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Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection applied to the determination of pesticides in food extracts

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Abstract

The separation provided by conventional gas chromatography (1D-GC) can be significantly enhanced by using comprehensive two-dimensional GC (GC×GC) instead. Combination with mass spectrometric detection is desirable for unambiguous confirmation of target compounds and the provisional identification of unknowns. A GC×GC system using a cryogenic modulator was coupled to a time-of-flight mass spectrometric (TOF MS) detector. With the determination of pesticides in vegetable extracts as an example, it was demonstrated that GC×GC improves the separation dramatically. All 58 pesticides of interest could be identified using their full-scan mass spectra, which was not possible when using 1D-GC–TOF MS. In addition, the high scan speed of the TOF MS allowed the deconvolution of compounds partly co-eluting in GC×GC.

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1. Introduction

Conventional one-dimensional gas chromatography (1D-GC) generally does not provide sufficient separation for highly complex mixtures. Examples of such complex mixtures are petrochemical samples, and toxaphene or PCBs as found in environmental samples. As another category, extracts of food, sediments or wastewater often contain rather high concentrations of numerous matrix constituents that can easily obscure the analytes of interest. For all such sample types complicated sample preparation techniques such as multi-step solid-phase extractions (SPE) [1] or column-switching techniques such as heart-cutting techniques [2], or the use of a PIONA multi-column analyzer for petrochemical samples [3], are required to create sufficient separation of the analytes of interest from the matrix.

A novel approach to distinctly enhance separation is to use comprehensive two-dimensional gas chromatography (GC×GC) [4]. As recent experience has shown, this technique can effect a much improved separation of analytes of interest from each other and/or the matrix background and can provide group-type separations. In the latter instance, the ordered structure of the final chromatogram facilitates analyte identification [5].

This paragraph describes briefly the processes in a

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cryogenic modulated GC×GC system, which is accepted to be the common type of modulators. A GC×GC system consists of two columns with different retention mechanisms, which are connected in series. The sample is separated on the first column using a conventional temperature programme of 1–5°C/min. During this separation, small successive adjacent fractions of the eluate of the first column are retained and focused at the beginning of the second column by means of a cryogenic modulator, which essentially works like a cold trap. After the trapping of each fraction, the modulator is switched off or moved away to effect the release of the retained compounds and their rapid injection on to the second column (for explanation see Fig. 1). The second column is much shorter and narrower than the first column, which results in a much faster separation (e.g. 3–10 s vs. 45–120 min). Since the oven temperature does not change much during the rapid separation on the second column, typically 0.1–0.5°C, the second-dimension separation is essentially isothermal.

In a truly multidimensional system, the separation mechanisms in the first and the second columns are independent of each other and the separation obtained in the first column is maintained during the modulation and separation in the second column. The combination of a polymethylsiloxane column in the first and a polyphenylmethylsiloxane column in the second dimension provides two (almost) independent separation mechanisms — in the first dimension according to the vapour pressure of the analytes and in the second dimension according to their activity coefficients (aromaticity). In order to preserve the separation obtained in the first dimension, experience shows that a peak eluting from the first-dimension column should be modulated (Fig. 2, step 1) into five or more fractions [6]. In addition, all compounds that are injected on to the second column in one specific fraction should elute during the same modulation cycle in order to prevent co-elution with analytes of the next fraction and, thus, a loss of resolution.

The raw GC×GC chromatogram consists of a large number of second-dimension chromatograms which are stacked side by side, or transformed (Fig. 2, step 2) to generate a two-dimensional (2D) chromatogram. The axes of this 2D chromatogram represent the retention times on the first and the second column, respectively. The most convenient way to visualize such chromatograms in order to

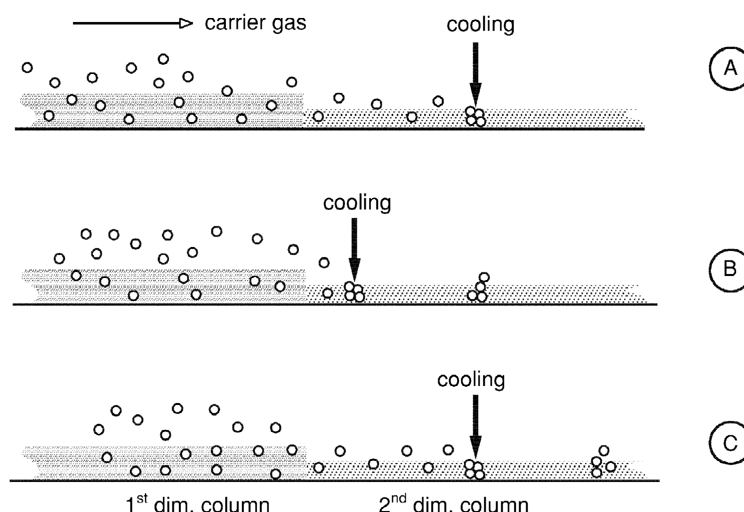

Fig. 1. Cryogenic modulation of a peak eluting from the first-dimension column. The black arrows indicate the part of the second-dimension column that is cooled by cold CO_2 gas. The temperature of that part is typically 100°C below the temperature of the GC oven. (A) The modulator retains part of a peak eluting from the first column. (B) The modulator is moved away, the cold spot heats up very quickly and the compounds are released and start to separate on the second column. Meanwhile, eluting material from the first column is prevented from interfering with the focused fraction. (C) The modulator is moved back to the trapping position.

