Supercritical Fluid Extraction of the Fortified Residues of Fluazifop-P-butyl (Fusilade II) and Its Major Metabolite, Fluazifop-P, in Onions

Yuk Y. Wigfield* and Monique Lanouette

Laboratory Services Division, Food Production and Inspection Branch, Agriculture Canada, Ottawa, Ontario K1A 0C6, Canada

A supercritical fluid extraction (SFE) procedure is described to isolate fluazifop-P-butyl and its major metabolite, fluazifop-P acid, directly from onions without any further cleanup procedures. A sample of onions is homogenized and freeze-dried. The dry sample is added to a SFE extraction vessel between two layers of silanized glass wool to prevent the clogging of the frits by fine particles in the sample. A modifier solvent (1 mL of methanol) is added with a pipet directly onto the sample, which is then extracted with supercritical fluid (SF) carbon dioxide at 80 °C and 400 atm for 10-min static followed by 60-min dynamic modes. The extract is trapped in three culture tubes connected in series, each containing methanol (3 mL). The methanol solutions are combined, evaporated, and analyzed by high-performance liquid chromatography (HPLC) with an ultraviolet (UV) detector. Alternately, the same extract may also be methylated and analyzed by a gas chromatograph (GC) with a mass selective detector (MSD). Using HPLC/UV, the average recoveries of fluazifop-P acid and the butyl ester at the fortification range 0.6–6.0 ppm are 94.4–78.3% and 92.8–77.8%, respectively, with a limit of detection (LOD) of 0.2 ppm. When the extract is methylated and determined by GC/MSD, the average recoveries at fortification range 0.06–0.6 ppm are 89.1–101.2% for the methyl ester and 96.9–100.6% for the butyl ester with a LOD of 0.02 ppm for both analytes.

INTRODUCTION

Fluazifop [(*R,S*)-2-[4-[5-(trifluoromethyl)-2-pyridyloxy]phenoxy]propionic acid] is a racemic mixture of *R*- and *S*-enantiomers; the butyl ester of the *R*-isomer, known as fluazifop-P-butyl, is the active herbicide. It was introduced by ICI with the trade name of Fusilade II and a code number of PP005. Its chemical structure is shown in Figure 1.

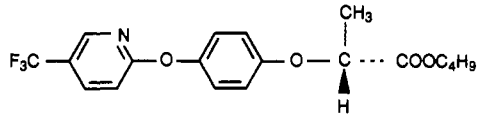

Figure 1. Chemical structure of fluazifop-P-butyl.

It is a potent selective herbicide used to control postemergent volunteer cereals and grass weeds in such crops as potatoes and onions (Worthing, 1987). It has been reported that fluazifop-P-butyl applied under field conditions degrades rapidly to the corresponding acid, which is conjugated in plant (Clegg, 1987; Smith, 1987). The published methods (Negre et al., 1987; Patumi et al., 1987; Clegg, 1987; Liu et al., 1991) used to determine the residues of fluazifop-P and its butyl ester in soil and crops are lengthy, labor-intensive, and solvent-consuming and can present many opportunities for sample loss. For crops (potatoes and soybeans), the residue method involves acid or base hydrolysis of the butyl ester to the acid, multiple extraction steps, methylation of the acid to the methyl ester, and Florisil column cleanup followed by gas chromatographic determination with a nitrogen–phosphorus detector (NPD) or with a mass-selective detector (MSD) (Clegg, 1987). Alternatively, after the extraction, the ester may be brominated and the acid converted into a pentafluorobenzyl derivative, followed by Florisil column cleanup and gas chromatographic determination using an electron capture detector (ECD) (Liu et al., 1991).

