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Evaluation of pesticide residue contents in fruit juice by solid-phase microextraction and multidimensional gas chromatography coupled with mass spectrometry

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ABSTRACT

A new method based on the use of SPME followed by the MDGC–MS analysis was developed to determine pesticides in fruit juice. Different pesticide mixture standards (i.e. Mix 101, 13 and 164) were initially analyzed to optimize the separation conditions. To evaluate the advantages of the two-dimensional system over monodimensional GC, a comparative study on relative standard deviations, detection limits and correlation coefficients was carried out. As a result, selective transfers of some pesticides from the first to the second dimension were at times essential to avoid overlapping. The selected separation conditions from the study with standards were applied to fruit juices spiked with some pesticide standards. The results found in this work prove that the employment of a multidimensional analysis technique permits to avoid false positives obtained frequently on monodimensional techniques as a consequence of interferences of the analytes with matrix components.

1. Introduction

Nowadays, the use of pesticides in agriculture has become a common practice to increase food production. Despite a number of benefits are obtained from the employment of pesticides, some of them have been recently prohibited because of their highly persistent properties and their bioaccumulation. In this sense, polychlorinated biphenyls (PCBs) have been reported to be ubiquitous environmental xenobiotics of particular persistent ability and toxicity [1,2]. One of the main characteristics of PCBs is, among others, their lipophilic character, which results in their accumulation in the liver. Although there are different sources from which pesticides can reach human body, the intake of contaminated foods is the principal pathway in comparison to other sources such as inhalation and other dermal contact [3].

The determination of pesticides generally requires the application of protocols that include selective extractions and clean-up procedures necessary to overcome matrix effect troubles. These conventional methods usually are time consuming, costly and tedious. Besides, they demand the use of contaminant organic solvents. The techniques such as multidimensional gas chromatography (MDGC) [4] progressing in the development of selector phases represent reliable and powerful methods to avoid peak overlapping. The application of MDGC in environmental analysis has been primarily limited to analysis of polychlorinated biphenyl congeners [5,6] and toxaphene [7]. MDGC is typically used with electron capture detector (ECD) [8,9]. However the combination of MDGC and MS has provided good examples of target qualitative and quantitative analyses of these congeners in foods [10]. The environmental analysis concerning the identification of pesticides and their metabolites has received considerable attention. The analysis of these types of compounds is difficult because of the wide variety of polarities and the potentially wide range of component concentration.

A number of sample preparation methods have been developed for the separation and enrichment of analytes. Pesticide matrices are usually enriched by liquid–liquid extraction (LLE) [11,12], dispersive liquid–liquid microextraction (DLLME) [10], SPE [13,14], and single-drop microextraction (SDME) [15]. LLE, SDME and SPE often are time consuming and need organic solvent. Also, dispersive solid–liquid microextraction [16] and direct solid sample introduction [17]. As an alternative, SPME has important advantages because it is a simple and rapid technique which minimizes the sample handling. The usefulness of using SPME has already been reported [18,19]. For instance the selectivity demanded to isolate effectively some compounds from complex matrices can be attained by using the appropriated coating. Different authors have published SPME applications to organophosphorus pesticide

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Table 1
Data obtained from the separation column placed on the first dimension in the MDGC–MS system. The first dimension (1D) involved the use of the first GC coupled to the FID and the second dimension (2D) involved the use of the second GC coupled to the MS detector. Relative standard deviation (%) from the absolute peak area ($n = 3$), correlation coefficient (R^2) for the linear calibration and detection limits (LDs, ng) are presented.