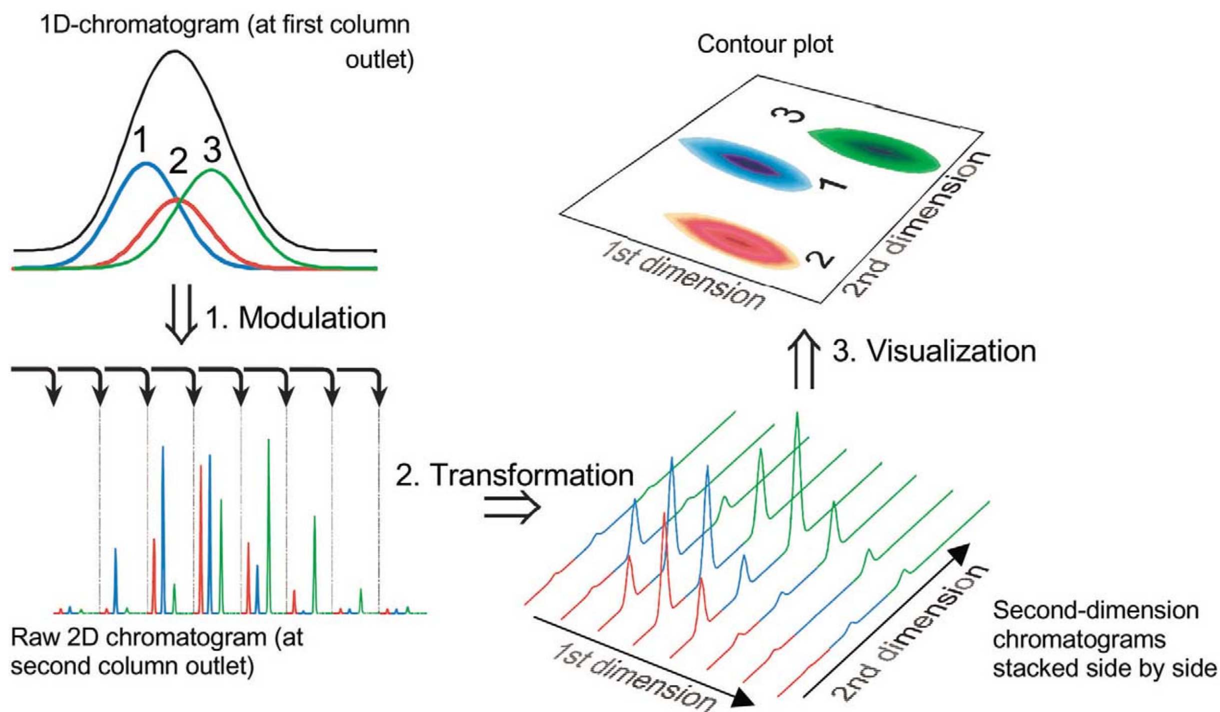

Fig. 2. Generation and visualization of a GC×GC chromatogram. For details of the progress of the operation see text.

facilitate interpretation, is by means of contour plots where colours and shading of the spots indicate the signal intensity.

The narrow peaks generated in the second dimension, with baseline widths of, typically, 60–600 ms, require the use of fast detectors to reconstruct the chromatograms properly. Until recently, detection in GC×GC therefore had to be done with single-channel detectors such as the FID [5,7] or ECD [8] since no fast mass-spectrometric (MS) detector was available. For most samples, however, an MS detector is highly desirable for the identification or identity confirmation of the analytes of interest. Recently, time-of-flight mass spectrometers (TOF MS) were introduced which can acquire 100 or more mass spectra per second as is required for GC×GC. Their speed, selectivity and sensitivity have been demonstrated for 1D-GC–TOF MS [9] and first results on the coupling of GC×GC and TOF MS have also been reported [10,11].

Unfortunately, at present there is no integrated software available to perform all three operations shown in Fig. 2, for data generated with GC×GC–TOF MS. Therefore, in this paper, three separate programmes were used: (i) GC–MS software for data acquisition, (ii) software for data transformation into a 2D array and (iii) software for data visualization in a contour plot. A brief explanation is given below.

Peaks, or spots, in the contour plot are identified by their retention times in the first and second dimension, i.e. by their coordinates in the contour plot. Mass spectra for target analyte confirmation and/or the identification of unknowns can at present be obtained only from the chromatogram of the raw data (''raw 2D-chromatogram'', cf. Fig. 2). For this purpose, as the first step, the total retention time of each peak of interest in the contour plot was calculated by adding the retention times from the first and second dimension. This total retention time is equivalent to the retention time in the raw 2D-chromatogram, where the peaks can be identified on the basis of their mass spectra, as is routinely done in 1D-GC–MS. Complex mixtures can easily contain

several hundreds or even thousands of compounds; therefore, an automated peak finding and identification routine is highly desirable. The 1D-GC–MS software used in this study can perform an automated qualitative analysis, i.e. it can deconvolute and identify peaks in an automated way. From the resulting peak table, the first- and second-dimension retention times (coordinates) were calculated to locate these peaks in the contour plot. Such a peak table may well contain a few thousand peaks.

Next to identification, also quantification was only possible using the raw 2D-chromatograms. Because the first-dimension peaks were modulated into 2–5 second-dimension peaks, the areas of these peaks had to be added prior to the actual calculation.

