1 *Running-Head Title: Pesticides detection by SPME MDGC-MS: strawberry jam*

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12 **New method based on Solid Phase Microextraction and**
13 **Multidimensional Gas Chromatography-Mass Spectrometry to**
14 **determine pesticides in strawberry jam**

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ABSTRACT

Although, the use of pesticides is necessary in agriculture to prevent crops destruction and to avoid the attack to leaves and stems of the plants, which cause quality defects of fruits and yield reduction, the control of pesticide is important in order to guarantee human safety. In the present study, a new method based on the use of solid-phase microextraction (SPME) followed by multidimensional gas chromatography-mass spectrometry (MDGC-MS) analysis was developed to detect pesticides in strawberry jam. Commercial and home-made jams as well as spiked non-spiked samples were included in the study. Relative Standard Deviation estimated from five replicates, was below 16%. Limit detection values varied from 0.11 to 0.42 ng/kg on the first dimension and from 0.013 and 0.093 ng/kg on the second dimension. These levels are considerably lower than the Maximum Residue Levels established for strawberry pesticides by EU Regulations. Also, the matrix effect of the strawberry jam on the effectiveness of the SPME extraction was evaluated. The data presented demonstrate that the method proposed is capable of detecting reliably very low concentrations of pesticides in strawberry jams between 0.013 and 0.093 ng/kg. Additional advantages of the method are its repeatability, rapidity, simplicity, selectivity and environmental friendly nature.

Keywords: Pesticides, Jam, Multidimensional Gas Chromatography / Mass Spectrometry, Solid Phase Microextraction.

1. Introduction

Currently, processing is one of the most common means used by the industry to preserve fruit for consumption during the fruit off-season. Jams are an intermediate moisture food prepared by boiling fruit pulp with sugar, pectin and other ingredients until obtaining a thick consistency (Touati, Tarazona-Díaz, & Aguayo, 2014). In particular strawberry jam is a good way to exit the excess of production, particularly in Spain since it is the world's bigger strawberry exporter. According to the European Commission (European Commission, 2014), fruit jams are classified as high sugar and low water content commodities, together with honey and dried fruits. These features of the fruit jams represent a challenge in pesticide determination.

The use of pesticides in agriculture is necessary to avoid the destruction of crops by controlling agricultural pests and to improve plant quality (EU, 2014). However, despite the benefits of pesticides to control pests and plagues, some of them have been forbidden due to their highly persistent properties, their bioaccumulation and biocide activity. In addition, some studies have recently revealed their potential risk for human health even at very low concentration level (Pakade, & Tewary, 2010). For these reasons several organizations, Reg (EU) No. 500/2010 (EU Regulations 2010) and United States Environmental Protection Agency, have established the Maximun Residue Limits (MRL) of different pesticides (EU, 2014). This makes it necessary the development of highly sensitive analytical methods capable of detecting very low content of pesticides.

The determination of pesticides is generally time consuming, costly and tedious. Various sample preparation methods have been proposed on the basis of different extraction techniques such as liquid-liquid extraction, solid phase extraction, single-drop microextraction, direct solid sample introduction (Ng ChIn, & Zhang X, 2011) and solid phase microextraction (SPME). There are also some reviews highlighting the particular

usefulness of all these extraction techniques to determine different types of pesticides (Pakade, & Tewary, 2010; Matamoros, Calderon-Preciado, Dominguez, & Bayona, 2012).

However, SPME possesses important advantages over other extraction techniques. Some of them are its solvent free nature, easy handling and low cost. SPME has been applied to the isolation of organophosphorus (OPPs), organochlorine (OCPs) and pesticides in fruits like mango (Filho, dos Santos, & de Paula Pereira, 2011; Kin, & Huat, 2009), strawberry (Kin, & Huat, 2010; Lambropoulou, & Albanis, 2002; Lambropoulou, & Albanis, 2003; Wennrich, Popp, Koller, & Breuste, 2001) and fruit juices (Wennrich, Popp, Koller, & Breuste, 2001). However, studies on the application of SPME to fruit jams have been exclusively focused on aroma compounds (Oliveira, de Pinho, Malhiero, Baptista, Pereira, 2011; Ravid, Elkabetz, Zamir, Cohen, Larkov, & Aly R, 2010). Reports on the use of SPME to extract pesticides from fruit jams have not been published in the literature as yet.