Compound	tr-1D (min)	Heart-cut (min)	RSD-1D	LD-1D (ng)	R^2-1D	tr-2D (min)	LD-2D (ng)	R^2-2D
15[a]. Alachlor[b]	24.42	24.30–24.60	0.63	4.485	0.9942	32.79	33.515	0.9997
10[c]. Ametryn	22.94	22.82–23.00	0.20	0.686	0.9989	30.78	0.610	0.9898
4. Atrazine	20.08	19.99–20.12	0.42	2.813	0.9950	21.59	0.238	0.9905
13. Chlorpyriphos	24.00	23.90–24.07	0.18	1.269	0.9953	32.18	1.360	0.9953
7. Diazinon	20.97	20.86–21.07	1.05	1.236	0.9941	27.47	0.833	0.9917
1. Molinate	15.93	15.84–16.07	0.21	1.034	0.9886	21.72	0.304	0.9942
14. Parathion-ethyl	24.23	24.12–24.29	0.37	1.403	0.9970	32.36	1.077	0.9962
9. Parathion-methyl	22.65	22.57–22.76	0.16	2.271	0.9978	30.77	0.352	0.9989
16. Pendimethalin	25.48	25.36–25.60	0.05	1.098	0.9964	33.53	1.154	0.9938
8. Pirimicarb	21.88	21.78–21.97	0.34	1.326	0.9958	26.74	0.026	0.9988
11. Prometryn	23.08	23.00–23.17	0.34	1.347	0.9737	30.69	0.326	0.9805
5. Propazine	20.21	20.12–20.30	0.09	1.786	0.9501	26.75	0.317	0.9967
3. Simazine	19.95	19.68–19.98	0.82	3.536	0.9935	26.80	0.809	0.9494
6. Terbuthylazine	20.57	20.41–20.72	0.12	1.759	0.9979	22.04	0.111	0.9724
12. Terbutryn	23.54	23.42–23.64	0.62	1.459	0.9998	31.36	0.352	0.9394
2. Trifluralin	18.64	18.54–18.72	0.18	1.155	0.9820	20.25	0.062	0.9116
23. PCB 28	22.50	22.47–22.75	0.28	0.895	0.9934	24.40	0.450	0.9928
25. PCB 52	23.71	23.66–23.85	0.26	0.738	0.9904	25.61	0.592	0.9923
32. PCB 101	26.72	26.69–26.84	0.41	0.765	0.9949	28.65	0.179	0.9723
38. PCB 138	28.54	28.47–28.63	0.25	1.210	0.9980	30.50	0.226	0.9924
41. PCB 153	29.55	29.51–29.70	0.30	1.035	0.9995	31.60	0.160	0.9934
45. PCB 180	32.69	32.62–32.82	0.46	1.007	0.9904	34.54	0.216	0.9907
26. Aldrin	24.28	24.22–24.40	0.18	0.846	0.9915	26.26	0.241	0.9924
30. cis-Chlordane	26.48	26.42–26.56	0.33	1.227	0.9997	21.12	0.228	0.9997
34. trans-Chlordane	27.00	26.96–27.10	0.21	1.212	0.9996	28.97	0.306	0.9998
29. oxy-Chlordane	25.70	25.75–25.90	0.51	1.250	0.9913	27.79	0.161	0.9992
37. 2,4′-DDD	27.98	27.92–28.13	0.17	0.685	0.9895	30.20	0.148	0.9935
38. 4,4′-DDD	29.09	29.03–29.16	0.38	0.740	0.9893	34.91	0.180	0.9944
42. 2,4′-DDE	26.63	26.58–26.68	0.38	1.672	0.9912	30.00	0.170	0.9944
35. 4,4′-DDE	27.69	27.64–27.74	0.76	0.683	0.9914	29.69	0.683	0.9991
31. 2,4′-DDT	29.22	29.17–29.35	0.33	0.822	0.9909	31.28	0.283	0.9975
40. 4,4′-DDT	30.33	30.27–30.43	0.85	0.877	0.9912	33.50	0.180	1
36. Dieldrin	27.80	27.75–27.89	0.24	1.095	0.9926	28.30	0.383	0.9989
33. α-Endosulfan	26.91	26.86–26.95	0.29	1.571	0.9986	28.90	0.352	0.9908
33. β-Endosulfan	26.91	26.86–26.95	0.72	1.485	0.9985	28.90	0.334	0.9967
17. α-HCH	19.24	19.20–19.35	0.32	1.483	0.9925	20.35	0.409	0.9964
19. β-HCH	20.20	20.17–20.30	0.41	3.085	0.9953	22.13	0.409	1
20. δ-HCH	21.27	21.24–21.40	0.21	1.420	0.9913	23.23	0.450	0.9971
21. γ-HCH	20.44	20.40–20.55	0.31	1.780	0.9905	21.85	0.264	0.9933
22. ε-HCH	21.64	21.60–21.75	0.40	1.796	0.9988	23.59	0.282	0.9546
24. Heptachlor	23.05	23.00–23.15	0.38	1.167	0.9922	25.01	0.592	0.9946
28. cis-Heptachlorepoxide	25.66	25.60–25.75	0.88	1.240	0.9938	27.66	0.209	0.9951
28. trans-Heptachlorepoxide	25.81	25.60–25.75	0.68	1.278	0.9966	30.98	0.236	0.9958
18. Hexachlorobenzene	19.56	19.53–19.70	0.56	1.545	0.9997	20.93	0.214	0.9928
27. Isoaldrin	25.29	25.22–25.39	1.15	0.940	0.9929	27.30	0.214	0.9772
46. Mirex	33.70	33.63–33.80	1.58	1.053	0.9927	36.86	0.216	0.9976
44. Methoxychlor	32.18	32.11–32.34	1.53	0.901	0.9823	33.25	0.216	0.9976

[a] Pesticides are numbered in elution order.
[b] Pesticide names are cited in alphabetic order.
[c] Pesticides 10 and 11 were transferred together.

residues in cow milk using headspace SPME [20], pesticides in aqueous samples [21] in solid food samples [22] and chlorophenols and organochlorine in aqueous samples [23]. To our knowledge, no analytical method combining the selectivity of SPME with the sensitivity of MDGC/MS to determine pesticides in fruit juice has been proposed to date.

In this paper, we develop a new analytical method to identify and quantify a high number of pesticides that are potentially present in fruit juice. This method was based on SPME as an extraction technique and MDGC–MS for the analysis of the extract. Advantages of this method over other methods reported in the literature are its reliability, rapidity, simplicity and sensitivity.