In the present paper, a GC×GC system with cryogenic modulation is described that was coupled to a time-of-flight mass spectrometer for the trace-level determination of pesticides in extracts of carrots and celeriac. The advantages of this approach over 1D–GC and GC×GC–FID are explained.

2. Experimental

The GC×GC–TOF MS system consisted of a HP 6890 (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph equipped with an Optic 2 programmable injector with a multicapillary liner (ATAS, Veldhoven, The Netherlands). The detector was a Pegasus II time-of-flight mass spectrometer (LECO, St Joseph, MI, USA).

A 15 m×0.25 mm I.D.×0.25 μm CP-SIL 5 CB low bleed/MS phase column (Varian-Chrompack, Middelburg, The Netherlands) was used as first-dimension column and a 80 cm×0.1 mm I.D.×0.1 μm BPX-50 phase column (SGE Europe, Milton Keynes, UK) as second-dimension column. The columns were connected with a press-fit connector (Varian universal quick seal, Varian-Chrompack).

The modulator is based on the longitudinally modulated cryogenic system of Dr P.J. Marriott (RMIT, Melbourne, Australia) [12]. Different from the original design, which uses the Joule–Thompson effect of expansion of liquid CO_2 for cooling inside the modulator, the CO_2 expansion and cooling is done outside the modulator. Therefore, the modulator in this set-up is cooled with cold gaseous CO_2 only. This enables a much better adjustment of the temperature of the modulator than with the original set-up.

The carrier gas was helium at a constant flow-rate of 1.3 ml/min. The temperature of the GC column was programmed from 50°C (4 min hold) to 280°C at 5°C/min. The modulation time was 6 s; the modulator temperature was kept 100°C below the oven temperature. The time-of-flight mass spectrometer was operated at a spectrum storage rate of 50 Hz, using a mass range of m/z 45–500 and a multi-channel plate voltage of −1800 V.

2.1. Analytes and samples

A standard mixture containing 40 nitrogen/phosphorus pesticides was obtained from J.T. Baker (Deventer, The Netherlands). A standard containing 58 pesticides and several food samples were a gift from the Dutch Inspectorate for Health Protection (Amsterdam, The Netherlands). The food samples were chopped and an aliquot of 2.5 g was added to a centrifuge tube; 2.5 g sodium sulphate and 5 ml ethyl acetate were added and the mixture was blended for 2–3 min in a Polytron blender (Kinematica, Littau-Lucerne, Switzerland) at 20 000 rpm. Next, the mixture was centrifuged at 5000 rpm for 10 min and 3–4 ml of the organic phase were pipetted off and transferred to a vial [13]. Approx. 1 g sodium sulphate was added to the ethyl acetate extract for drying. Finally, 1 or 10 μl of the extract were analyzed by GC×GC–TOF MS, which is equivalent to 0.5 or 5 mg fruit sample, respectively.

3. Results and discussion

3.1. Large volume injection

The carrier gas flow through the injector and column in a GC×GC system is similar to that of a conventional 1D-GC system, i.e. 1–3 ml/min. The dimensions and phase ratio of the first column are also similar to those of a conventional system, e.g. 0.25 mm I.D. and 0.25 μm film thickness. Therefore, all injection techniques of 1D-GC can also be used in GC×GC, e.g. split, hot and cold splitless, and large-volume injections.

In order to achieve better analyte detectability than with 1-μl cold splitless injections, 10 μl of the fruit extracts were injected using a PTV injector in the solvent-vent mode. For ethyl acetate as a solvent, a vent time of 55 s was used (at 40°C injector temperature, 70 ml/min vent flow and 7.2 p.s.i. vent pressure). In the example shown in Fig. 6, the chlorfenvinphos contamination could not be detected using a 1 μl cold splitless injection.

3.2. Identification of pesticides in food extracts

The essentially non-selective sample preparation used in the present study yielded extracts that contained rather high concentrations of matrix compounds. As expected, a 1D-GC separation could not separate all analytes of interest from the matrix and/or from each other. Admittedly, in many cases the mass spectrometer could deconvolute the peaks of partly co-eluting analytes. In some cases, however, matrix compounds completely obscured the analytes of interest. As an example of the potential of the GC×GC technique, Fig. 3 shows the most crowded part of the GC×GC–TOF MS chromatogram for a celeriac extract spiked with 58 pesticides (Table 1). It is obvious that the extract contains a number of matrix components at high concentrations (peaks labelled A–E and the three compounds tentatively identified — on the basis of their mass spectra — as bergaptan, psoralen and hexadecanoic acid). If 1D-GC–TOF MS was used, out of the mixture of 58 pesticides, four could not be identified and two other pesticides gave poor mass spectral match factors (Table 2). For example, triadimefon had exactly the same retention time as hexadecanoic acid when separated on a DB-1 column (Fig. 4a) and could not be identified by 1D-GC–TOF MS since no clean mass spectrum could be obtained nor by deconvolution or by baseline subtraction (Fig. 4c). Therefore the compound was incorrectly identified to be hexadecanoic acid. However, when using GC× GC–TOF MS, a clear separation of triadimefon from the matrix constituent was obtained due to the different activity coefficients of the two compounds on the second-dimension column (Fig. 4b). The mass spectrum now obtained was of a very good quality and triadimefon could be identified with a high similarity match factor (Fig. 4e,f).

