

## Supercritical Fluid Extraction of Pesticides from a Table-Ready Food Composite of Plant Origin (Gazpacho)

ANA AGUILERA, MARÍA BROTONS, MARIANO RODRÍGUEZ, AND  
ANTONIO VALVERDE\*

Pesticide Residue Research Group, Faculty of Experimental Sciences, University of Almería,  
04071 Almería, Spain

Supercritical fluid carbon dioxide extraction (SFE) has been evaluated for the extraction of 17 organohalogen and organophosphate pesticides in gazpacho (a table-ready food composite containing crude vegetables, white bread, vegetable oil, water, and other minor components) using anhydrous magnesium sulfate as drying agent. The effects of different parameters, such as fat content in gazpacho composites, magnesium sulfate/gazpacho ratio, supercritical fluid volume, pressure, temperature, and static modifier additions, on SFE recoveries from spiked gazpacho samples have been studied. Analyses were performed by gas chromatography (GC) with flame photometric (FPD), electron capture (ECD), and mass spectrometry (MSD) detectors. In most experiments, recoveries obtained for the nonpolar organohalogen pesticides were lower than those obtained for the most polar organophosphate pesticides, but overall pesticide recoveries determined by using the optimal SFE conditions indicate that SFE could be used to determine pesticide residue levels in gazpacho.

**KEYWORDS:** Gazpacho; pesticides; SFE

### INTRODUCTION

The determination of pesticide residues in foods has become an increasingly essential requirement for consumers, producers, and authorities responsible for food quality control. As a consequence, the need has arisen to set up fast and simple analysis methods which can provide the largest possible range of results. In the traditional methods for pesticide residue analysis, sample preparation often requires more than 50% of the analyst's time and consumes large quantities of diverse hazardous organic solvents (1–3). To avoid these limitations, during the last 10 years, a number of new extraction technologies have been assessed to be applied in the analysis of pesticide residues in foods, supercritical fluid extraction (SFE) being one generating more interest in this area of analytical chemistry (4). Today, it has been demonstrated that SFE is a suitable alternative to conventional methods for the extraction of different classes of pesticides from a variety of foodstuffs, including cereals (5–7), meat (8, 9), eggs (10), honeybees (11), and baby foods (12). Likewise, although SFE presents some inherent difficulties in its application to high water content samples (13), some authors have demonstrated that this technique is also a suitable alternative to conventional extraction methods in the analysis of pesticide residues in fruits and vegetables when samples are previously mixed with an appropriate drying agent (14–19). In fact, the method proposed by Lehotay for the determination of pesticides in nonfatty fruits and vegetables using SFE and

GC/MS has been recently adopted as “First Action Official Method” within the AOAC Official Methods Program (20).

In general, supercritical carbon dioxide extraction methods developed for analysis of pesticide residues in vegetables are faster, simpler, less expensive, and environmentally safer than conventional solvent-based methods, but one important disadvantage of SFE is the large number of variables to control, which means that the development and validation of SFE methods can be costly and very time-consuming. In addition, results obtained in the above-referenced papers indicate that SFE of pesticides from these types of samples presents an elevated matrix dependence, and the variables related to the preparation of the SFE sample are, in general, more critical than those affecting the extraction process. In fact, all the SFE methods proposed up to now for multiresidue analysis of pesticides in vegetables use very similar extraction conditions (supercritical carbon dioxide at 300–350 atm pressure and 50–60 °C temperature), the real factors that determine the effectiveness of the method being the type and amount of material added to the vegetable sample and the presence of water, salts, or modifiers in the SFE sample (18, 21).

In this study, supercritical carbon dioxide extraction has been evaluated for the extraction of different organohalogen and organophosphate pesticides in gazpacho, using anhydrous magnesium sulfate as drying material. Gazpacho is a typical Andalusian dish, largely consumed in Spanish homes and restaurants during the summer season, which can be defined as a table-ready food composite containing 70–80% crude vegetables (tomato, cucumber, and pepper), 5–10% white bread,

\* To whom correspondence should be addressed. Fax: +34 950 015008.  
E-mail: avalverd@ual.es.

2–10% vegetable oil, and other minor components (onion, garlic, vinegar, and salt). Pesticides included in this study were selected within those routinely monitored by the pesticide residues laboratory of the Spanish Ministry of Agriculture, Fisheries and Food in Almería, Spain. All the selected pesticides are insecticides or fungicides authorized to be used on tomato, pepper, and/or cucumbers, except vinclozoline and chlorothalonil, which are fungicides used on onion and garlic, and dichlorvos, which is an insecticide used as a greenhouse disinfectant (22). This paper is mainly devoted to evaluating the effects of different sample preparation parameters, such as fat content of the composite, magnesium sulfate/composite ratio, and static modifier additions, on pesticide recoveries from spiked gazpacho samples.