2. Experimental

2.1. Samples

Different pesticide mixtures purposed by Dr. Ehrenstorfer GmbH were analyzed. Three standard solutions with different pesticides were studied. *Mixture 101* [Alachlor, Ametryn, Atrazine, Chlorpyriphos, Diazinon, Molinate, Parathion-ethyl, Parathion-methyl, Pendimethalin, Pirimicarb, Prometryn, Propazine, Simazine, Terbuthylazine, Terbutryn, Trifluralin] (50 ng/μl each component), pesticide *Mix 164* (10 ng/μl each component) (2,4′-DDD, 2,2′-DDD, 2,4′-DDE, 4,4′-DDE, 2,4′-DDT, 4,4′-DDT), *Mix 13* [PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180, Aldrin, cis-Chlordane, trans-Chlordane, oxy-Chlordane, 2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 4,4′-DDE, 2,4′-DDT, 4,4′-DDT, Dieldrin, α-Endosulfan, β-Endosulfan, α-HCH, β-HCH, γ-HCH, δ-HCH, ε-HCH, Heptachlor, cis-Heptachlorepoxide, trans-Heptachlorepoxide, Hexachlorobenzene, Isodrin, Methoxychlor, Mirex] (10 ng/μl each component). Also three fruit juices (peach, orange and pineapple) purchased from local shops were analyzed.

2.2. Solid phase microextraction (SPME)

A SPME holder (Supelco, Bellefonte, PA) was utilized to perform the experimentation. A fused silica fiber coated with a 65-μm

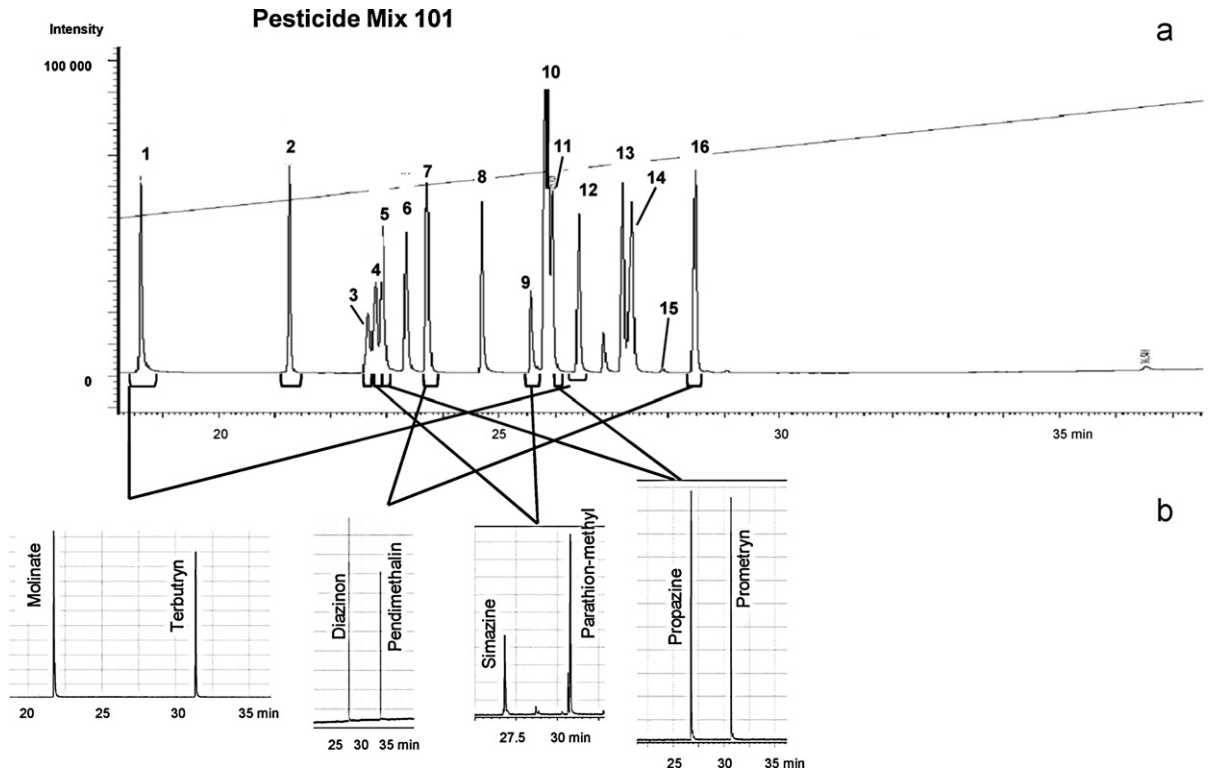

Fig. 1. (a) First dimension chromatogram showing the trace of the Mix 101 pesticides. (b) Second dimension chromatogram showing the separation of eight compounds of the Mix 101 pesticides.