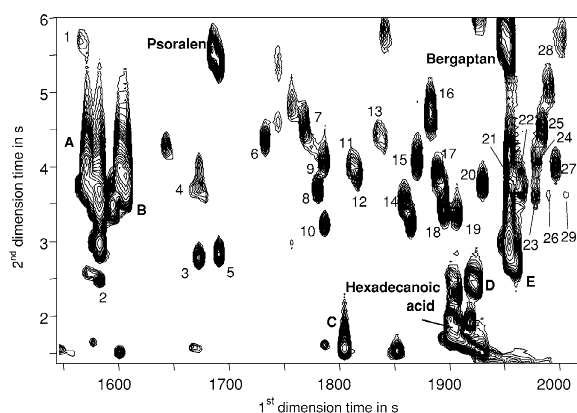

Fig. 3. Detail of the GC×GC–full-scan TOF MS chromatogram of an extract of celeriac, spiked with pesticides at a level of 0.16 ng/μl (0.32 mg/kg celeriac); for peak assignment, see Table 1; A–E, non-identified matrix compounds.

Similar results were obtained for the other five pesticides. As Table 2 indicates, dimethoate, profenvinphos and bupirimate could not be detected with 1D-GC–TOF MS either, since they co-eluted with matrix compounds or other analytes, while no problems were encountered once GC×GC–TOF MS was used as an alternative. With triadimenol (1) and pyridaphenthion, rather poor GC–MS results were found to be considerably improved using the GC× GC set-up.

It is interesting to add, whereas in 1D-GC with conventional MS detection identification is usually based on two to four qualifier ions and quantification is performed using a selective, but not always intense, single ion trace, GC×GC–TOF MS instead uses the complete mass spectrum for identification and enables quantification at more intense but less selective quantification masses which results in improved detectability.

The identification of non-target compounds such as bergaptan, psoralen and hexadecanoic acid in Fig. 3 requires high-quality mass spectra. Here, the much better resolution of GC×GC compared with 1D-GC analysis, which causes co-elution to be less severe, has a beneficial influence.

In the celeriac extract of Fig. 3 all analytes were identified by GC×GC–TOF MS using a non-target rather than the (more straightforward and simpler) target approach. In other words, the TOF MS software did not specifically search for these analytes

Table 1
Retention times of the 58-pesticide mixture

No.[a]	Name	t_R (s)		No.[a]	Name	t_R (s)	
		1st dim.	2nd dim.			1st dim.	2nd dim.
–	Biphenyl	1130	2.6	22	Chlorfenvinphos (α-)	1963	3.8
–	Mevinphos	1187	4.0	23	Chlozolinate	1978	3.6
–	Propham	1244	2.8	24	Chlorfenvinphos (β-)	1981	4.2
–	Phenylphenol (ortho-)	1316	3.2	25	Quinalphos	1981	4.6
–	Heptenophos	1394	3.6	26	Triadimenol (1)[b]	1997	3.7
–	Ethoprophos	1472	3.1	27	Procymidone	1999	4.0
–	Diphenylamine	1454	3.8	28	Methidathion	1999	5.8
–	Chlorpropham	1508	3.0	29	Triadimenol (2)[b]	2011	3.7
1	Dimethoate	1568	5.7	–	Profenophos	2080	4.5
2	Hexachlorobenzene	1580	2.6	–	Prothiophos	2083	3.7
3	Propyzamide	1675	2.8	–	Flusilazole	2116	4.3
4	Pyrimethanil	1675	3.7	–	Bupirimate	2125	4.6
5	Diazinon	1690	2.9	–	Oxadixyl	2176	1.9
6	Pirimicarb	1735	4.3	–	Ethion	2185	4.7
7	Parathion-methyl	1771	4.4	–	Propargite	2302	4.5
8	Chlorpyriphos-methyl	1777	3.8	–	Phosmet	2335	2.5
9	Tolclofos-methyl	1783	4.2	–	Pyridaphenthion	2344	1.4
10	Vinclozolin	1786	3.3	–	Iprodione	2344	5.6
11	Metalaxyl	1810	4.0	–	Bromopropylate	2365	4.8
12	Prometryn	1816	3.9	–	Bifenthrin	2383	3.9
13	Fenitrothion	1837	4.5	–	Fenpropathrin	2392	5.2
14	Pirimiphos-methyl	1855	3.6	–	Tetradifon	2413	0.7
15	Malathion	1867	4.2	–	Phosalone	2427	0.5
16	Fenthion	1885	4.7	–	Fenarimol	2487	1.0
17	Parathion-ethyl	1888	4.0	–	Cyhalothrin (lambda)	2493	4.8
18	Chlorpyriphos-ethyl	1891	3.5	–	Pyrazophos	2511	0.7
19	Triadimefon	1906	3.4	–	Pyridaben	2577	0.8
20	Fenpropimorph	1918	1.9	–	Permethrin (*cis*)	2571	0.8
21	Bromophos-methyl	1930	3.9	–	Permethrin (*trans*)	2589	0.5

[a] Peak assignment in Fig. 3.
[b] The fungicide triadimenol consists of two diastereoisomers.

