both SPE (aqueous phase) and SPME (headspace) coupled to a GC × GC system, is a promising and versatile technique for the rapid and wide-ranging screening of flavours and fragrances in food.

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