## EXPERIMENTAL PROCEDURES

**Reagents and Apparatus.** (a) Pesticide standards of acephate, bromopropylate, chlorpyrifos, chlorpyrifos-methyl, chlorothalonil, diazinon, dichlorvos, endosulfan I, endosulfan II, endosulfan sulfate, lindane, methamidophos, phosalone, procymidone, pyrazophos, triazophos, and vinclozoline (purity >98%) were supplied by Riedel de Haën (Seelze, Germany). For each pesticide, a stock standard solution (about 500 mg/L) was prepared in acetone. Spiking standard solution, containing 50 mg/L of each pesticide, was prepared in acetone from the stock standard solutions.

(b) All the solvents were Panreac (Barcelona, Spain) pesticide residue grade. Carbon dioxide, 99.995% purity, was supplied by SEO (Madrid, Spain). Anhydrous magnesium sulfate (>99% purity) was obtained from Fluka (Buchs, Switzerland).

(c) Chopper Dito-Sama K-35 (Aubusson, France); high-speed blender Omni mixer 17106 (Waterbury, CT).

(d) An Isco SFE system, consisting of one Model 260D syringe pump and controller, an SFX 2-10 extractor with restrictor heater set at 70 °C, and 10 mL stainless steel extraction cartridges with removable 2  $\mu$ m frits, was used in this study. An uncoated and deactivated fused silica capillary column, 30 cm length  $\times$  50  $\mu$ m i.d., was used as restrictor, and 10 mL graduated test tubes, immersed in a 15–20 °C water bath and containing 3 or 5 mL of ethyl acetate, were used as the collection system.

(e) Gas chromatograph, Hewlett-Packard 5890 series II (Palo Alto, CA), equipped with an HP-5 fused-silica capillary column (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness), attached to a  $^{63}$ Ni electron capture detector (ECD). The operating conditions were as follows: injector temperature, 240 °C; detector temperature, 325 °C; oven temperature program, 150 °C, hold for 1 min, 20 °C/min to 190 °C, hold for 4 min, 5 °C/min to 220 °C, hold for 2 min, 20 °C/min to 260 °C, hold for 8 min; argon/methane flow rate, 1 mL/min (carrier), 50 mL/min (make up), and 10 mL/min (split), splitless time 0.75 min.

(f) A gas chromatograph, Perkin-Elmer 8700 (Norwalk, CT) with flame photometric detector (FPD) in phosphorus mode, equipped with a BP10 wide-bore fused-silica column (30 m  $\times$  0.53 mm i.d.  $\times$  1.0  $\mu$ m film thickness). The operating conditions were as follows: injector and detector temperature, 300 °C; oven temperature program, 180 °C, hold for 2 min, 30 °C/min to 190 °C, 5 °C/min to 270 °C, hold for 7 min; carrier gas flow (nitrogen) 10 mL/min.

(g) A gas chromatograph, Hewlett-Packard 5890 Series II, equipped with a quadrupole mass selective detector (MSD HP-5971), a split/splitless injector, and an HP-5 fused-silica capillary column (30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness). The operating conditions were as follows: injector temperature, 280 °C; transfer line temperature, 300 °C; oven temperature program, 55 °C, hold for 1 min, 40 °C/min to 140 °C, hold for 1 min, 5 °C/min to 260 °C, hold for 10 min; carrier (helium) flow rate, 0.8 mL/min; split flow rate, 10 mL/min; splitless time 0.75 min; solvent delay, 3 min. GC-MSD analysis was carried out in selected ion monitoring (SIM) mode with the following program for ions (*m/z*) and time windows: ions 109 (dichlorvos), 94 (methamidophos), and 136 (acephate) from 3 to 12 min; ions 183 (lindane), 179 (diazinon), 266 (chlorothalonil), 286 (chlorpyrifos-methyl), and 212 (vinclozolin) from 12 to 18 min; ions 314 (chlorpyrifos), 96

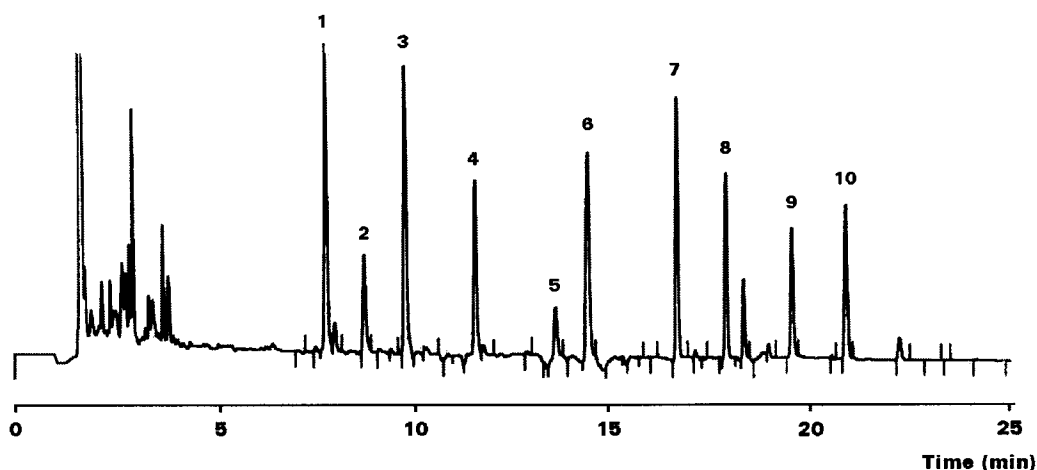
(procymidone), and 195 (endosulfan I) from 18 to 22 min; ions 195 (endosulfan II), 161 (triazophos), and 272 (endosulfan sulfate) from 22 to 26 min; ions 183 (bromopropylate), 182 (phosalone), and 221 (pyrazophos) from 26 to 31 min.