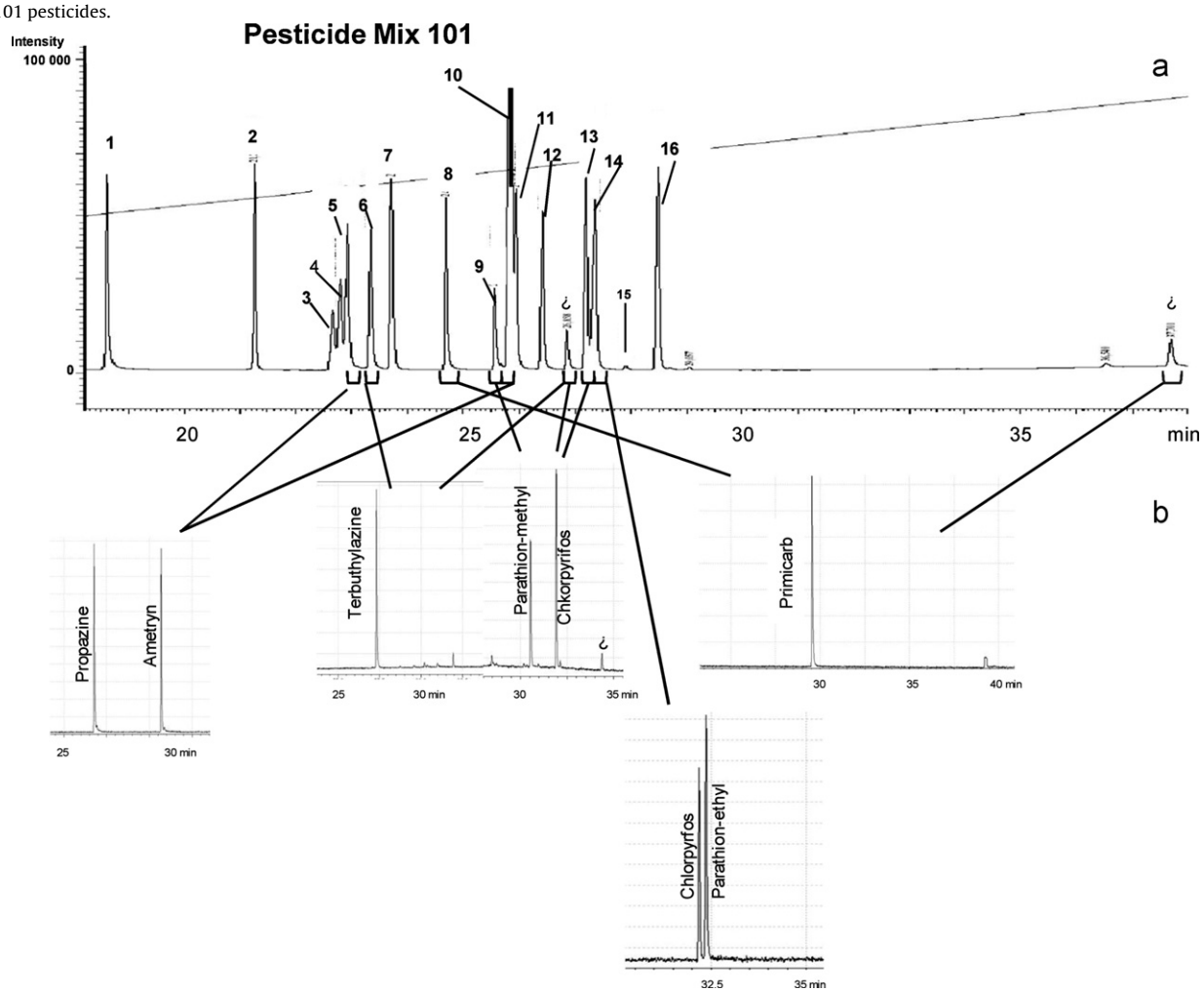

Fig. 2. (a) First dimension chromatogram showing the trace of the Mix 101 pesticides. (b) Second dimension chromatogram showing the separation of twelve compounds of the Mix 101 pesticides.

