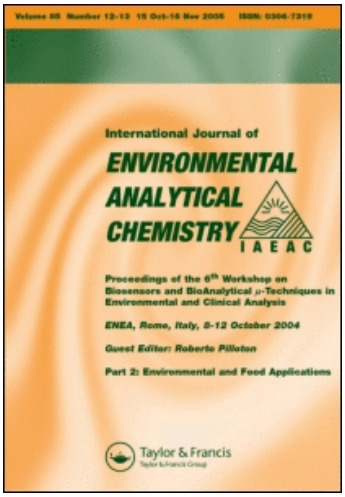

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Multiresidue determination in soil of pesticides used in tomato crops by sonication-assisted extraction in small columns and gas chromatography

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MULTIRESIDUE DETERMINATION IN SOIL OF PESTICIDES USED IN TOMATO CROPS BY SONICATION-ASSISTED EXTRACTION IN SMALL COLUMNS AND GAS CHROMATOGRAPHY

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Various herbicides and insecticides belonging to different chemical groups and used in tomato crops were determined in soil. The proposed analytical method was based on the sonication-assisted extraction in small columns (SAESC) of pesticides using ethyl acetate. All pesticides were determined by capillary gas chromatography with electron-capture detection (GC-ECD) and their identity was confirmed by gas chromatography coupled with mass spectrometry (GC-MS). Recoveries obtained for all compounds in the two soils studied varied from 81 to 106% with a relative standard deviation between 2 and 9%. The limit of detection in the conditions assayed was at least 0.01 μg/g for all compounds. The developed procedure was applied to the analysis of real samples, obtained after tomato harvest, from 18 commercial fields in Spain, and residue levels of pendimethalin (0.018–0.650 μg/g) endosulfan-I (0.011–0.032 μg/g), endosulfan-II (0.014–0.178 μg/g) and endosulfan-sulfate (0.010–0.135 μg/g) were found.

Keywords: Pesticides; Soil; Tomato; SAESC extraction; Environmental analysis

INTRODUCTION

Various pesticides, mainly herbicides and insecticides, are usually employed to control weeds and pests in tomato crops. Some compounds, such as herbicides, are applied directly to the soil while others, like foliar insecticides, are applied to the plant. In both cases, a variable amount of the pesticides applied reaches the soil, where it remains for a certain time according to the environmental conditions and the cultural practices.

Information on pesticide levels in soil is usually required for efficacy studies of soil-applied compounds. In addition, concern about the environmental contamination caused by the use of pesticides makes necessary their determination in that matrix besides other environmental compartments.

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Various analytical methods have been employed in the determination of pesticide residues in soil. In these methods pesticides are mainly extracted from soil matrixes using conventional techniques such as shaking or Soxhlet extraction [1–3] where high volumes of toxic solvents are involved and a large amount of glassware is normally required. Alternative methods have been developed to overcome these drawbacks, such as supercritical fluid extraction (SFE) [4,5], accelerated solvent extraction (ASE) [6,7] and microwave assisted extraction (MAE) [8].

Other methods, such as solid-phase microextraction (SPME) and ultrasonic solvent extraction, have also been applied, with good results, to the extraction of pesticides from soil samples [9–11]. Recently, a method based on the sonication-assisted extraction in small columns (SAESC) of pesticides was developed for determination of the residue in soil of various pesticides [12–14].

The aim of this work was to develop a multiresidue method for the analysis, in soil samples, of pesticides commonly used in tomato crops. This method is based on the SAESC extraction of pesticide residues and their determination by gas chromatography. The pesticides selected for the study belong to various chemical groups: chlorpyrifos is an organophosphorus insecticide, endosulfan-I, endosulfan-II and endosulfan-sulfate are organochlorine insecticides while the herbicides ethalfluralin, trifluralin, dinitramine, butralin and pendimethalin belong to the group of dinitroanilines. The chemical structures of the pesticides studied are presented in Fig. 1.