Table 2
Comparison of mass spectral match factors[a] for GC–TOF MS and GC×GC–TOF MS of selected pesticides

Analyte	CAS No.	GC–TOF MS		GC×GC–TOF MS	
		Similarity	Reverse	Similarity	Reverse
Dimethoate	60-51-5	nf	nf	957	965
Triadimefon	43121-43-3	nf	nf	943	942
Triadimenol (1)	5519-65-3	616	757	911	911
Profenophos	41198-08-7	nf	nf	901	907
Bupirimate	41483-43-6	nf	nf	797	872
Pyridaphenthion	119-12-0	532	650	746	797

Sample: celeriac extract spiked with pesticides at a level of 0.16 ng/μl (0.32 mg/kg celeriac); nf, not found.
[a] "Similarity" and "Reverse" are MS match factors provided by the NIST search algorithm, which are between 0 and 999, where higher numbers mean better fit. The similarity factor describes how well the library hit matches the peak using all masses. The reverse factor describes how well the library hit matches the peak using only the masses present in the NIST database mass spectrum.

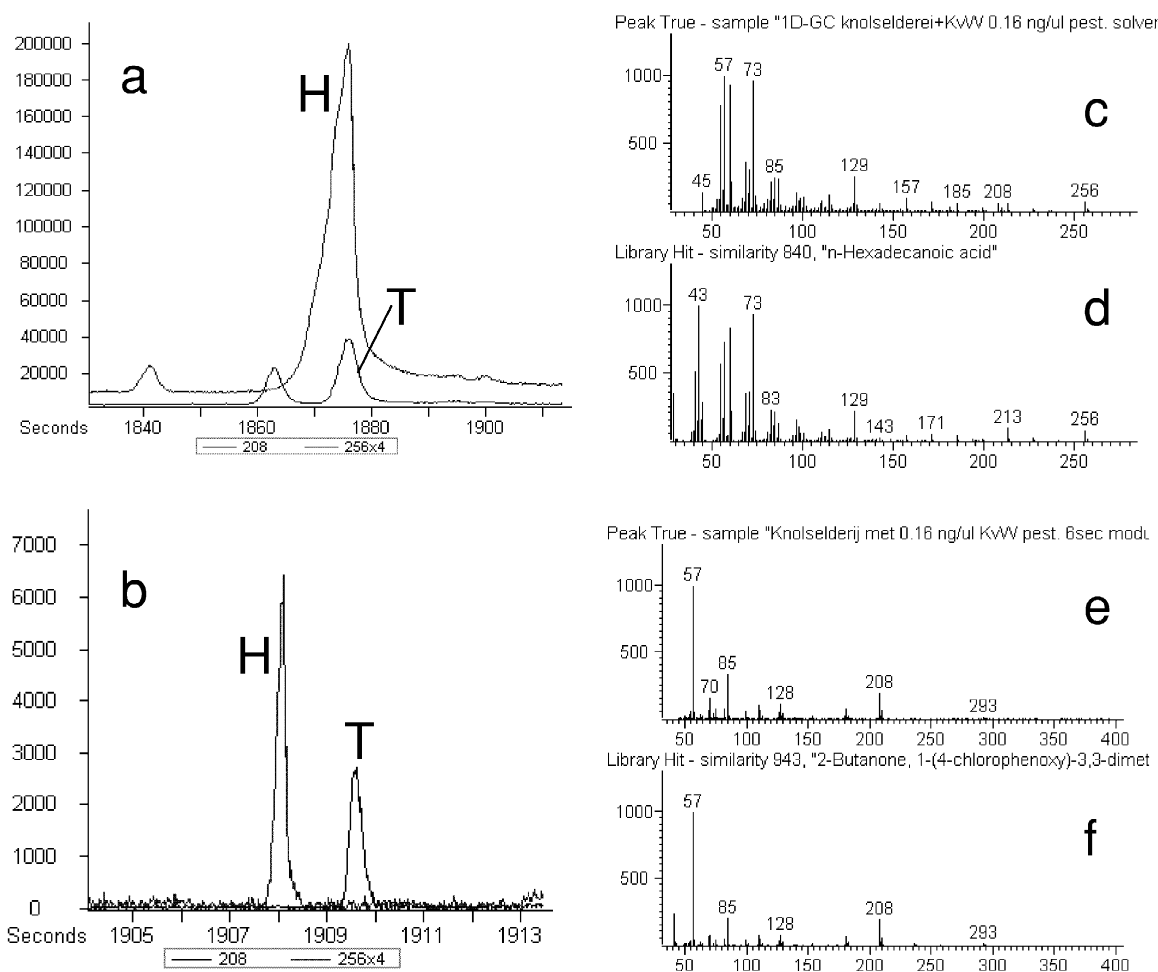

Fig. 4. Details of chromatograms of a celeriac extract, spiked with pesticides at a level of 0.16 ng/μl (0.32 mg/kg celeriac). (a) Conventional 1D-GC–TOF MS chromatogram: the matrix compound (H, hexadecanoic acid, m/z 256) and the analyte (T, triadimefon, m/z 208 scaled to 400%) co-elute. Identification of triadimefon (mass spectrum c) was not possible (library hit d — hexadecanoic acid). (b) Second-dimension chromatogram of GC×GC–TOF MS shows separation of triadimefon from hexadecanoic acid. Triadimefon could be easily identified (mass spectrum, e; library spectrum, f).

but, rather, for all sample constituents. As a consequence, the software generated a peak table containing the 2000 largest peaks found in the chromatogram with their (deconvoluted) mass spectra and mass spectral library search results. In this peak table all pesticides were identified, most of them with similarity factors of better than 900. Although this suggests the possibility of a non-target approach in routine analysis instead of the commonly used target analysis, a more extensive study is definitely required. In this paper, a target approach was used to obtain analytical performance data for selected analytes (see Section 3.4). A non-target analysis was generally preferred because of its flexibility during method development. In routine analysis, a target analysis supplemented by a non-target analysis using the same data file could be a promising approach. A more detailed explanation of target and non-target analysis (screening) with the emphasis on (semi)-automated data processing can be found in Ref. [14].