On the other hand, the application of Multidimensional Gas Chromatography (MDGC) to the separation of PCBs, pesticides and their metabolites in different matrices has received considerable attention in the last years (Gomara, Bordajandi, & Gonzalez, 2007; Munoz-Arnanz, Bosch, Fernandez, Grimalt, & Jimenez, 2009; de Alencastro, Grandjean, & Tarradellas, 2003; Kmellar, Pareja, Ferrer, Fodor, & Fernandez-Alba, 2011). This technique enables the usual troubles found on the pesticides separation to be overcome. In particular, the use of a two-dimensional technique allows a wide variety of polarities and concentrations to be determined. To our knowledge, some authors have been proposed a single MDGC method to determine pesticides, it is based on a modified single-drop microextraction method for the determination of organochlorine pesticides in jams (Fernandez, Subramanian, Mateus, Domingues, & Delerue-Matos, 2012).

In this paper, the aim of the study was to develop a new analytical method to identify and quantify simultaneously sixteen pesticides potentially occurring in strawberry jam. This approach combines the simplicity of SPME as an extraction procedure with the selective separation technique MDGC and MS as a sensibility detection technique enabling very low contents to be detected. An additional advantage of the proposed method is the possibility of obtaining all target pesticides in just one single run, which shortens considerably the analysis time.

2. Materials and Methods

2.1. Samples

Mixture 101 with different pesticides [Alachlor, Ametryn, Atrazine, Chlorpyrifos, Diazinon, Molinate, Parathion-ethyl, Parathion-methyl, Pendimethalin, Pirimicarb, Prometryn, Propazine, Simazine, Terbutylazine, Terbutryn, Trifluralin] (50 ng/μl each component) by Dr. Ehrenstorfer GmbH (Augsburg, Germany) was used as a standard solution. The water used for the standard solutions was collected from a Milli-Q water purification system (Millipore, Milford, MA). Three different strawberry jams and strawberry fruits (Virtue variety, caliber 22) were purchased from local shops (Madrid, Spain) to include three home-made jams in the study.

Six different types of samples were considered in this study: three commercial strawberry jams (sample 1), three home-made strawberry jams elaborated from fresh strawberry fruit (Huelva, Spain) were made (sample 2), three home-made strawberry jams elaborated from spiked strawberry fruit (sample 3), three spiked commercial strawberry jam (sample 4), three spiked home-made strawberry jams (sample 5). Also, Mix 101 model solution

(sample 6a), and Mix 101 model subjected to the jam elaboration conditions, (sample 6b) were used as references.

The home-made strawberry jam (sample 2) was made by the following procedure: 200g strawberries were placed into a bowl and this bowl was placed into another one with warm H₂O Milli Q. Then the strawberries were covered with cling film and it was brought up until boiled (80-90°C, 660 m over sea level). Stirring was applied until the jam surface wrinkled (2 h). When the setting point was reached, the heating was turned off. The jam was finally cooled and kept at 5°C until its analysis.

With a view to evaluating the capability of the SPME-MDGC-MS method proposed to detect pesticides in strawberry jams when added to the fruit, we faced this study by elaborating home-made strawberry jam from berries spiked with Mix 101 (sample 3) at three different amounts of added Mix 101 (ie, 1.8 µl, 6 µl and 12 µl).

In order to study the matrix effect of strawberry jam, we spiked the commercial and home-made jams with the Mix 101 standard (Samples 4 and 5) and they were prepared by spiking 0.1 mg of each pesticide/kg. To study the effect of the jam preparation procedure on the pesticides, the same experimental conditions used in jam elaboration were applied to a standard solution (ie, 12 µl of Mix 101 standard in 3 mL of water Milli Q in a 20 mL vial (sample 6a) and then heated at 80-90°C for 2h (sample 6b)).

2.2. Solid phase microextraction (SPME)

The SPME conditions used were based on modifications of the extraction method elsewhere reported (Ruiz del Castillo, Rodríguez-Valenciano, de la Peña Moreno, & Blanch, 2012). A SPME holder (Supelco, Bellefonte, PA) was utilized to perform the experimentation and a poly(dimethylsiloxane) / divinylbenzene (PDMS/DVB, 65-µm layer) fused silica fiber was employed. The SPME fiber was initially conditioned in the

injector of the gas chromatograph at 250°C for 30 min. The commercial and home-made strawberry jams (6 g) and samples spiked with Mix 101, were placed in a 20.0 mL vial. Before the actual extraction, the sample was heated at 40°C for 2 min to enrich the headspace in the target compounds. The extraction time was 30 min at 40°C. The extract was thermally desorbed into the GC injector at 250°C for 5 min in splitless mode and analyzed, as explained below.