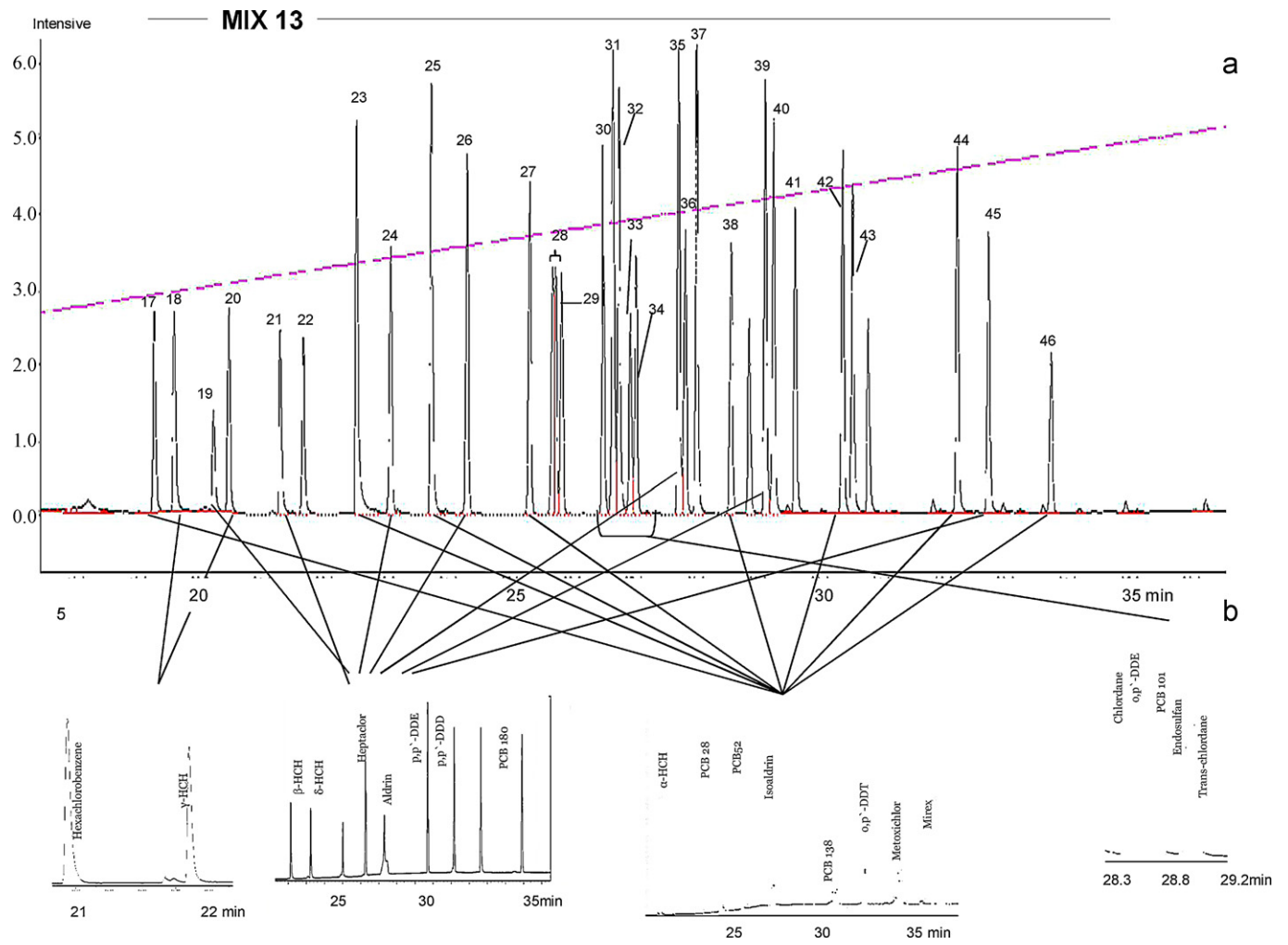

Fig. 3. (a) First dimension chromatogram showing the trace of the Mix 13 pesticides. (b) Second dimension chromatogram showing the separation of eight compounds of the Mix 13 pesticides.

layer of poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) was employed to retain the compound of interest. Before the SPME fiber was used, it was conditioned in the injector of the gas chromatograph at 250 °C for 30 min. A 1.0-mL volume of water was spiked with 1 μl of Mix 101 and was placed in a 5.0-mL vial that was sealed with a plastic film. Prior to the actual extraction, the sample was heated at 40 °C for 2 min to enrich the headspace in the target compounds. Then the fiber was exposed to the sample headspace for 30 min at 40 °C. The SPME conditions used were based on modifications of the extraction method reported by other authors [21]. The pesticides were thermally desorbed into the GC injector at 250 °C for 5 min and analyzed by multidimensional gas chromatography coupled to a mass spectrometer (MDGC–MS).

2.3. Multidimensional gas chromatography coupled to a mass spectrometer (MDGC–MS)

The MDGC system consisted of two independent gas chromatographs (Shimadzu model GC-2010), GC-1 and GC-2, GC-1 is equipped with split/splitless injector and a flame ionization detector (FID) and GC-2 with a mass spectrometer (MS) detector (Shimadzu model MS-QP2010 Plus). The automatic split/splitless injector (Shimadzu model AOC-20i) operated at 250 °C in the splitless was used to detect the analytes and helium served as the carrier gas at an approximate speed of 1 mL/min and the FID operated at 250 °C. Both GC are connected through a transfer line, in which two columns of different characteristics were placed. The two columns were serially coupled through a Deans-based switching system [24] and the transfer line, which was maintained at 300 °C throughout the experimentation. The connection of the Deans switch with FID was performed by means of stainless steel tubing. A scheme of the transfer employed has been described elsewhere [25]. The gas chromatographic analysis of the samples was performed using the GC-1 a 30 m × 0.25 mm ID capillary fused silica column coated with a 0.25 μm film of TRB-5 (Teknokroma, Spain). The oven was temperature-programmed from 60 °C (2 min) to 140 °C at 12 °C/min and then to 320 °C at 6 °C/min, the final temperature being maintained for 5 min. In the GC-2 a 30 m × 0.25 mm ID capillary fused silica column coated with 0.1 μm film of TRB-50 (Teknokroma, Spain) was used. This column has one end connected to the Deans switch and the other end connected to the MS detector. The selection of this stationary phase was based on the literature [1,2]. The column temperature was increased from 90 °C (10 min) to 120 °C at 12 °C/min and then to 170 °C at 3 °C/min. The ion source temperature of the MS was 230 °C, mass range 50–550 amu, scan speed 1666 amu/s, interface temperature 230 °C. The scan mode was used for the analyses. An advanced pressure control supplied helium at constant pressure (95 kPa) to the interface.

Analyses of spiked samples were accomplished to verify the identification in the first dimension as well as the transfer time of the fraction to the second GC. In all cases, analyses were made, at least, in triplicate.