**Preparation of Gazpacho Composites.** Most recovery experiments were carried on gazpacho composites containing 6% olive oil, which were prepared in a blender jar by mixing 400 g of tomato, 300 g of cucumber, 75 g of pepper, 50 g of white bread, 30 g of onion, 10 g of garlic, 10 g of vinegar, 5 g of salt, 60 g of olive oil, and 60 g of water. The mixture was thoroughly blended until obtaining a homogeneous composite. Gazpacho composites containing 2.5% and 8.5% of olive oil were prepared in the same way but using 25 g of oil and 95 g of water and 85 g of oil and 35 g of water, respectively. In all cases, tomato, cucumber, and pepper samples used in the preparation of gazpacho composites were provided by the pesticide residues laboratory of the Spanish Ministry of Agriculture, Fisheries and Food in Almería, Spain, where the vegetable samples were previously analyzed by using a conventional ethyl acetate–sodium sulfate-based extraction method and GC/FPD-ECD-MSD and determined not to contain any detectable residue of the studied pesticides.

**Preparation of Spiked Samples and SFE Recovery Studies.** Recovery tests were conducted on gazpacho samples fortified with 0.1 mg/kg of acephate, bromopropylate, chlorpyrifos, chlorpyrifos-methyl, chlorothalonil, diazinon, dichlorvos, endosulfan I, endosulfan II, endosulfan sulfate, lindane, methamidophos, phosalone, procymidone, pyrazophos, triazophos, and vinclozoline. Spiked samples were obtained by addition of 200  $\mu$ L of spiking standard solution to 100 g of the corresponding gazpacho composite and further homogenization. Gazpacho samples were prepared for SFE following the method described by Valverde et al. (17, 18), who used anhydrous magnesium sulfate as the drying agent in SFE of pesticide residues from vegetables. Specifically, 20 g of gazpacho was thoroughly mixed with 28 g of anhydrous magnesium sulfate in a glass beaker immersed in an ice/water bath. After 5 min, this gazpacho–magnesium sulfate (5:7) mixture was thoroughly pounded in a porcelain mortar until obtaining a dry and homogeneous powdered mixture (“standard” sample preparation method). A number of recovery tests were carried out on gazpacho–magnesium sulfate (1:1) mixtures, which were prepared as described before but mixing 28 g of gazpacho and 28 g of magnesium sulfate. In all cases, gazpacho–magnesium sulfate mixtures (named SFE samples) were kept frozen until extraction.

Extractions were done in 10 mL extraction cartridges packed with 8.0 g of SFE sample (6.6 g in the experiments carried out with gazpacho–magnesium sulfate (1:1) mixtures), first placing 1 g of anhydrous magnesium sulfate at the bottom of the cartridge to bind any water that migrated during extraction. All the extractions were performed with supercritical carbon dioxide, in dynamic mode, after a 5 min static equilibrium period. The assessed extraction conditions (CO<sub>2</sub> volume, pressure, temperature, and static modifier) are specified in the Results and Discussion, but most experiments were performed with 15 mL of CO<sub>2</sub> at 300 atm, 50 °C, and 200  $\mu$ L of methanol as static modifier (“standard” extraction method).

**Chromatographic Analysis.** After extraction, the volume of ethyl acetate extracts was adjusted to 1.5 mL by evaporation with a nitrogen stream or addition of ethyl acetate and then diluted to 3 mL with cyclohexane and analyzed by GC-FPD and GC-MSD; 0.5 mL of these extracts was further diluted to 1 mL with ethyl acetate/cyclohexane (1:1) and then analyzed by GC-ECD. In all cases, GC-FPD and GC-MSD analytical extracts contained 1.1 g of gazpacho sample/mL, whereas the GC-ECD extracts contained 0.55 g/mL. Quantitative analysis of lindane, chlorothalonil, procymidone, endosulfans, bromopropylate, and phosalone was carried out by GC-ECD, whereas dichlorvos, methamidophos, acephate, diazinon, chlorpyrifos-methyl, chlorpyrifos, triazophos, and pyrazophos were quantified by GC-FPD. Since chlorpyrifos-methyl gave a GC-ECD signal at the same retention time as vinclozoline, this last pesticide was determined by GC-MSD (ion 212). Pesticide standard solutions to make external calibrations were prepared by suitable dilution of the spiking standard solution with ethyl acetate/cyclohexane (1:1).