2.3. Multidimensional Gas Chromatography coupled to a Mass Spectrometer (MDGC-MS)

The MDGC system, lent by Izasa (Madrid, Spain) has two independent gas chromatographs (Shimadzu model GC-2010), GC-1 and GC-2. The two GCs are coupled through a transfer line at 300°C through a Deans-based switching system (Sciarrone, Costa, Ragonese, Quinto, Tranchita, Tedone, Sant, Dugo, Dugo, & Mondello, 2011). The first GC has a split/splitless injector (Shimadzu model AOC-20i) operated at 250°C and a flame ionization detector (FID, 250°C) and the second GC is coupled to MS (Shimadzu model MS-QP 2010 Plus). Two columns of different characteristics were placed in both GCs. The columns were coupled through a Deans-based switching system (Deans, 1981). The connection of the Deans switch with FID was performed by means of stainless steel tubing. The selection of the stationary phases was based on a previous study (Ruiz del Castillo, Rodríguez-Valenciano, de la Peña Moreno, & Blanch, 2012). A TRB-5 column (Teknokroma, Spain) was placed in the GC-1, it has a 30 m x 0.25 mm ID capillary fused silica column coated with a 0.25µm film of 5%-phenyl-95%-dimethylpolysiloxane. The oven temperature was 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 was maintained for 5 min. A TRB-50 column (Teknokroma, Spain) was used in the GC-2, it has 30 m x 0.25 mm ID capillary fused silica column coated with 0.1 µm film of 50%-phenyl-50%-

dimethylpolysiloxane. The TRB-50 was connected to the Deans switch and to the MS detector. 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. Helium was used as carrier gas at 1 mL/min. The different chromatographic signals eluted in the first dimension were transferred to the second dimension to identify their nature. The MS conditions were as follows: 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. To verify the identities of the target compounds in the first dimension as well as the transfer time of the fraction from the first to the second dimension the spiked samples were analyzed. All the analyses were made at least in triplicate.

3. Results and Discussion

3.1. Commercial and home-made strawberry jams

Fig.1a and 1b correspond to the chromatograms obtained from the first dimension of the SPME-MDGC-MS analysis of commercial (a) and home-made (b) strawberry jams (samples 1 and 2). The MS detection indicated that all chromatographic signals extracted and analysed corresponded to aroma compounds present in both commercial and home-made strawberry jams. All the detected compounds have already been described in the literature as typical volatile compounds of strawberry jam (Schipilliti, Dugo, Bonaccorsi, & Mondello, 2011). As observed in Fig.1a and 1b, the volatile profile of both jams was not particularly rich. This is not surprising taking into account that the extraction conditions applied were optimized for the analysis of pesticides. However, initially pesticides were not detected in either commercial or home-made strawberry jam. This might reflect that either no pesticides were added to the strawberry fruit used in the

preparation of both jams or the SPME-MDGC-MS method here developed was not valid for the determination of pesticides in strawberry jam.

3.2. Making-jam processing effect on pesticides

The evaluation of the SPME-MDGC-MS method proposed to detect pesticides in strawberry jams were made by elaborating home-made strawberry jam from berries spiked with Mix 101 (Sample 3) at three different amounts as is detailed in Section 2.1. This is an usual procedure to validate a method when the target compounds do not occur in the specific samples analysed (Kakimoto, Takatori, Okihashi, Kajimura, Toriba, & Hayakawa, 2016). Fig.2a shows the chromatogram corresponding to jam prepared from the fruit added with 12 µl of Mix 101. As observed, most pesticides were hardly detected even when the highest concentration of standards were added. The explanation for this is possibly that the pesticides are degraded, evaporated or reacted with other compounds coming from the strawberry fruit during making-jam processing. To evaluate these hypotheses, sample 6a was analysed by SPME-GC-MS. The chromatogram obtained as a result of this analysis is shown in Fig.2b. In this case almost all pesticides were extracted, analysed and detected. Specifically, the compounds identified by the MS detector were: (1) Molinate, (2) Trifluralin, (7) Diazinon, (14) Pirimicarb and (16) Pendimethalin. They were all recovered properly. In line with this experiment, sample 6b (12 µl Mix 101 3ml water heated at 80-90°C) was analysed. The chromatogram resulting from this last experiment is shown in Fig.2c. As can be seen in this figure, the target pesticides could not be any longer detected after heating. This implies that the pesticides studied are lost by evaporation in the home-made strawberry prepared from spiked fruits (see Fig.2a) as a consequence of the high temperatures utilized during relatively prolonged periods.