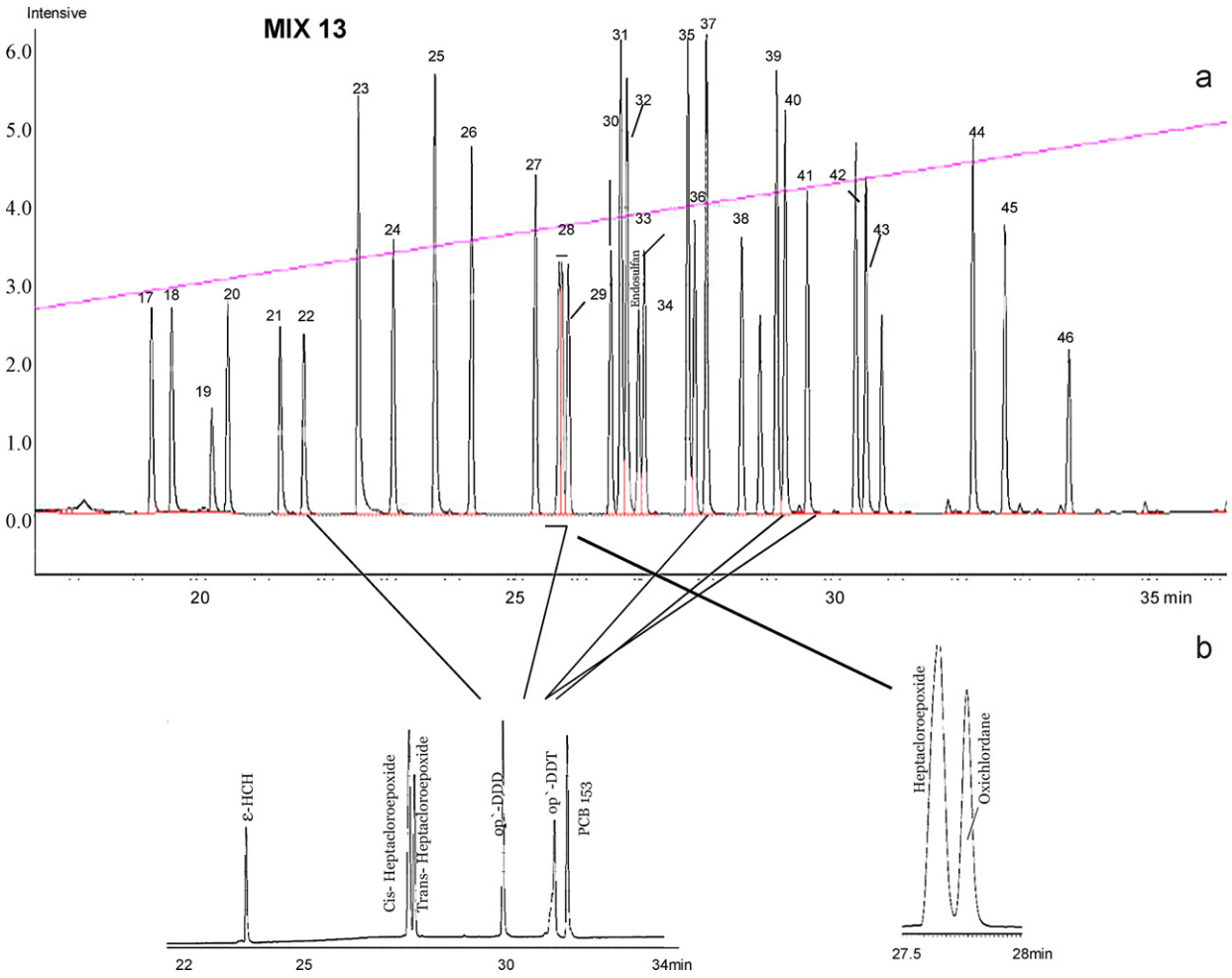

Fig. 4. (a) First dimension chromatogram showing the trace of the Mix 13 pesticides. (b) Second dimension chromatogram showing the separation of twelve compounds of the Mix 13 pesticides.

2.4. Calibration curve

Calibration curves were constructed for each compound to be quantified. To that end, linearity was evaluated in solution in a concentration range of 1–80 ng. The quantitative data were corrected to surrogate recovery. A blank sample was included with each set of six samples.

3. Results and discussion

The usefulness of the multidimensional technique was evaluated by comparing the results provided by one-dimensional GC and two-dimensional GC. Table 1 indicates the repeatability (expressed as relative standard deviation, RSD), detection limit (LD) and linearity (R^2) obtained from the separation of the target compounds on the first dimension in the MDGC–MS system. The first dimension involved the use of the first GC coupled to the FID. All these estimations were made from the standard solutions of both Mix 101 and Mix 13. The RSD was calculated from three replicates and a signal/noise ratio of 5 was employed for the calculation of the LD. As seen in Table 1, the RSD values were lower than 1.0% for most compounds. Higher values were only obtained for Diazinon, Isoaldrin, Mirex and Metoxychlor, which exhibited RSDs ranging between 1.0 and 1.6%. In any case, the repeatability of the one-dimensional GC method (i.e. on the first dimension of the multidimensional system) was considered satisfactory. The LDs varied in general from 0.683 to 2.271 ng. Higher values were however obtained for Atrazine, Simazine and Alachlor (i.e. 2.813, 3.536 and 4.485 ng respectively). The LD values obtained for Atrazine and Simazine are due probably to the possible error in the area measurement as a consequence of their co-elution with other components on the first chromatographic column. The LD of 4.485 ng obtained for Alachlor can however be owing to lower FID response. Regarding the linearity, the method was found to be linear over a range of 0.6–15.0 ng with a correlation coefficient (R^2) higher than 0.9904 for all compounds. From these results, the repeatability, detection limit and linearity for the studied compounds on the first column were satisfactory.