The separation of agricultural chemical residues from plant materials is a fundamental problem in residue analysis. This problem may be effectively addressed by supercritical fluid extraction (SFE) to isolate the active ingredients and their metabolites from these matrices. SFE is a separation technique based on the enhanced solvating power of supercritical fluids (SFs) above their critical points. The SFs have several characteristics that make them suitable for extraction purposes (Brogle, 1982). Their low viscosity and high diffusivity make the mass transfer during extraction rapid. Furthermore, the solvating power of a SF can be controlled by changing the extraction pressure and, to some extent, the extraction temperature. At present, carbon dioxide with or without modifier is the most popular SF used for SFE. The use of carbon dioxide has several advantages. Because of its extreme volatility, it can be easily and completely separated from any solutes. It has low critical point (74 bar, 31 °C) and is nontoxic at the levels used in the laboratories, nonflammable, and inexpensive; it causes no environmental problems in comparison with other SFs such as the chlorofluorohydrocarbons and also has no disposal cost.

SFE has shown great potential in offering shorter extraction times with higher recoveries and low consumption of organic solvents. It has recently been applied to pesticides in soil and plant material (Capriel et al., 1986; McNally and Wheeler, 1988; Wheeler and McNally, 1989), pesticides from sand (Lopez-Avila et al., 1990; Raymer and Velez, 1991) and from fatty and nonfatty foods (Hopper and King, 1991), polychlorinated dibenzo-*p*-dioxins from fly ash (Alexandrou and Pawliszyn, 1989) and from sediments (Onuska and Terry, 1989a), polychlorinated biphenyls from sediments (Onuska and Terry, 1989b), and polynuclear aromatic hydrocarbons from coal (Lancas et al., 1991). Adding small amounts of polar modifiers such as methanol or ethanol can greatly enhance SFE of polar solutes adsorbed on a polar matrix. Very

* Author to whom correspondence should be addressed.

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little sample preparation is usually required, which produces savings in terms of analysis time, labor, and cost and also reduces the potential for sample loss.

The purpose of this paper is to present a SFE procedure for isolating fluazifop-P-butyl and its metabolite, fluazifop-P, from onion samples. The levels of analytes were determined by high-performance liquid chromatography with a UV detector (HPLC/UV). Alternately, it could be methylated and determined by gas chromatography and a mass-selective detector (GC/MSD) (see Figure 2). Effects of extraction temperature, pressure, and extraction phase additives on the extraction efficiencies were examined.

EXPERIMENTAL PROCEDURES

Chemicals. All solvents (Caledon Laboratories Ltd., Georgetown, ON, Canada) used were of high purity and suitable for use in residue analysis. Fluazifop-P-butyl (86.5%) and fluazifop-P (99.3%) were from ICI Chemicals and provided by Chipman Inc. (Stoney Creek, ON) and were used without further purification. These compounds were dissolved in methanol to give a stock standard solution of 0.1 μg/μL of each. The SFC-grade (supercritical fluid chromatography) carbon dioxide was purchased from Scott Specialty Gases (Plumsteadville, PA). A buffer solution containing KH_2PO_4 (0.005 M) and methanol (4%) of pH 2.3 was used as a component of the mobile phase.

Supercritical Fluid Extraction System. The SFE system was a Suprex (Pittsburgh, PA) Model MPS 225 SFE-SFC consisting of a 250-mL syringe pump with the necessary valves and connecting lines to the extraction vessel, a control module containing a microprocessor for controlling the SFE system and able to store up to 24 methods; and an oven module consisting of an extraction oven, an extraction vessel, and a four-port valve configured with the electronic actuators for automated operation. The extraction vessels (Quick Change, 3 or 5 mL) were purchased from Suprex. Supercritical pressure was maintained inside the extraction vessel by using an uncoated fused silica restrictor (50 μm i.d. and 375 μm o.d. × 1 m long) from Suprex. The restrictor was kept inside a copper tubing (1/8 in. o.d. × 20 in. long), which was maintained at a constant temperature of 75–80 °C. Collection of the extract was performed by inserting the outlet restrictor through a needle into the first of three culture tubes (13 × 100 mm), each containing 3 mL of methanol. These culture tubes were connected in series using stainless steel tubing ($^1/_{16}$ in. o.d., 0.02 in. i.d. × 30 cm long).