Another illustrative example of the separation power of GC×GC–TOF MS can be found in the

identification of a (very) low concentration of a chlorfenvinphos contamination in an extract of carrots. The extract contained approx. 10 pg/μl of chlorfenvinphos (equivalent to 0.02 mg/kg of carrot, quantified by the Health Inspectorate Amsterdam by 1D-GC–ion trap MS; maximum residue level set by European Commission is 0.5 mg/kg) in a very complex matrix. Fig. 5 shows a contour plot of the GC×GC chromatogram of that sample, which contained several hundred fully resolved peaks. On the basis of their mass spectra, many of these could be identified as flavours. The two very intense and strongly tailing major peaks were found to be hexadecanoic (A16) and octadecadienoic (A18) acid. Due to the separation power of GC×GC, the elongated tails of both acids can be clearly identified as two intense curving bands starting at approx. 1700 and 1900 s, respectively. In 1D-GC, a major part of these tails could not be recognized: they were part of a high and somewhat variable background. Here and elsewhere in the GC×GC chromatograms, the recognition of peaks and, in this instance, tails is improved considerably by the peak compression invariably effected by refocusing during modulation (cf. Refs. [15,16]). Fractions of the tail (in the present example being 6 s wide) eluting from the first-dimension column typically were only 200 ms wide in the second-dimension chromatogram.

When 1D-GC–TOF MS was used, there was no possibility to separate chlorfenvinphos from many other, interfering compounds, although a small peak was observed at the characteristic mass, m/z 323 (Fig. 6b). However, the mass spectrum obtained at that retention time (Fig. 6e) was not characteristic at all for the analyte (library spectrum in Fig. 6d). GC×GC–TOF MS dramatically improved the separation from the matrix, as is evident from Fig. 6a; the sample matrix shows up as a thick, continuous band at the bottom of the contour plot. The mass spectrum obtained from the now almost fully resolved analyte peak, was of good quality (Fig. 6c) and allowed the identification of chlorfenvinphos.

3.3. Deconvolution

In conventional 1D-GC–MS, the mass spectral

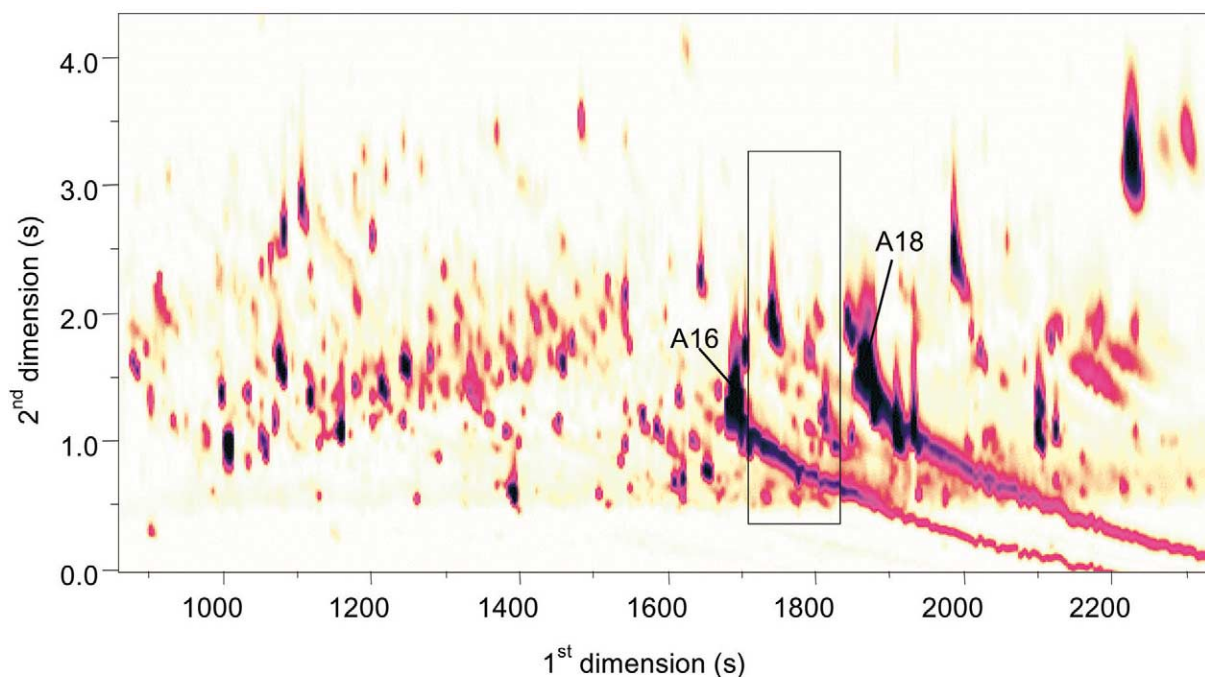

Fig. 5. Detail of the GC×GC–TOF MS TIC-chromatogram of a (non-spiked) carrot extract. A blow-up of the marked area is shown in Fig. 6a.