3.3. Matrix effect on the SPME extraction of pesticides

Samples 4 and 5 were analysed in order to study the matrix effect. Since the pesticide MRLs in strawberry jam have not been reported, we prepared the spiked samples on the basis of the MRL data described for strawberry fruit, which were used as a reference ([EU Regulations N.600/2010](#)).

The levels were lower than the range of the MRLs established. Fig.3a and 3b show the first dimension chromatograms resulting from commercial and home-made strawberry jams spiked with the mixtures of pesticides, respectively. As seen, the compounds detected were (1) Molinate, (2) Trifluralin, (7) Diazinon, (10) + (11) Prometryn + Ametryn, (13) Chlorpyrifos, (15) Alachlor and (16) Pendimethalin. All these compounds were properly extracted and determined. However, the compounds (3) Simazine, (4) Atrazine, (5) Propazine, (8) Pirimicarb, (9) Parathion methyl, (12) Terbutryn and (14) Parathion ethyl could not be identified. This can be due to the lower extraction yield. The recovery observed for these compounds from the standard mixture has been previously studied in water. These authors reported more satisfactory results than those found in the present study ([Wennrich, Popp, Koller, & Breuste, 2001](#)). This is most likely because of the matrix effect. The strawberry components compete with the target pesticides for the absorption on the SPME fibre in such a way that when the fibre is saturated no more compounds can be retained. SPME allows selectivity to be improved by choosing the extraction conditions, particularly the SPME fibre, adequate for the studied compounds. However, even so, interference compounds are usually extracted together with the analytes.

On the other hand, as can be observed in Fig. 3, co-elutions with matrix components also occurred. Specifically, Trifluralin (2) and Terbutylazine (6) overlapped with some other jam components. For this reason, the use of a multidimensional technique, like MDGC,

along with mass spectrometric detection, is necessary to reliably quantify the overlapped chromatographic signals (Fig.4a, 4b). From this figure, it can be clearly appreciated that the resolution of both Trifluralin and Tertbutylazine was improved by the use of MDGC. This enhancement in the resolution allowed its reliable quantification to be carried out. As shown in Fig.4, by using MDGC-MS system it is possible to transfer several compounds from the first to the second dimension in just one single analysis. The peaks selected to perform the transfer were (1) Molinate, (2) Trifluoralin, (7) Diazinon, (14) Parathion ethyl, (15) Alachlor and (16) Pendimethalin (fig.4a). Fig.4b shows the chromatogram obtained as a result of the transfer of the peaks 3, 6, 10 and 11, from the first to the second dimension. Specifically, the identification of the peaks was as follows: (3) Atrazine, (6) Tertbutylazine, (10+11) Ametryn+Prometryn. Also the transfer of (7) Diazinon and (15) Alachlor was performed (fig.4c). It is worth highlighting that the compounds (10) and (11) were transferred together, in only one heart-cut, to the second dimension since their chromatographic resolution on the first dimension was not possible. It is also interesting that the rest of the compounds (ie, 4, 5, 8, 9, 12 and 13) were transferred together to the second dimension. However, their detection was based only on retention time data since their small size did not enable the mass spectrometric detection to be accomplished.

Table 1 indicates the retention times obtained on the first dimension for all the components as well as on the second dimension for those compounds whose identification was certain. The heart-cut carried out on the first dimension is also shown. Specifically, the time comprised between 0.08 and 0.30 min is transferred from the first to the second dimension for all components. Ametryn and Prometryn (peaks 10 and 11) had to necessarily be transferred together as a one heart cut from 22.82 to 23.06 min, as shown in fig.3a. As seen in the figure, the transfer of five or six pesticides in just one run

was possible (fig.4a). The repeatability (expressed as Relative Standard Deviation, RSD) for the separation of the target compounds on the first dimension as well as Detection Limits (LD) for the separation of the studied pesticides on both first and second dimensions were estimated in the MDGC-MS system (Table 1). The RSD values were calculated from three replicates. A signal/noise ratio of 5 was employed for the calculation of the LD. The RSD values on the first dimension were higher than the values previously found from the study performed with the Mix 101 standard in water and juice (Ruiz del Castillo, Rodríguez-Valenciano, de la Peña Moreno, & Blanch, 2012). As observed in Table 1, the RSD values found in the present study were, in all cases, lower than 16%. RSD values previously described for these same compounds by the same analytical method were lower than 2% when working with model solutions. The higher RSD values now obtained are clearly due to the matrix effect. Some compounds naturally occurring in jams are slightly overlapped with the target pesticides and the measurement of the peak area is less precise. It is also important to highlight that the RSD of some minor peaks could not be properly calculated due to their low concentration.