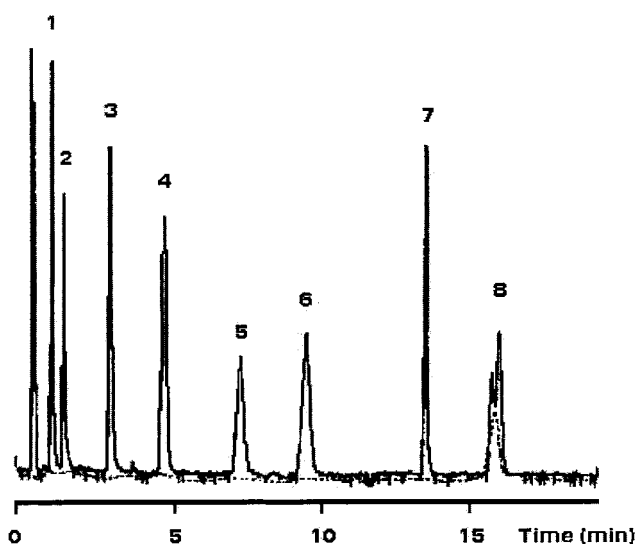
**Figure 1.** ECD chromatogram obtained for an spiked gazpacho sample (6% vegetable oil, 0.1 mg/kg spiking level) by applying the "standard" sample preparation and SFE methods: (1) lindane; (2) chlorothalonil; (3) chlorpyrifos-methyl + vinclozoline; (4) chlorpyrifos; (5) procymidone; (6) endosulfan I; (7) endosulfan II; (8) endosulfan sulfate; (9) bromopropylate; (10) phosalone.

**Table 1.** Pesticide Mean Recoveries Obtained by Applying the "Standard" Sample Preparation and Extraction Methods to Spiked Gazpacho Composites (0.1 mg/kg) Containing Different Percentages of Vegetable Oil

pesticide	mean recovery, % (RSD, %)			overall mean recovery, % (RSD, %)
	2.5% oil	6% oil	8.5% oil	
acephate	121 (13)	92 (21)	105 (7)	106 (14)
bromopropylate	85 (15)	67 (12)	65 (5)	72 (15)
chlorothalonil	90 (9)	76 (21)	83 (7)	83 (8)
chlorpyrifos	85 (15)	66 (9)	72 (10)	74 (13)
chlorpyrifos-methyl	78 (8)	88 (8)	78 (10)	81 (7)
diazinon	70 (6)	66 (11)	62 (15)	66 (6)
dichlorvos	75 (28)	60 (20)	61 (15)	65 (13)
endosulfan I	84 (10)	71 (14)	73 (3)	76 (9)
endosulfan II	73 (7)	74 (13)	61 (2)	69 (10)
endosulfan sulfate	77 (6)	73 (19)	65 (9)	72 (9)
lindane	91 (7)	85 (11)	72 (8)	83 (12)
methamidophos	119 (18)	121 (14)	91 (16)	110 (15)
phosalone	76 (7)	65 (8)	66 (9)	69 (9)
procymidone	113 (4)	107 (26)	93 (6)	104 (10)
pyrazophos	74 (5)	63 (7)	64 (9)	67 (9)
triazophos	83 (6)	72 (16)	73 (10)	76 (8)
vinclozoline	85 (7)	72 (8)	74 (18)	77 (9)

## RESULTS AND DISCUSSION

**Pesticide Recoveries in Gazpacho Samples with Different Oil Contents.** To evaluate the influence of the oil content on the extraction of the studied pesticides from gazpacho by SFE, a number of recovery tests were performed on gazpacho samples containing 2.5%, 6%, and 8.5% of olive oil, at a spiking level of 0.1 mg/kg for all the pesticides. In all cases, recovery tests were carried out using the standard sample preparation and extraction methods (gazpacho–magnesium sulfate (5:7) mixtures; 15 mL of CO<sub>2</sub>, 300 atm, 50 °C, 200 μL of methanol). Mean recovery and RSD values obtained for all the pesticides are indicated in **Table 1**, and the FPD, ECD, and some MSD chromatograms obtained for a gazpacho sample with 6% olive oil are shown in **Figures 1–3**, respectively. Recoveries correspond to triplicate extraction of two different SFE samples in the case of gazpacho with 6% oil and triplicate extraction of one SFE sample in the other cases. As can be seen in **Table 1**, mean recoveries in 2.5% oil samples were in all cases higher than 70% and ranged between 70 and 121%, whereas mean recoveries in 6% and 8.5% oil samples ranged between 60 and 121% and 61–105%, respectively. In **Table 1**, the overall mean



**Figure 2.** FPD chromatogram obtained for an spiked gazpacho sample (6% vegetable oil, 0.1 mg/kg spiking level) by applying the "standard" sample preparation and SFE methods: (1) dichlorvos; (2) methamidophos; (3) acephate; (4) diazinon; (5) chlorpyrifos-methyl; (6) chlorpyrifos; (7) triazophos; (8) pyrazophos.

recovery obtained for each pesticide is indicated, which ranged between 65 and 69% for dichlorvos, diazinon, pyrazophos, phosalone, and endosulfan II; 104 and 110% for procymidone, acephate, and methamidophos, and 72 and 83% for all the other pesticides.