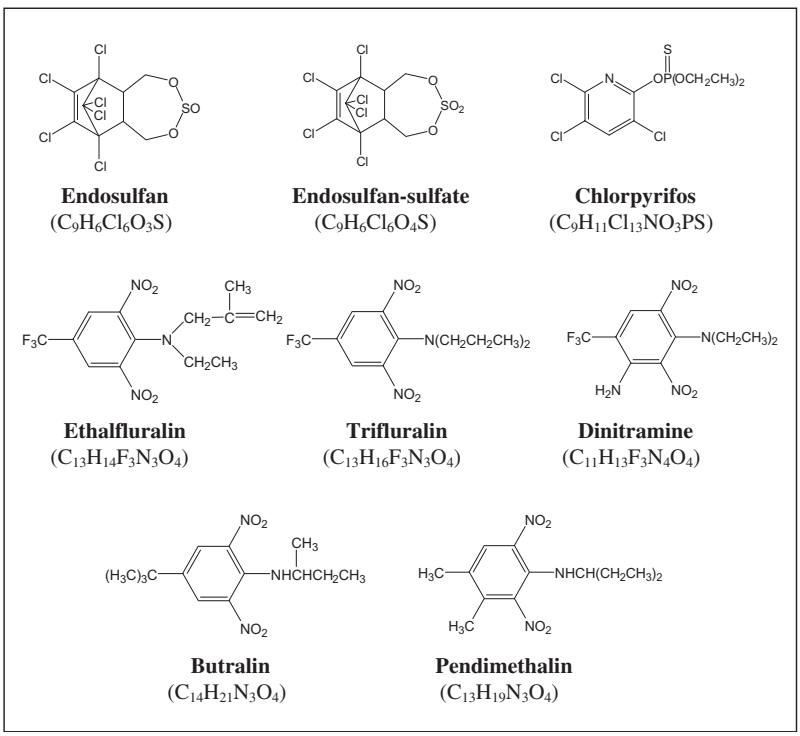

FIGURE 1 Pesticides analysed in this study.

EXPERIMENTAL

Chemicals and Solvents

Herbicide and insecticide standards were obtained from commercial sources: ethalfluralin and trifluralin from Eli Lilly (USA), dinitramine and butralin from Condor (UK), and pendimethalin, chlorpyrifos, endosulfan-I, endosulfan-II and endosulfan-sulfate from Reidel-de Häen (Germany). Purities were >98% for all the standards. Ethyl acetate was for pesticide residue analysis (Scharlau, Spain) and anhydrous sodium sulfate was purchased from Merck (Germany).

Soil Samples

The main physical–chemical properties (organic matter, pH, texture and field capacity) of soils are given in Table I. Soil samples were collected from the plough layer (0–10 cm) of two experimental plots located in the region of Madrid (Spain). These samples were sieved (2 mm) and stored at room temperature until fortified.

Extraction Equipment and Columns

An ultrasonic water bath (Raypa, Spain) was used in the extraction procedure. The generator of this apparatus has an output of 150 W and a frequency of 33 kHz.

A 12-port vacuum manifold (Supelco, Spain) was employed for the filtration of the extracting solvent, and polypropylene columns (20 mL), purchased from Becton Dickinson (Spain) with Whatman No.1 filter paper circles of 2 cm diameter at the end, were used in the extraction step.

Determination

A Hewlett-Packard 5890 Series II gas chromatograph equipped with an electron-capture detector (ECD) and automatic injection was used for the analysis of pesticides. A non-polar fused silica capillary column, HP-1 (30 m × 0.25 mm i.d. and 0.25 μm film thickness), was employed, with helium as carrier gas at 1 mL/min. The column temperature was maintained at 80°C for 1 min, then programmed at 8°C/min to 220°C, held 10 min and programmed at 10°C/min to 260°C, held 2 min. The injector port was maintained at 270°C and the detector temperature was 300°C. A 2 μL volume was injected in the splitless mode.