Sample Extraction. Samples of onions were homogenized using a Hobart food chopper (Robot Coupe, Jackson, MS) followed by freeze-drying using the Labconco Stoppering tray dryer (Labconco Corp., Kansas City, MO) at 10–30 μmHg, −4 to 0 °C for 9 h and then overnight at room temperature in a desiccator containing $MgSO_4$. The dried sample was ground into the granular form. The granular sample (1 g) was introduced into an extraction vessel (5-mL size) between two layers of silanized glass wool to prevent clogging of the frits by fine particles in the matrix. The sample was fortified with a standard solution of fluazifop-P acid and the butyl ester in methanol and was allowed to sit at room temperature for 15 min; methanol (1.0 mL) was then pipetted into the vessel. The vessel was then positioned inside the extraction oven. The sample was extracted with CO_2 at 80 °C and 400 atm for 10-min static followed by 60-min dynamic extractions. After extraction, the extracts in the three culture tubes were combined and evaporated under N_2 to 1 mL, which was transferred to a volumetric flask (5-mL size) and diluted to volume with methanol.

HPLC/UV Determination. An aliquot (1 mL) of methanol extract was transferred to a volumetric flask (2-mL size), diluted to volume with the buffer solution, and filtered through a 0.45-μm filter. An aliquot (25 μL) of this solution was injected into the HPLC/UV system consisting of a Spectra System P4000 pump equipped with an autosampler (Spectra System AS3000), an UV detector (Spectroflow 783, ABI Analytical Kratos Division) with wavelength set at 270 nm (Negre et al., 1987), and a Chrom Jet 400 integrator (Spectra Physics) with attenuation set at 16 and chart speed at 0.5 cm/min. An HPLC column (Zorbax ODS, 4.6 mm × 25 cm, Du Pont Instrument), which was preceded by a RP-18 (0.5 μm) guard column cartridge (Brownlee), was used. After the injection, the columns were eluted with methanol and buffer (60 + 40) for 5 min, which was then linearly increased to 75 + 25 in 15 min and kept there for 3 min, linearly increased to 90 + 10 in 2 min and kept there for 2 min, and then returned to the original ratio of 60 + 40 in 3 min and kept at this ratio for 5 min. The flow rate was maintained at 1 mL/min. Under these conditions, the retention time for acid was 13.05 min and for ester was 28.8 min (see Figure 3).

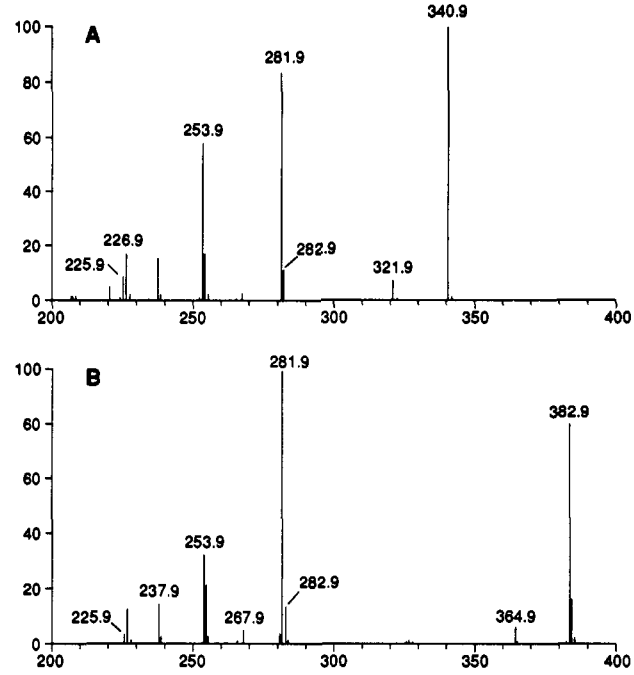

Figure 2. Mass spectra of (A) fluazifop-P-methyl and (B) fluazifop-P-butyl.