**Influence of Modifier.** Studies on the influence of different static modifier conditions on pesticide recoveries were conducted on gazpacho samples with 6% olive oil spiked with 0.1 mg/kg of all the pesticides, applying the standard sample preparation and extraction methods, but using 200 μL of ethyl acetate or no modifier instead of 200 μL of methanol. Recovery tests without modifier were performed by triplicate extraction of two different SFE samples, whereas recovery tests with 200 μL of ethyl acetate as modifier were performed by triplicate extraction of one SFE sample. Mean recovery and standard deviation values obtained in these experiments are compared in **Figure 4** with those previously obtained for 6% oil gazpacho samples using the standard sample preparation and extraction methods. In all cases, recoveries obtained without modifier were less than those obtained using methanol as modifier, except for vinclo-

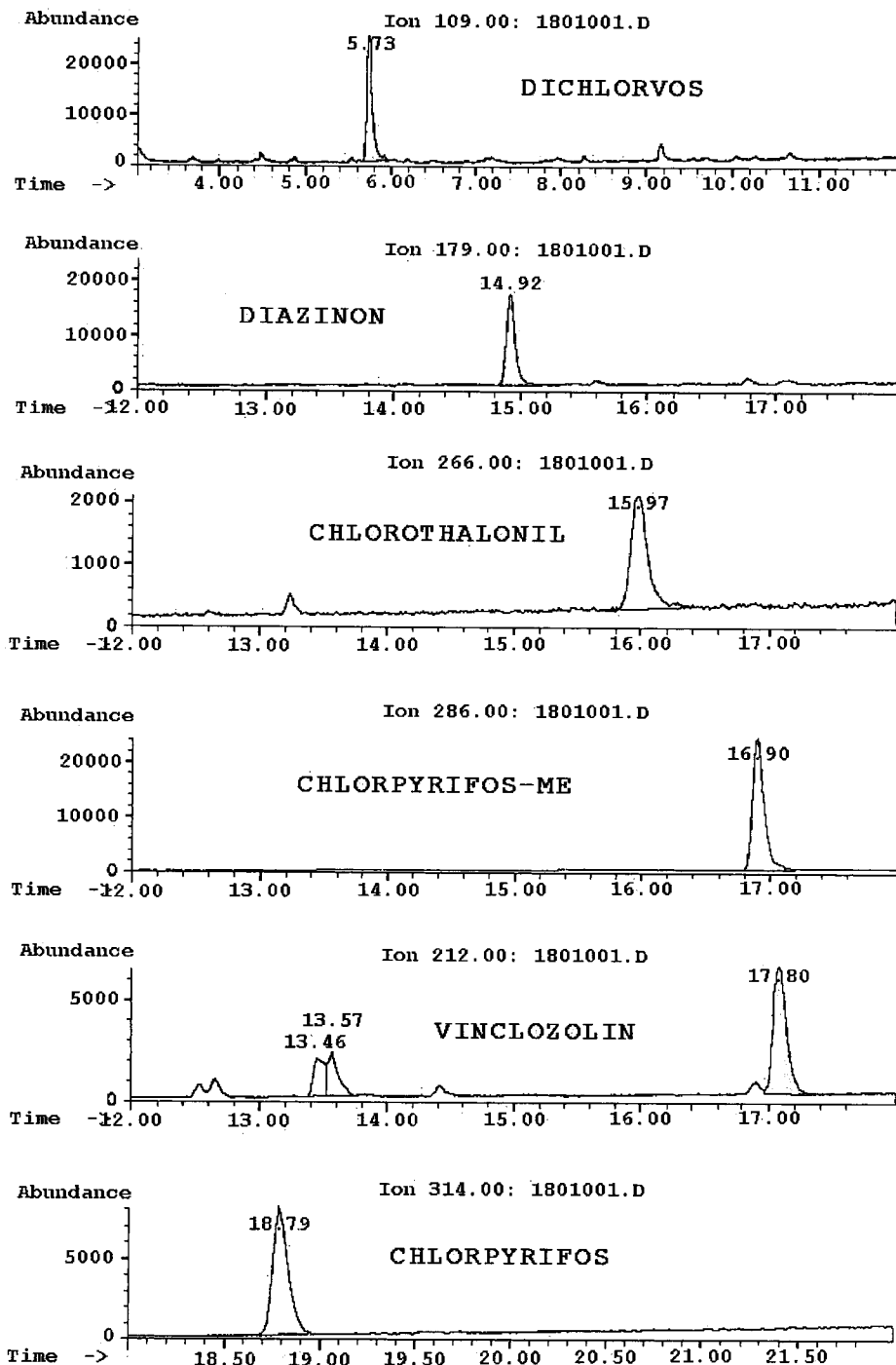
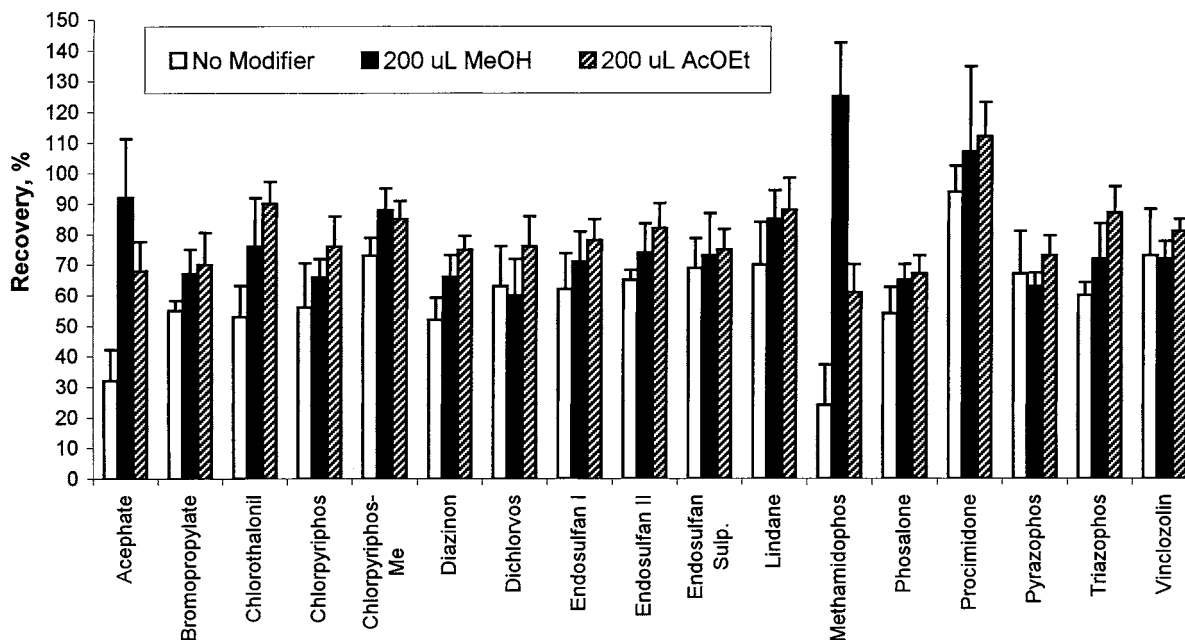