Figs. 1a and 2a depict the original chromatogram obtained on the first dimension of the separation of pesticides forming Mix 101. As can be seen in the chromatogram, although the most compounds were adequately resolved, several chromatographic signals appeared to overlap. In this sense, peaks 3, 4 and 5 as well as peaks 10 and 11 could not be properly separated by using one-dimensional GC. This problem was overcome by using the MDGC system, which allowed us to transfer selected cuts from the first to the second column. Parts (b) of both Figs. 1 and 2 illustrate the chromatograms corresponding to the pesticides transferred from the first to the second dimension in each case. The transfer of Symazine, Atrazine, Propazine (peaks 3, 4, 5 in Fig. 1a) as well as of Ametryn and Prometryn (peaks 10 and 11 in Fig. 2a) in single cuts did not still enable the target compounds to be satisfactorily resolved. This is due most likely to the inappropriate chromatographic selectivity of the second column to these compounds. For this reason, these

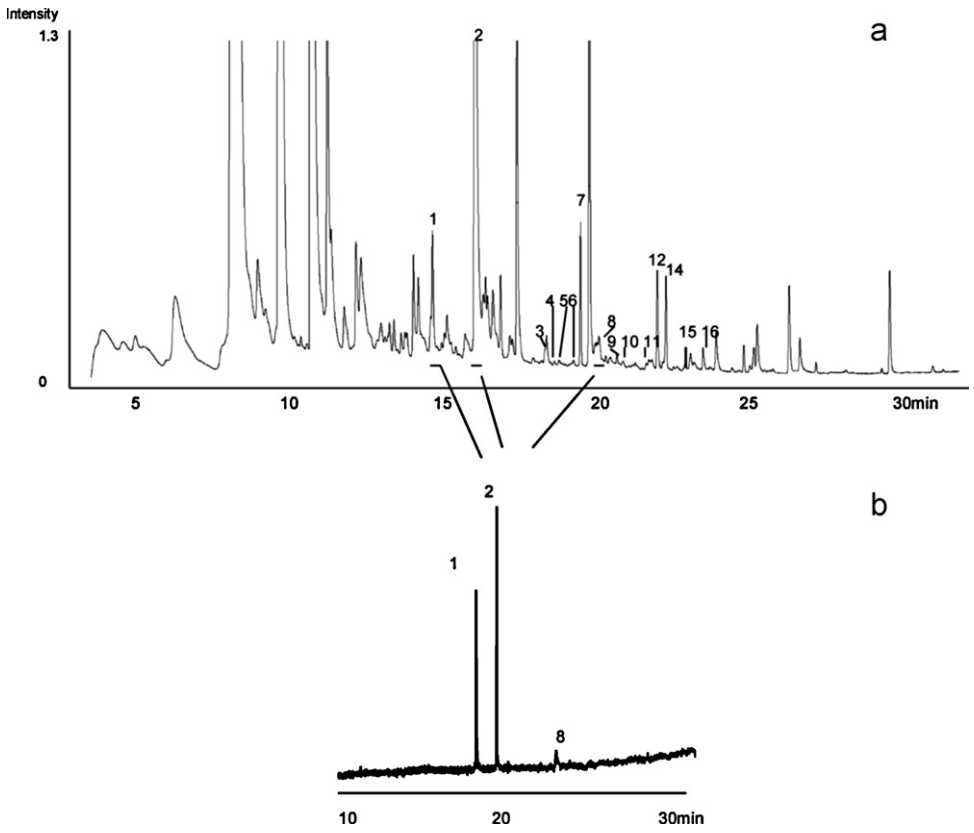

Fig. 5. (a) First dimension chromatogram of a commercial apricot juice spiked with Mix 101 standard. (b) Transfer from the first to the second dimension. Peak identification as in Table 1.

pesticides had to necessarily be transferred individually from the first to the second dimension. The chromatograms obtained on the second column as a result of these cuts are displayed in Figs. 1b and 2b.

Similarly, Figs. 3a and 4a represent the whole chromatogram obtained on the first dimension of the separation of pesticides forming Mix 13. Equally to Mix 101 (Figs. 1 and 2) several chromatographic signals co-eluted with other compounds on the first dimension. This made it necessary to use MDGC and, hence, the transfer of pesticides forming Mix 13 from the first to the second dimension. Parts (b) in both Figs. 3 and 4 display the peaks corresponding to the compounds transferred to the second column in each case. As can be seen in Fig. 4b, cis/trans-Heptachlorepoxide (peak 28) was not properly separated on just one dimension. However, the cut of these two geometrical isomers from the first to the second dimension in the MDGC system permitted to satisfactorily resolve them on the second column. On the contrary, the transfer of peaks 30, 31, 32, 33 and 34 in just a single fraction (see Fig. 3b), did not allow us to improve the resolution achieved on the first column. As also previously carried out, the individual transfer of each pesticide was required to reach a good chromatographic resolution of these five compounds. Consequently, it may be stated that MDGC permits to avoid co-elution of the target compounds with matrix components by means of the transfer of extremely small cuts, even single compounds. It is also important to bear in mind, that the employment of MDGC enables complicated separations to be resolved through the selection of a chromatographic column for the second dimension chemically different from that employed for the first dimension.

In addition to the overlapping problems, MDGC also demonstrated to be useful in confirming uncertain identities of some target pesticides. In particular, the difficulty of identifying reliably DDT compounds and their isomers in the Mix 101 standard (peaks 31, 35, 37, 38, 40 and 42 in Figs. 1a and 2a), was sorted out by the transfer of a new standard mixture (i.e. Mix 164) from the first to the second dimensions in MDGC.