GC/MSD Determination. An aliquot (1 mL) of the methanol extract was transferred to a 5-mL centrifuge tube and was evaporated under N_2. Isooctane (200 μL), used to keep the analytes in solution, and diethyl ester were added to the tube, and the mixture was evaporated to remove all methanol. The acid in the extract was derivatized to methyl ester using diazomethane generated from Diazald (99% *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) (Sigma Chemical Co., St. Louis, MO). The diazoalkanes are toxic, and the preparation should be carried out in a fume hood with adequate protection to prevent inhalation or contact of the diazomethane solution with skin. The resulting solution was evaporated to near dryness (200 μL), diluted to 1 mL with hexane, and injected (2 μL) into a gas chromatograph (Hewlett-Packard 5890 Series II) equipped with an autosampler, a mass-selective detector (Hewlett-Packard 5971A), and a GC column (30 m × 0.25 mm) coated with DB-1701 (0.25 μm). The GC parameters were as follows: injector, 250 °C; oven, 70 °C for 1.5 min then increased to 280 °C at 20 °C/min and kept at 280 °C for 3 min; detector, 280 °C; carrier gas, He at 7 psi. Under these conditions, the retention times of fluazifop-P-methyl and fluazifop-P-butyl were 12.28 and 13.46 min, respectively. For quantitation, the two analytes were monitored at mass numbers of 341 (molecular ion of methyl ester) and 254 (single ion from butyl ester), respectively (see Figure 4). These mass numbers were chosen for their intensity of response (see Figures 2 and 4) and were free of interferences from the coextractive. For confirmation, SIM of mass numbers 254, 282, 341, and 342 for methyl ester and 254, 282, 364, and 383 for butyl ester was used.

RESULTS AND DISCUSSION

Initially, the plan of this study was to perform on-line SFE-SFC/NPD to determine the residues of these two analytes. However, while it was possible to chromatograph the ester, it was impossible to chromatograph the more polar analyte (the acid) using commercially available SFC columns such as a Deltabond CN (5 μm) column (100 ×

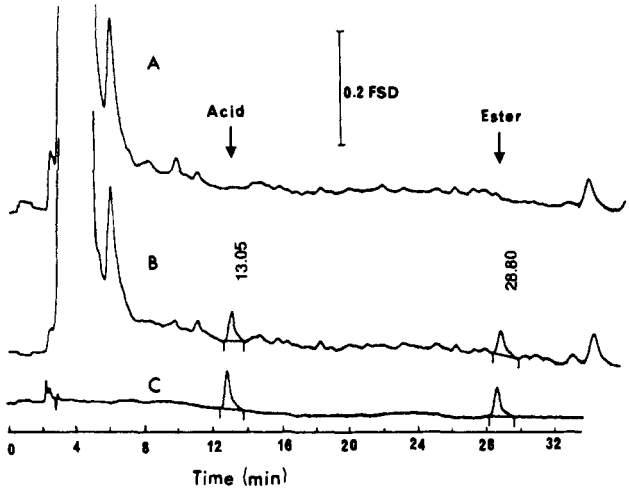

Figure 3. LC/UV chromatograms of (A) blank onion extract, (B) fortified (1.0 ppm) onion extract, and (C) standard solution (1.0 ppm).

0.25 mm) or a Deltabond PEG (5 μm) column (100 × 0.25 mm) (Keystone Scientific, Bellefonte, PA) and pure carbon dioxide as mobile phase. Thus, an off-line extraction with solvent (methanol) trapping was performed instead.

The sample weight was reduced to 12 ± 0.4% (n = 12) of the original weight after the freeze-dry process. Throughout this study, the fortification levels refer to the concentration of analytes relative to the actual sample weight before the freeze-drying. The analytes fortified on the samples were not lost from the freeze-dry process under the reported conditions. The recoveries of the acid and butyl ester at 2 ppm fortification level were 99.2 ± 5.6% (n = 9) and 86.5 ± 4.9% (n = 9) respectively. Approximately 10–20% loss of the butyl ester occurred after 16 h, and 20–30% loss occurred after 4 days. The acid was not lost under any conditions.

Optimization of SFE. The extraction efficiency was assessed by the following variables: (1) modifiers to the CO_2 fluid, (2) pressures at constant temperature, and (3) temperatures at constant pressure and (4) at constant density. Initial extraction using pure CO_2 yielded 0% of both analytes. Thus, modifier (methanol, ethanol, or water) was added to the extraction vessel to enhance the polarity of the extraction fluid and therefore the efficiency. As shown in Table I, recovery results were comparable at 80 °C and 350 atm. It was decided to use methanol because it has the lowest boiling point, which results in shorter evaporation time.