GC-MS analysis was performed with a Hewlett-Packard 6890 gas chromatograph equipped with an automatic split-splitless injector model HP 7683, and a mass spectrometric detector (MSD) model HP 5973. A fused silica capillary column (HP-5MS), diphenyl dimethylpolysiloxane as non-polar stationary phase (30 m × 0.25 mm i.d.

TABLE I Characteristics of the soils used in the recovery assays

Soil	*pH*	*Organic matter* (%)	*Sand* (%)	*Silt* (%)	*Clay* (%)	*Field capacity* (% at −33 kPa)
A	7.69	0.97	44.34	37.44	18.22	14.76
B	6.70	1.75	64.81	23.65	11.54	13.30

and 0.25 μm film thickness) was employed, with helium as carrier gas at a flow-rate of 1 mL/min. The injection port and detector temperatures were 270 and 250°C, respectively. The oven temperature was held at 80°C for 1 min, then programmed at 8°C/min to 220°C, held for 10 min and programmed at 10°C/min to 260°C, held 3 min (total time 35.5 min).

Mass spectrometric parameters: electron impact ionisation with 70 eV energy; ion source temperature 230°C; MS Quad temperature 150°C, mass range m/z 50–450; scan rate 3.62 s per scan, 2-μscans; EM voltage 1600 V; solvent delay 5 min.

Procedure

Two filter paper circles were placed at the end of the plastic column and 2 g of anhydrous sodium sulfate was added, then 5 g of the sieved soil was placed in the columns. Once contained in the columns the soil samples were fortified and extracted after 15 min, to allow solvent evaporation. The first extraction was performed with 5 mL of ethyl acetate for 15 min in an ultrasonic water bath at room temperature. The water level in the bath was adjusted to equal the extraction solvent level inside the columns, which were supported upright in a tube rack and closed with screw-type valves. After extraction, the columns were placed on the multiport vacuum manifold where the solvent was filtered and collected in graduated tubes. Soil samples were extracted again with another 4 mL of ethyl acetate (15 min). The extracting solvent was filtered and the soil samples washed with 1 mL of additional solvent. The total extract collected was adjusted to 10 mL and analysed by GC-ECD.

RESULTS AND DISCUSSION

Recovery Assays

To study pesticide recoveries, soils were fortified with 1 mL of a mixture of the different compounds to reach final concentrations of 0.1, 0.5 and 1 μg/g. Ethyl acetate was employed to extract pesticides from soil samples, based on the good results reported previously using this solvent [12–14]. The recoveries obtained are depicted in Fig. 2.

The recovery of these compounds varied from 84 to 104% with relative standard deviations between 3 and 9% for soil A and from 81 to 106% with relative standard deviations between 2 and 9% for soil B. These values show a high recovery of the pesticides studied and a good reproducibility of the results obtained.

Detection Limit and Linearity

The linearity of the method was tested by analysing solutions of the studied pesticides with concentrations between 0.05 and 0.5 μg/mL. A representative chromatogram of a mixture of standards is depicted in Fig. 3(A).

A good separation of the studied compounds was accomplished with the temperature programme describe above. Results of the calibration assay are compiled in Table II. The detector response was linear in the assayed range of concentrations. The limit of detection (LOD) of the proposed method was at least 0.01 μg/g for the compounds