Figure 3. Selected single-ion chromatograms (MSD-SIM) obtained for an spiked gazpacho sample (6% vegetable oil, 0.1 mg/kg spiking level) by applying the "standard" sample preparation and SFE methods.

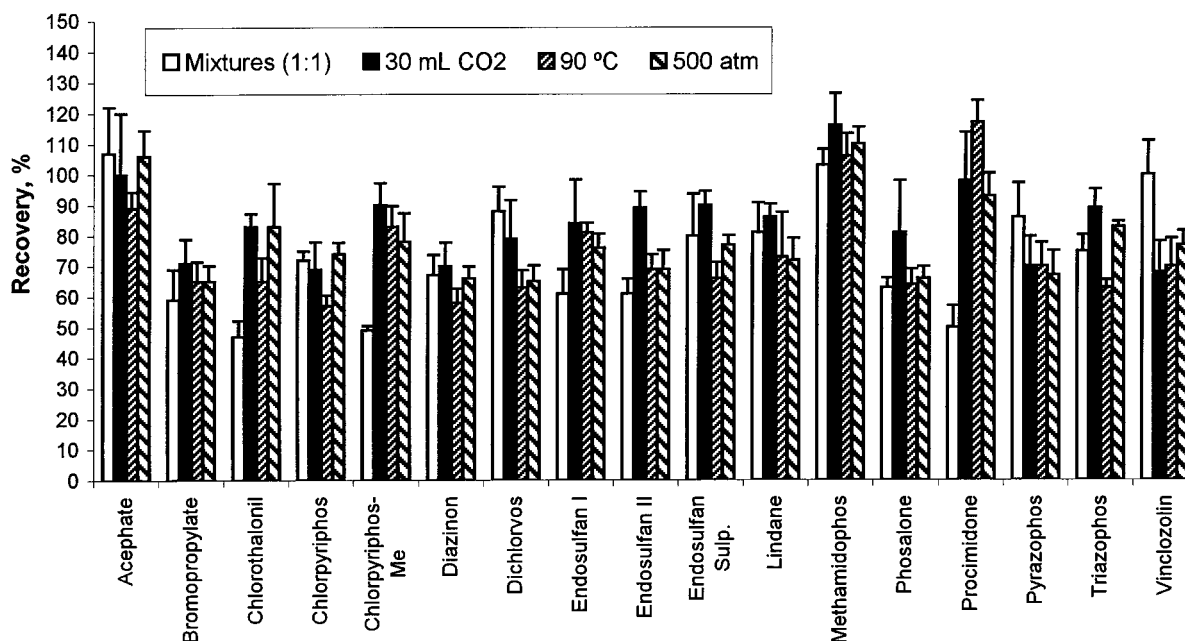
zolin, dichlorvos, and pyrazophos, pesticides for which the mean recoveries obtained without modifier were slightly higher. The two very polar phosphoramidothioate pesticides, methamidophos and acephate, gave poor recoveries in absence of modifier (<30%), which is in agreement with some of the results reported by Valverde et al. (17) on SFE of methamidophos from different vegetables. On the other hand, recoveries obtained by using ethyl acetate as modifier were, in general, slightly higher than those obtained with methanol, except again for the most polar pesticides methamidophos and acephate, for which recoveries >70% were only obtained by using methanol as modifier.