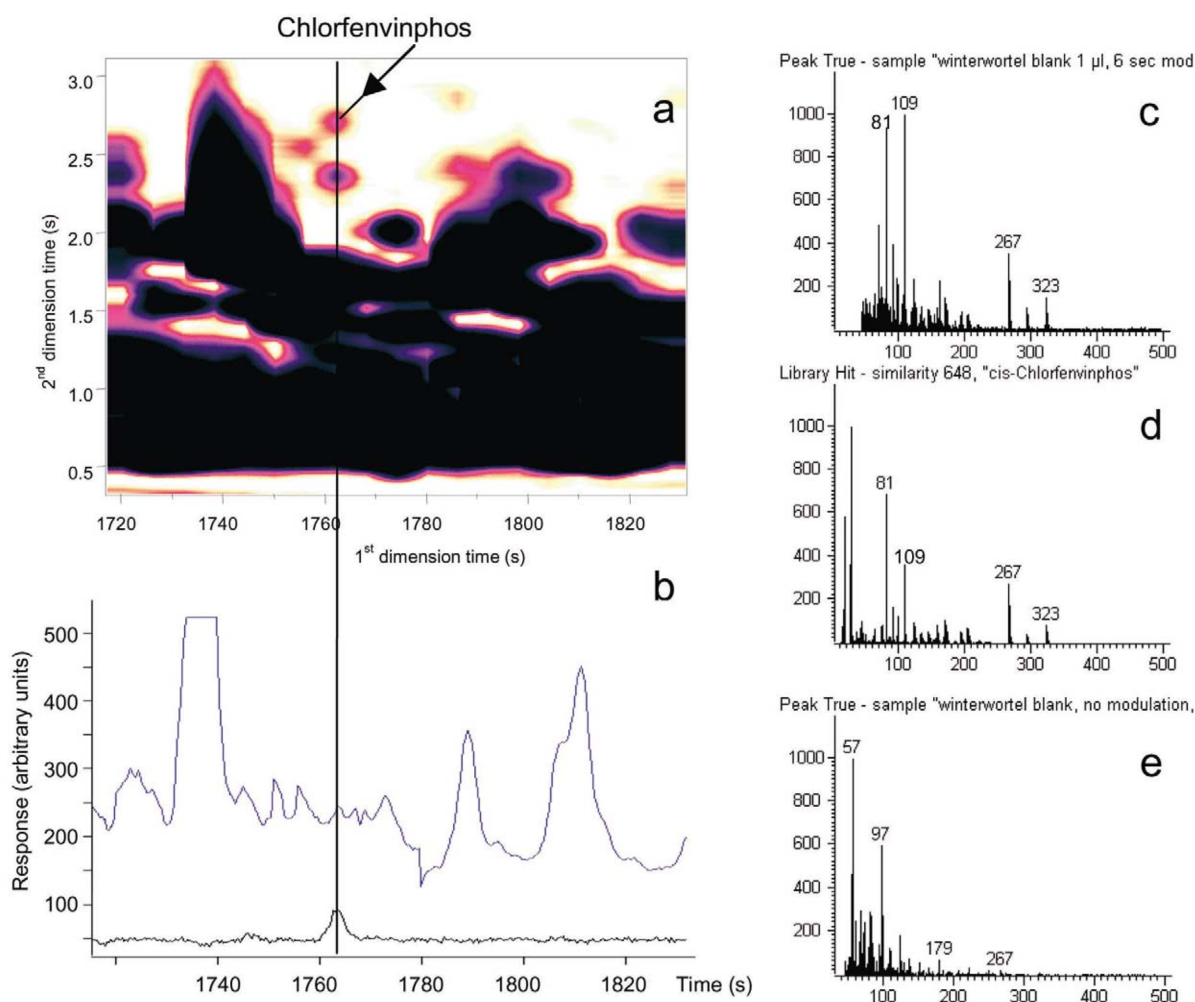

Fig. 6. GC×GC–TOF MS versus 1D-GC–TOF MS for the analysis of a carrot extract. (a) GC×GC–TOF MS contour plot. (b) 1D-GC–TOF MS chromatogram of the same region; upper trace, TIC scaled to 1%; lower trace, m/z 323 ion trace. (c) Mass spectrum obtained after GC×GC separation showing the characteristic m/z values of chlorfenvinphos (m/z 81, 109, 267, 295, 323). (d) Library spectrum of chlorfenvinphos and (e) spectrum obtained at the retention time of chlorfenvinphos after 1D-GC separation.

information can be used to mathematically separate (i.e. deconvolute) partly co-eluting chromatographic peaks to obtain ''purified spectra'' [17]. The GC–MS software used in this paper for data acquisition and processing can deconvolute two overlapping peaks when their apexes are separated by three scans. Since we used a scan rate of 50 Hz, this means ''purified'' deconvoluted mass spectra could be obtained from peaks that were separated by only 0.06 s. Since peaks obtained in GC×GC had between 0.2 and 0.6 s baseline widths, this means that the number of identifiable peaks can be increased 3- to 10-fold compared to GC×GC–FID. Such deconvolution requires that the mass spectra of each of the co-eluting analytes display characteristic m/z values. In our experience, most pesticides have sufficiently characteristic mass spectra — consequently, partial co-elution causes no serious problems in terms of analyte identification or confirmation. Still, one should consider that deconvolution is an *additional* tool to aid separation. Complex samples require a good chromatographic separation in the first place, as