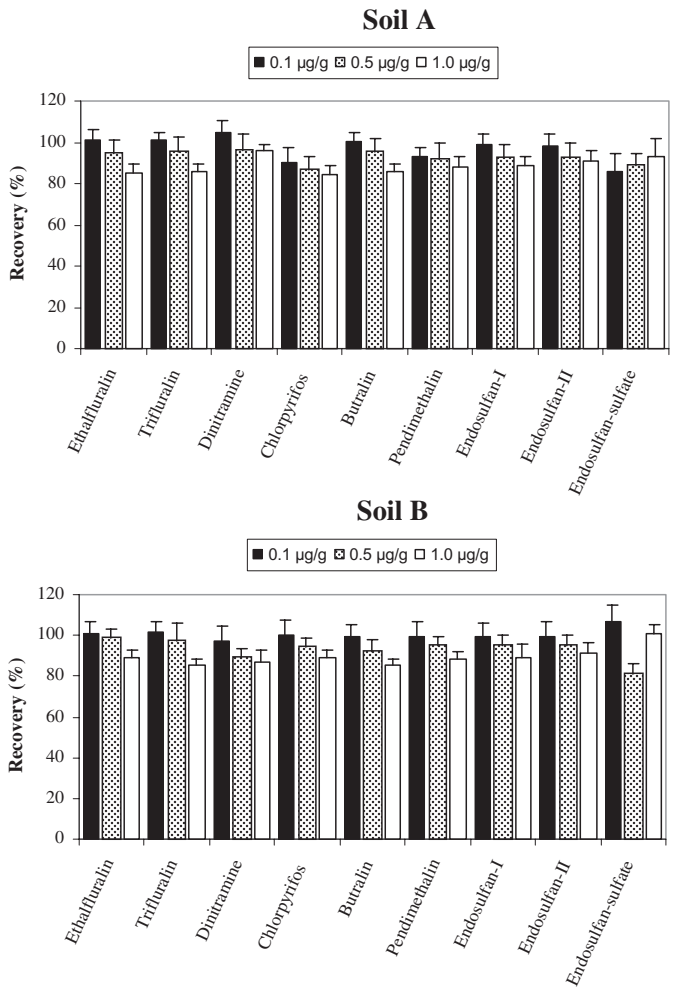

FIGURE 2 Pesticide recoveries obtained from soils A and B fortified at the three studied levels (0.1, 0.5 and 1 µg/g).

analysed, considering a signal-to-noise ratio equal to or higher than three. A lower LOD can be obtained for some pesticides, such as endosulfan, because of their higher response factor. The absence of coextracted interferences was confirmed by analysis of blank extracts.

Results obtained with the proposed extraction method are comparable with those reported when using other new sample preparation methods, such as MAE, ASE and SPME. Recoveries obtained with these procedures for organochlorine and organophosphorus pesticides ranged, in general, from 77 to 119% and are similar to the ones obtained with the SAESC method [7,8,15]. LODs were also variable, and levels of 0.01 µg/g for the ASE procedure were reported [7], as well as values from 0.06 to 0.65 ng/g for the SPME analysis of some organochlorine pesticides [9]. Nevertheless, those methods use more expensive equipment and require careful optimisation of the extraction procedure for routine analysis of real samples.