**Influence of Temperature, Pressure, CO<sub>2</sub> Volume, and Gazpacho–Magnesium Sulfate Ratio.** Additional recovery

tests were performed on 6% olive oil gazpacho samples spiked with 0.1 mg/kg of all the pesticides, applying the standard sample preparation and extraction methods (gazpacho–magnesium sulfate (5:7) mixtures; 15 mL of CO<sub>2</sub>, 300 atm, 50 °C, 200 μL of methanol) but changing just one of the following variables and keeping all the others constant: (i) gazpacho–magnesium sulfate (1:1) mixture; (ii) 30 mL of CO<sub>2</sub> volume; (iii) 90 °C temperature; (iv) 500 atm pressure. These recovery tests were carried out by triplicate extraction of one SFE sample. Mean recovery and standard deviation values obtained in these experiments are indicated in Figure 5. Table 2 shows the mean recoveries obtained for each pesticide in these tests after being normalized to (that is to say, divided by) the corresponding mean



**Figure 4.** Pesticide mean recoveries, and standard deviations, obtained from 6% olive oil gazpacho samples by applying the “standard” sample preparation and SFE methods but using different static modifier conditions (no modifier, 200  $\mu$ L of methanol and 200  $\mu$ L of ethyl acetate).



**Figure 5.** Pesticide mean recoveries, and standard deviations, obtained from 6% olive oil gazpacho samples by applying the “standard” sample preparation and SFE methods but using (i) gazpacho–magnesium sulfate mixtures (1:1) (ii) 30 mL of CO<sub>2</sub>, (iii) 90 °C temperature, or (iv) 500 atm pressure.

recovery value previously obtained on 6% oil gazpacho samples by using the standard sample preparation and extraction methods (see **Table 1**). As can be seen in **Table 2**, increasing the extraction temperature from 50 to 90 °C or the extraction pressure from 300 to 500 atm did not have a remarkable influence on the recovery of the studied pesticides (all the normalized mean recoveries obtained at 90 °C, or at 500 atm, were within the range 0.85–1.15). On the other hand, normalized mean recoveries obtained in the 30 mL CO<sub>2</sub> extractions were higher than 1.15 only for dichlorvos, endosulfans, phosalone, and triazophos, for the rest of the pesticides ranging between 0.9 and 1.1. Finally, the composition of the gazpacho–magnesium sulfate mixture seems to be a more critical factor in the extraction of some of the studied pesticides. Thus, decreasing the amount of anhydrous magnesium sulfate in the

gazpacho–magnesium sulfate mixture (SFE sample) from a 5:7 ratio to a 1:1 ratio led to remarkably higher recoveries for dichlorvos, pyrazophos, and vinclozolin (normalized recoveries 1.4–1.5), but lower recoveries were obtained for chlorothalonil, chlorpyrifos-methyl, and procymidone (normalized recoveries 0.5–0.6).

We can conclude that the “standard” sample preparation and SFE methods assessed in this work are adequate for the analysis of pesticide residues in gazpacho composites, yielding acceptable recoveries for most of the studied pesticides and SFE extracts ready for GC analysis without additional cleanup. In addition, results obtained in this study confirmed that SFE of pesticides from gazpacho present an elevated matrix dependence, the variables related to the preparation of the SFE sample being more critical than those affecting the SFE process.

**Table 2.** Mean Recoveries (Normalized to the Average Recovery for the "Standard" Sample Preparation and Extraction Methods) Obtained by Applying the Standard Methodology but Using: (i) Gazpacho Composite–Magnesium Sulfate Mixtures (1:1) as SFE Samples, (ii) 30 mL of CO<sub>2</sub>, (iii) 90 °C Temperature, or (iv) 500 atm

pesticide	normalized mean recovery			
	mixtures (1:1)	30 mL of CO <sub>2</sub>	90 °C	500 atm
acephate	1.16	1.09	0.97	1.15
bromopropylate	0.88	1.06	0.97	0.97
chlorothalonil	<b>0.64</b>	1.09	0.85	1.09
chlorpyrifos	1.09	1.05	0.87	1.12
chlorpyrifos-methyl	<b>0.56</b>	1.02	0.94	0.89
diazinon	1.01	1.06	0.88	1.00
dichlorvos	<b>1.47</b>	1.32	1.05	1.08
endosulfan I	0.86	1.18	1.14	1.07
endosulfan II	0.82	1.20	0.93	0.93
endosulfan sulfate	1.09	1.23	0.91	1.05
lindane	0.95	1.01	0.86	0.85
methamidophos	0.85	0.96	0.88	0.91
phosalone	0.97	1.25	0.98	1.02
procimydone	<b>0.47</b>	0.92	1.09	0.87
pyrazophos	<b>1.37</b>	1.11	1.11	1.06
triazophos	1.04	1.24	0.88	1.15
vinclozoline	<b>1.39</b>	0.94	0.97	1.07