Besides, an additional difficulty of the separation of DDT compounds is the degradation of DDT (i.e. 2,4′-DDT) into DDD (i.e. 2,4′-DDD) during GC injection owing theoretically to the employment of the split/splitless injector [26]. Some authors have proposed the use of the PTV injection to solve this inconvenience [9]. However, this injection technique has to necessarily be applied just to the determination of DDT compounds with no interferences of other types of pesticides. Hence, we meant to analyze DDT compounds by MDGC together with the other target pesticides and, therefore, by using split/splitless injection. Specifically, we accomplished the GC injection of DDD, DDT and DDE at four different temperatures (i.e. 100 °C, 150 °C, 220 °C and 250 °C). Table 2 summaries the relative areas of DDD, DDE and DDT at different injection temperatures. The value of 100 °C could not be included in the table since this temperature did not enable the compounds to be desorbed from the SPME fiber. As seen in Table 2, the use of 250 °C as the injection temperature resulted in slight degradation of the target compounds. However, DDT compounds did not show

Table 2
Relative areas of DDD, DDE and DDT compounds at different injection temperatures.

Compound	Injection temperature		
	250 °C	220 °C	150 °C
2,4′-DDE	21.98	20.21	23.18
4,4′-DDE	20.90	19.06	19.38
2,4′-DDD	22.71	21.02	19.93
4,4′-DDD	18.20	17.57	11.42
2,4′-DDT	11.16	13.44	16.26
4,4′-DDT	5.00	8.69	9.82

apparent decomposition either at 150 °C or at 220 °C. As a conclusion, we can state that if one means to determine just DDT compounds, the use of PTV injection or, alternatively, split/splitless at 150 °C or 220 °C is recommended. However, if DDTs occur together with a pesticide mixture, split/splitless at 250 °C would be preferable as long as small degradations can be admitted.

The LD and linearity values of the pesticides on the second column of the two-dimensional system are also shown in Table 1. The LD values lower than 0.6 ng were obtained for all compounds except for Alachlor whose LD was considerably high. As already mentioned it is possible that FID and MS detector possess low response to this compound. Equally to the first dimension, the method was found to be linear over a range of 0.6–10.5 ng with correlation coefficients (R^2) higher than 0.998 for most components. By comparing LDs on the first column (LD-1D) and on the second column (LD-2D) in Table 1, the values obtained on the second dimension were lower for most of the compounds than those provided by the first dimension. This can be easily explained by the higher sensitivity of the mass spectrometer with respect to that of FID detection. Furthermore, the RSD (%) value estimated was satisfactory ranging between 3 and 6% for all pesticides.

With a view to evaluating the applicability of the developed method to real-life samples, the determination of pesticides in fruit juices was accomplished. As commented in Section 2, the selection of the SPME conditions was based on bibliographic studies about the SPME of pesticides from fruit juices [26–29]. In brief, the extraction conditions used were: PDMS/DVB as the SPME fiber, 60 °C as the extraction temperature and 60 min as the exposure time. As a result of this study, pesticide compounds were not detected in the three fruit juice samples analyzed. Therefore spiked fruit juices were analyzed to study the matrix effect. Recently, some authors have determined fifty-three pesticide residues by LC–MS/MS in thirteen types of fruit juices encountering that 43% of the analyses carried out gave positive results. However, this study and ours only had three pesticides in common [30]. The repeatability of the method for real-life samples was calculated from the SPME-MDGC–MS analysis of three juices in the mentioned experimental conditions. The RSD values obtained were in all cases lower than 10%.

Fig. 5a represents the chromatogram obtained from the SPME followed by the MDGC/MS analysis of apricot juice spiked with the pesticide standards on the first dimension. As can be seen most of the pesticides were extracted, separated and detected by MS. However, a high number of compounds co-eluted with other matrix compounds. Specifically, the chromatographic signal corresponding to Trifluralin (peak no. 2 in Fig. 5) overlapped with one or more components of the juice. In this case it is obvious that the use of MDGC was necessary to quantify properly this pesticide. Fig. 5b displays the chromatogram obtained from the transfer of Trifluralin from the first to the second column. It can be clearly appreciated that the resolution of Trifluralin was improved by the use of MDGC, which enabled its reliable quantification to be carried out. In contrast, some other pesticides, such as Diazinon, Parathion-ethyl and Terbutryn (peak nos. 7, 12 and 14 in Fig. 5a), seem to be perfectly resolved on the first column with no need for their transfer to the second column. In any case, individual transfers of these pesticides from the first to the second column were also performed to confirm the quantification performed on the first dimension. It is worth mentioning that in general terms pesticides Atrazine, Propazine, Terbuthylazine, Ametryn and Prometryn (peaks 4, 5, 6, 10 and 11 in Fig. 5a) were poorly recovered in comparison with the results obtained from the standard mixtures. This reflects the matrix effect and, thus, the competition of other juice components for the absorption in the SPME fiber. In this regard, it is known that SPME is an equilibrium technique in such a way that when the equilibrium between the sample headspace and the fiber is reached, no more compounds can be further retained. A more selective fiber to these specific pesticides would be convenient to overcome this limitation.

In conclusion, a new method based on the use of SPME followed by the MDGC–MS analysis is proposed for the isolation, separation and quantification of a large number of pesticides in both standard mixtures and complex real-life samples. This approach combines the simplicity, speed and low economic cost of the SPME with the selectivity and sensitivity of MDGC/MS. The employment of a multidimensional analysis technique permits to avoid false positives frequently obtained on monodimensional techniques as a consequence of interferences of the analytes with matrix components.

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