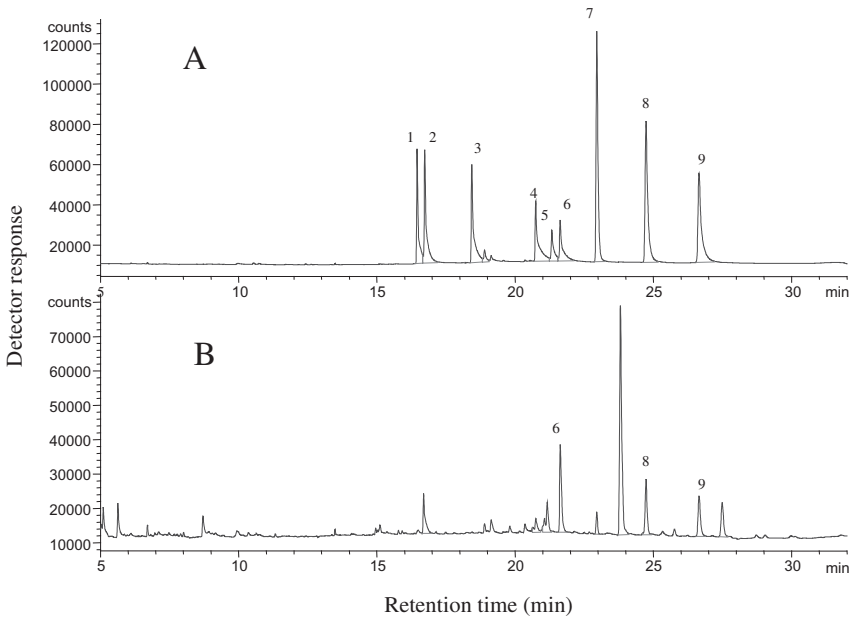

FIGURE 3 (A) GC-ECD chromatogram of a mixture of the pesticides studied at a concentration of 0.1 μg/mL, 1 = ethalfluralin, 2 = trifluralin, 3 = dinitramine, 4 = chlorpyrifos, 5 = butralin, 6 = pendimethalin, 7 = endosulfan-I, 8 = endosulfan-II and 9 = endosulfan-sulfate. (B) GC-ECD chromatogram of a real soil sample where some pesticides were found at levels higher than the LOD (0.01 μg/g): pendimethalin (0.120 μg/g), endosulfan-II (0.024 μg/g) and endosulfan-sulfate (0.016 μg/g).

TABLE II Calibration data for the pesticides analysed by GC-ECD

Compound	*Equation*	R^2
Ethalfluralin	$y = 2.30 \times 10^6 x + 67540.25$	0.9925
Trifluralin	$y = 2.50 \times 10^6 x + 69460.67$	0.9929
Dinitramine	$y = 2.33 \times 10^6 x + 40541.03$	0.9941
Chlorpyrifos	$y = 2.32 \times 10^6 x + 44072.50$	0.9917
Butralin	$y = 0.85 \times 10^6 x + 25164.47$	0.9913
Pendimethalin	$y = 1.21 \times 10^6 x + 23964.57$	0.9959
Endosulfan-I	$y = 6.03 \times 10^6 x + 116622.89$	0.9910
Endosulfan-II	$y = 5.2 \times 10^6 x + 67274.63$	0.9948
Endosulfan-sulfate	$y = 1.80 \times 10^6 x - 9892.61$	0.9976

Confirmation of Pesticide Residues

Confirmation of the pesticide identities was performed by GC-MS. Table III summarizes pesticide retention times together with the main ions for each compound and their relative abundances. Figure 4 shows a GS-MS chromatogram of endosulfan-I, endosulfan-II and endosulfan-sulfate at 25 ppb where the main ions obtained for endosulfan-II can be observed.

The main ions found in the mass spectra of these compounds are in agreement with those obtained previously by other authors [1,3,16–18]. All compounds studied can be identified by their mass spectra, in the PEST library, at levels near 10 ppb per compound.

TABLE III Retention times and main ions and their relative abundance in the mass spectra of the pesticides studied

Compound	t_r (min)	m/z (%)
Ethalfluralin	15.80	276 (100), 316 (81), 292 (46)
Trifluralin	16.05	306 (100), 264 (79), 290 (12), 335[a] (6)
Dinitramine	17.98	305 (100), 261 (23), 232 (17)
Chlorpyrifos	20.54	197 (100), 97 (80), 314 (60)
Butralin	21.07	266 (100), 224 (15), 295[a] (9)
Pendimethalin	21.70	252 (100), 162 (18), 281[a] (15)
Endosulfan-I	23.38	207 (100), 241 (98), 265 (64), 339 (37)
Endosulfan-II	26.47	195 (100), 241 (80), 265 (60), 339 (36)
Endosulfan-sulfate	29.44	274 (100), 272 (83), 229 (63), 387 (52)

[a]Molecular ion.