#### LITERATURE CITED

- Andersson, A.; Palsheden, H. Multi-residue Method for Analysis of Pesticides in Fruits and Vegetables Using Ethyl Acetate Extraction, GPC Cleanup and GC Determination. *Livsmedelverket Rapport* **1998**, *17*, 9–41.
- General Inspectorate for Health Protection. *Analytical Methods for Pesticide Residues in Foodstuffs*, 6th ed.; Ministry of Public Health, Welfare and Sport: Bilthoven, The Netherlands, 1996.
- US Food and Drug Administration. *Pesticide Analytical Manual*, 3rd ed.; US Department of Health and Human Services: Washington, DC, 1994; Vol. I.
- Lehotay, S. J. New Technologies Applied in Pesticide Residue Analysis. In *Pesticide Residues'96*; Valverde, A., Ed.; Almeria Studies Institute/University of Almeria: Almeria, Spain, 1998.
- Kim, D. H.; Heo, G. S.; Lee, D. W. Determination of organophosphorus pesticides in wheat flour by supercritical fluid extraction and gas chromatography with nitrogen–phosphorus detection. *J. Chromatogr. A* **1998**, *824*, 63–70.
- Norman, K. N. T.; Panton, S. H. W. Supercritical fluid extraction and quantitative determination of organophosphorus pesticide residues in wheat and maize using gas chromatography with flame photometric and mass spectrometric detection. *J. Chromatogr. A* **2001**, *907*, 247–255.
- Ohlin, B.; Valverde, A.; Declercq, B.; Norman, K. N. T.; Österdahl, B. G.; Elgerud, C.; Aguilera, A.; Rodriguez, M.; Brotons, M.; Panton, S. H. W. Supercritical fluid extraction of pesticides on dry foodstuffs. *Livsmedelverket Rapport* **2001**, *10*, 1–73.
- Argauer, R. J.; Eller, K. I.; Pfeil, R. M.; Brown, R. T. Determining ten synthetic pyrethroids in lettuce and ground meat by using ion trap mass spectrometry and electron-capture gas chromatography. *J. Agric. Food Chem.* **1997**, *45*, 180–184.
- Juhler, R. K. Supercritical fluid extraction of pesticides from meat: a systematic approach for optimisation. *Analyst* **1998**, *123*, 1551–1556.
- Fiddler, W.; Pensabene, J. W.; Gates, R. A.; Donoghue, D. J. Supercritical fluid extraction of organochlorine pesticides in eggs. *J. Agric. Food Chem.* **1999**, *47*, 206–211.
- Jones, A.; McCoy, C. Supercritical fluid extraction of organophosphate and carbamate insecticides in honeybees. *J. Agric. Food Chem.* **1997**, *45*, 2143–2147.
- Chuang, J. C.; Hart, K.; Chang, J. S.; Boman, L. E.; Van Emon, J. M.; Reed, A. W. Evaluation of analytical methods for determining pesticides in baby foods and adult duplicate-diet samples. *Anal. Chim. Acta* **2001**, *444*, 87–95.
- Taylor, L. T. Strategies for analytical SFE. *Anal. Chem.* **1995**, *67*, 364A–370A.
- Lehotay, S. J.; Aharonson, N.; Pfeil, E.; Ibrahim, M. A. Development of a sample preparation technique for supercritical fluid extraction for multiresidue analysis of pesticides in produce. *J. AOAC Int.* **1995**, *78*, 831–838.
- Lehotay, S. J.; Eller, K. I. Development of a method of analysis for 46 pesticides in fruits and vegetables by supercritical fluid extraction and gas chromatography/ion trap mass spectrometry. *J. AOAC Int.* **1995**, *78*, 821–830.
- Lehotay, S. J.; Ibrahim, M. A. Supercritical fluid extraction and gas chromatography/ion trap mass spectrometry of pentachloronitrobenzene pesticides in vegetables. *J. AOAC Int.* **1995**, *78*, 445–452.
- Valverde, A.; Fernández-Alba, A. R.; Agüera, A.; Contreras, M. Extraction of methamidophos residues from vegetables with supercritical fluid carbon dioxide. *J. AOAC Int.* **1995**, *78*, 867–873.
- Valverde, A.; Fernández-Alba, A. R.; Contreras, M.; Agüera, A. Supercritical fluid extraction of pesticides from vegetables using anhydrous magnesium sulfate for sample preparation. *J. Agric. Food Chem.* **1996**, *44*, 1780–1784.
- Lehotay, S. J.; Valverde, A. Evaluation of different solid-phase traps for automated collection and cleanup in the analysis of multiple pesticides in fruits and vegetables after supercritical fluid extraction. *J. Chromatogr. A* **1997**, *765*, 69–84.
- AOAC International, Inside Laboratory Management, September/October 2002, p 29.
- Lehotay, S. J. Supercritical fluid extraction of pesticides in foods. *J. Chromatogr. A* **1997**, *785*, 289–312.
- Liñán y Vicente, C. *Vademecum de Productos Fitosanitarios y Nutricionales*; Carlos Liñán y Vicente: Madrid, Spain, 2002.

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