The LDs for the pesticides indentified varied from 0.11 to 0.42 ng on the first dimension and from 0.013 to 0.093 ng on the second one. Regarding the identification, the transfer from the first to the second chromatographic column enabled the mass spectrometry identification of 10 compounds to be carried out. Since, as already mentioned, no regulation on jams has been published, the results obtained had to be compared with those reported for strawberry fruit and accepted by the EU. Therefore, the LDs for all pesticides eluted on the second column and detected by the mass spectrometer were much lower than the strawberry pesticide MRLs reported for strawberry and accepted by the EU.

4. Conclusions

The approach here proposed based on the use of SPME followed by the MDGC-MS analysis combines the simplicity, speed and low economic cost of the SPME with the selectivity of MDGC and high sensitivity of MS. The method developed showed good repeatability and it is capable of detecting pesticides in strawberry jam samples occurring at very low concentrations. In addition, the proposed method showed that pesticides present in contaminated strawberries seems to be lost by evaporation during jam preparation.

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Compliance with Ethical Standards

Conflict of Interest The authors declare no conflict of interest.

Ethical Approval This article does not contain any studies with human participants or animals performed by any of the authors.

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Legends to figures

Fig1. SPME-MDGC/MS first dimension chromatogram of commercial strawberry jam, sample 1, (a) and home-made strawberry jam, sample 2, (b).

Fig.2. SPME-MDGC/MS first dimension chromatogram of strawberry spiked strawberry and jam elaborated, sample 3, (a), 3ml of H₂O Milli spiked with 12µl of Mix 101, sample 6a, (b) and 3ml of H₂O spiked with 12µl of Mix 101 and heated at 80-90°C during 2h, sample 6b, (c) Peak identification as in Table 1.

Fig.3. SPME-MDGC/MS first dimension chromatogram of strawberry jam spiked with the Mix 101 standard of commercial, sample 4, (a) and home-made strawberry jam, sample 5, (b). Peak identification as in Table 1.

Fig.4. SPME-MDGC/MS second dimension chromatograms of different transfers (a), (b) and (c) from the first to the second dimension by MDGC-MS of commercial strawberry jam spiked with the Mix 101, sample 4. Peak identification as in Table 1.

Table 1. Data obtained from the commercial strawberry jam spiked with Mix 101 by MDGC-MS. First dimension (*1D*) involved the use of the first GC coupled to the FID Detector 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) and detection limits (LD, ng) are presented.

<i>Compound^a</i>	<i>tr-1D</i> (min)	<i>Heart-cut</i> (min)	<i>RSD-1D</i>	<i>LD-1D</i> (ng/kg)	<i>tr-2D</i> (min)	<i>LD-2D</i> (ng/kg)
1. Molinate	16.04	15.97-16.21	15.2	0,25	17.48	0.061
2. Trifluralin	18.75	18.63-18.84	11.6	0,24	20.08	0.087
3. Simazine	19.94	19.90-19.99	16.0	0.29	22.02	0.051
4. Atrazine	20.02	20.05- 20.14	-	0.33	-	-
5. Propazine	20.23	20.20-20.31	-	0.42	-	-
6. Terbutylazine	20.60	20.55-20.77	12.7	0.29	22.15	0.048
7. Diazinon	21.04	20.95-21.25	5.5	0.25	22.45	0.013
8. Pirimicarb	22.03	21.94-22.13	-	0.23	-	-
9. Parathion-methyl	22.71	22.64-22.84	-	0.51	-	-
10. Ametryn	22.95	22.85-23.00	1.9	0.11	24.46	0.080
11. Prometryn	22.95	22.90-23.06	1.9	0.11	25.79	0.082
12. Terbutryn	23.57	23.54-23.66	-	0.24	-	-
13. Chlorpyrifos	24.02	23.97-24.11	-	0.18	-	-
14. Parathion-ethyl	24.25	24.19-24.33	5.5	0.29	25.89	0.093
15. Alachlor	24.42	24.34-24.60	-	0.16	26.91	0.110
16. Pendimethalin	25.53	25.45-25.75	10.4	0.19	27.00	0.053

^a Pesticides are numbered in elution order
tr, retention time