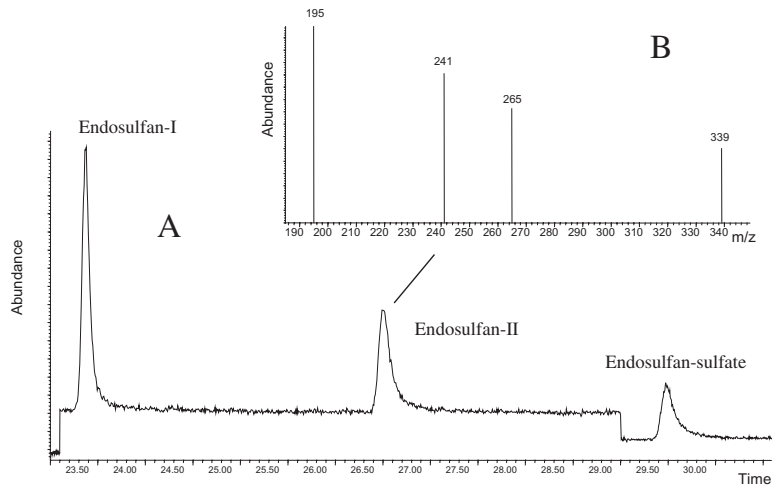

FIGURE 4 (A) GC-MS chromatogram of a standard solution of endosulfan-I, endosulfan-II and endosulfan-sulfate at a concentration of 25 ppb obtained in the selected ion monitoring mode. (B) Main ions of the mass spectra of endosulfan-II.

Real Samples

The proposed method was applied to the analysis of real samples collected from 18 commercial orchards located in the west of Spain. These fields were treated with chlorpyrifos, pendimethalin and endosulfan. Soil samples were taken, from the plough layer (0–10 cm), around two months after tomato harvest and the results obtained are presented in Table IV.

The results obtained indicate that no chlorpyrifos residues were detected two months after harvest, but levels of pendimethalin, endosulfan, and endosulfan-sulfate were found in soil in most of the fields. Figure 3(B) shows a chromatogram of a real soil sample where residues of pendimethalin, endosulfan-II and endosulfan-sulfate were found at levels higher than the LOD (0.01 μg/g).

Pendimethalin values varied from 0.018 to 0.650 μg/g, endosulfan-I levels varied from 0.011 to 0.032 μg/g, endosulfan-II ranged from 0.014 to 0.178 μg/g and the main endosulfan metabolite, endosulfan-sulfate, varied from 0.010 to 0.135 μg/g. In general, endosulfan-II, the most persistent isomer [19,20] and endosulfan-sulfate were found in

TABLE IV Residue levels found in real soil samples obtained from tomato fields (μg/g)

Field	*Pendimethalin*	*Endosulfan-I*	*Endosulfan-II*	*Endosulfan-sulfate*
A	0.027 ± 0.018	nd	0.028 ± 0.009	0.019 ± 0.009
B	0.125 ± 0.055	nd	0.024 ± 0.006	0.018 ± 0.003
C	0.061 ± 0.022	nd	0.014 ± 0.005	0.020 ± 0.011
D	0.046 ± 0.021	nd	nd	0.010 ± 0.006
E	0.085 ± 0.074	nd	0.028 ± 0.018	0.056 ± 0.003
F	0.293 ± 0.091	nd	0.032 ± 0.023	0.033 ± 0.016
G	0.172 ± 0.041	0.016 ± 0.002	0.130 ± 0.042	0.124 ± 0.027
H	0.018 ± 0.012	nd	0.022 ± 0.006	0.015 ± 0.005
I	nd	0.032 ± 0.020	0.140 ± 0.109	0.052 ± 0.029
J	nd	nd	0.037 ± 0.009	0.042 ± 0.017
K	0.124 ± 0.035	0.018 ± 0.013	0.138 ± 0.094	0.113 ± 0.080
L	nd	nd	0.056 ± 0.023	0.044 ± 0.027
M	0.650 ± 0.105	0.017 ± 0.007	0.178 ± 0.064	0.135 ± 0.053
N	0.078 ± 0.025	nd	0.073 ± 0.046	0.065 ± 0.027
Ñ	0.081 ± 0.065	nd	0.053 ± 0.042	0.085 ± 0.038
O	0.051 ± 0.011	0.011 ± 0.005	0.119 ± 0.054	0.129 ± 0.059
P	0.221 ± 0.081	nd	0.019 ± 0.017	0.029 ± 0.025
Q	0.104 ± 0.040	nd	0.050 ± 0.016	0.080 ± 0.041

Results are the mean of five samples taken in each field ± standard deviation; nd = below the detection limit (0.01 μg/g).

almost all the fields sampled. On the contrary, endosulfan-I levels were very low or undetectable and pendimethalin values showed a high variation, with non-detectable levels in some fields while in others detected values were rather high.