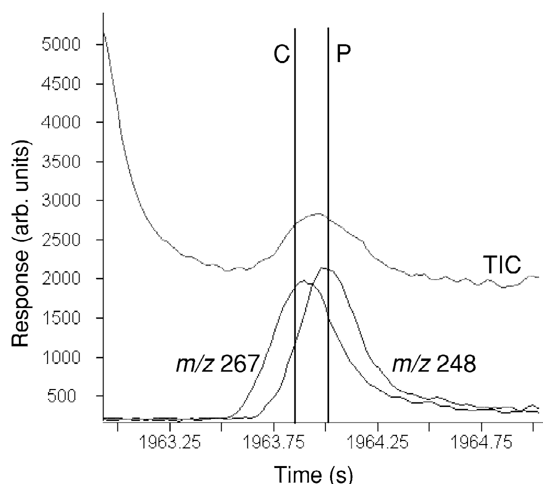

Fig. 7. GC×GC–TOF MS chromatograms of a celeriac extract spiked at 0.16 ng/μl (equivalent to 0.32 mg/kg celeriac) with several pesticides. Second-dimension chromatogram of the ion traces *m/z* 267 and 248 for α-chlorfenvinphos (C) and penconazole (P), respectively, and the TIC (scaled to 2%).

obtained by GC×GC. The compounds listed in Table 2 could not be identified by 1D-GC–TOF MS despite the use of the deconvolution algorithm.

To quote an example of the potential of deconvolution, penconazole and α-chlorfenvinphos were found to co-elute in the present GC×GC system: their peak apexes were only separated by 0.1 s in the second dimension. Fig. 7 shows the co-eluting peaks, viz. the total ion current (TIC) trace as well as the characteristic *m/z* 267 and 248 traces of the second-dimension chromatogram. With the total ion trace of Fig. 7 — or, for that matter, GC×GC–FID — there is no possibility to distinguish the two analytes. The deconvolution algorithm, however, automatically recognized the different peak apexes (for instance, for the ion traces *m/z* 267 and 248) and calculated the mass spectra for both compounds, which were then identified with similarity factors of 817 and 850, respectively.

3.4. Analytical performance data

The pesticides molinate, trifluralin, prometryn, metolachlor, stirofos, and butachlor were selected to determine linearity and detection limits. Table 3 summarizes relevant analytical data. Calibration plots were found to be linear over the entire 0.01–3 ng range tested: correlation coefficients were 0.998 or higher in all instances (1 μl injections; seven data points; $n=2$). The detection limits (LODs) were between 3 and 23 pg. As has been explained in Refs. [14,18], the LODs are affected by the number of modulations across the first-dimension peak (and, of course, also by the second-dimension peak width). In the present case, the LODs were calculated for the highest second-dimension modulation peak. The relative standard deviations of the peak areas were 5–11% (100 pg injections, $n=5$). The repeatability of the retention times for these selected analytes was 0.11–0.16 s with peak widths of 0.2–0.6 s and second-dimension retention times of 1.0–2.9 s. No additional correction of the retention time was required, since modulation and data acquisition were synchronized at the beginning of each run.

For a recent extensive study on analytical performance data in GC×GC–TOF MS, the reader is referred to Ref. [14]. A discussion about detection

Table 3
Analytical data of selected pesticides

Analyte	t_R (s)		Quantitation mass (Da)	LOD (pg)[c]	Correlation coefficient[a]	RSD of peak area (%)[b]	Standard deviation of 2nd dimension retention time (s)
	1st dim.	2nd dim.					
Molinate	881	2.4	126	5	0.9994	11	0.11
Trifluralin	1097	1.0	264	7	0.9994	8	0.11
Prometryn	1355	2.9	241	12	0.9978	7	0.16
Metolachlor	1427	2.2	162	5	0.9988	6	0.11
Stirofos	1577	3.2	109	23	0.9981	9	0.16
Butachlor	1601	2.0	160	7	0.9996	5	0.14

[a] Range, 0.01–3 ng/μl; seven data points in duplicate.
[b] Determined at a level of 100 pg, $n=5$.
[c] Experimentally determined at 10–30 pg level for the highest second-dimension peak, 3× peak-to-peak noise.

limits in GC×GC compared to 1D-GC on a theoretical basis can be found in Ref. [18].

4. Conclusions

GC×GC–TOF MS is a powerful separation and identification technique, which is very suitable for the analysis of complex food samples, which often contain hundreds, or even thousands, of GC-amenable compounds. When using GC×GC, the analytes of interest can be better separated from each other but, what is more important, also from matrix compounds, which tend to seriously interfere in 1D-GC–MS procedures. Consequently, the quality of the TOF MS mass spectra obtained by GC×GC is much better than those obtained with 1D-GC, as was illustrated in this study for a series of pesticides. The recording of two, rather than one, retention time(s) and the excellent analyte detectability effected by the peak sharpening during modulation, add to the attractiveness of GC×GC-based analyses. To put it differently, GC×GC–TOF MS can be used to simplify cumbersome sample preparation procedures via analyte/matrix pre-separation.

In the near future, the data handling and visualization routines of GC×GC–TOF MS will have to be improved. Most importantly, the quantification procedures will have to be redesigned, given the fact that the first-dimension peaks are split (during modulation) into three or more second-dimension peaks whose areas have to be added.

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