CONCLUSIONS

The results of this study show that the proposed method, based on the sonication-assisted extraction of the pesticides in small columns using low volumes of organic solvent, provides a rapid and economic procedure for the multiresidue determination of the pesticides applied to tomato crops. Recoveries higher than 80% for all compounds were obtained in the soils studied and the method detection limit was at least 0.01 μg/g for the pesticides analysed. Satisfactory results were achieved in the routine analysis of real samples, confirming the reliability and efficacy of this method. The identity of pesticide residues found in soil was confirmed by GC-MS.

References

[1] C. Sánchez-Brunete, L. Martínez and J.L. Tadeo, *J. Agric. Food Chem.*, **42**, 2210–2214 (1994).
[2] E. Papadopoulou-Mourkidou, J. Patsias and A. Kotopolou, *J. AOAC International*, **80**, 447–454 (1997).
[3] E.J. Aigner, A.D. Leone and R.L. Falconer, *Environ. Sci. Technol.*, **32**, 1162–1168 (1998).
[4] J.L. Snyder, R.L. Grob, M.E. McNally and T.S. Oostdyk, *J. Environ. Sci. Health A*, **29**, 1801–1816 (1994).
[5] S.U. Khan, *J. Agric. Food Chem.*, **43**, 1718–1723 (1995).
[6] B.E. Ritcher, J.L. Ezzell, D. Felix, K.A. Roberts and D.W. Later, *Am. Lab.*, February, 24–28 (1995).
[7] E. Conte, R. Milani, M. Giulia and F. Abballe, *J. Chromatogr. A*, **765**, 121–125 (1997).
[8] V. Lopez-Avila and J. Benedicto, *J. AOAC International*, **81**, 1224–1232 (1998).
[9] R.-A. Doong and P.-L. Liao, *J. Chromatogr. A*, **918**, 177–188 (2001).
[10] R.E. Johnsen and R.I. Starr, *J. Agr. Food Chem.*, **20**, 48–50 (1972).
[11] S. Babić, M. Petrović and M. Kaštelan-Macan, *J. Chromatogr. A*, **823**, 3–9 (1998).

[12] C. Sánchez-Brunete, R.A Pérez, E. Miguel and J.L. Tadeo, *J. Chromatogr. A*, **823**, 17–24 (1998).
[13] J. Castro, C. Sánchez-Brunete and J.L. Tadeo. *J. Chromatogr. A*, **918**, 371–380 (2001).
[14] C. Sánchez-Brunete, E. Miguel and J.L. Tadeo, *J. Chromatogr. A*, **976**, 319–327 (2002).
[15] J.L. Ezzell, B.E. Richter, W.D. Felix, S.R. Black and J.E. Meikle, *LC-GC International*, May, 390–397 (1995).
[16] A. Agüera, M. Contreras and A.R. Fernandez-Alba, *J. Chromatogr. A*, **655**, 293–300 (1993).
[17] A.I. García-Valcarcel, C. Sánchez-Brunete, L. Martínez and J.L. Tadeo, *J. Chromatogr. A*, **719**, 113–119 (1996).
[18] J. Fillion, R. Hindle, M. Lacroix and J. Selwyn, *J. AOAC International*., **78**, 1252–1266 (1995).
[19] Shalini-Singh, P. Dureja, S. Kumar and M.C. Jain, *J. Environ. Sci. Health B*, **34**, 965–974 (1999).
[20] J.J. Cerón, C. Gutierrez-Panizo, A. Barba and M.A. Cámara, *J. Environ. Sci. Health B*, **30**, 221–232 (1995).