The influence of the extraction pressure on the extraction efficiency was assessed at two different pressures (350 and 400 atm), 80 °C, and 0.6 ppm fortification level. There was a marked difference in recoveries between 350 and 400 atm. Results in Table II show that the fluid density (hence the solvent strength) and the extraction recoveries increased as the pressure increased. Attempts to perform extraction at 450 atm were unsuccessful because at that pressure the SF CO_2 leaked through the extraction vessel very readily.

The influence of temperature on the extraction efficiency was performed by extracting fortified sample (2.4 ppm) at four different temperatures (50, 60, 80, and 90 °C) while the pressure was kept constant at 400 atm. The extraction recoveries remained similar (see Table III) at 60, 80, and 90 °C; those at 50 °C were lower even though the density was higher than the former three. The influence of temperatures (50, 70, and 80 °C) on the recovery (see Table IV) at constant density (0.824 g/mL) was assessed. It was found that at constant density the recoveries increased slightly as the pressures and temperatures increased. This observation is consistent with the findings of Wheeler and McNally (1989) and Anderson et al. (1989).

It was necessary to use three culture tubes to completely trap the two analytes exiting from the restrictor since it was found that as much as 30% of the butyl ester was carried over from the first tube to the second tube.

The problems of plugging the restrictor outlet after several extractions, resulting in a drastic drop of flow rate and low recoveries, have been reported (Wong et al., 1991; Onuska and Terry, 1989a). The former group solved the problems by using a new restrictor after every four or five extractions and the latter every second extraction. In this study, the problem was solved (1) by keeping the extraction vessel restrictor outlet inside a copper tubing maintained at 75–80 °C to prevent internal precipitation of organic material and (2) by connecting the restrictor to a 3-mL extraction vessel containing glass wool and methanol (0.5 mL) after every sample extraction and flushing the entire

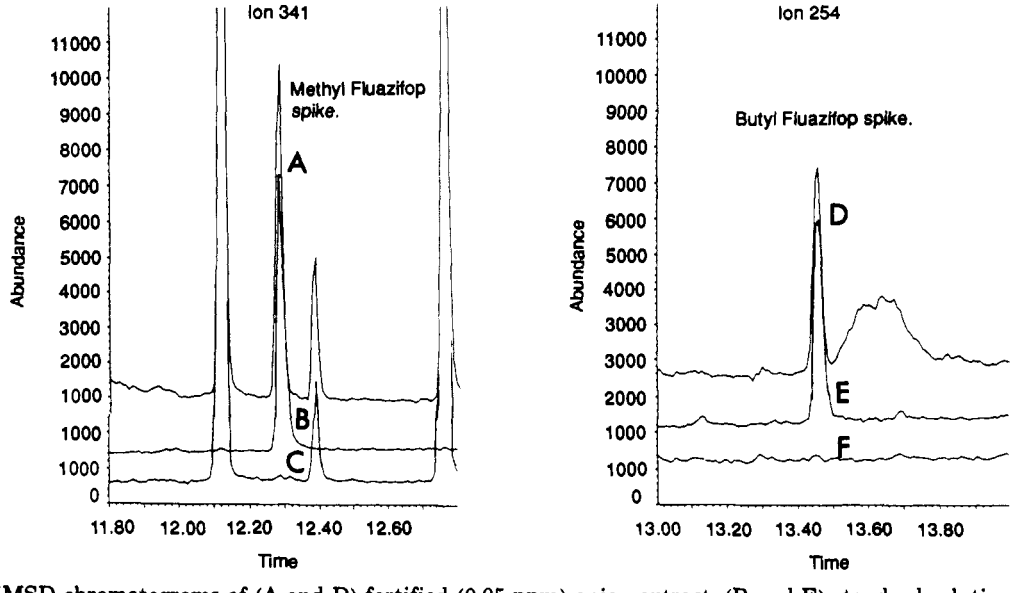

Figure 4. GC/MSD chromatograms of (A and D) fortified (0.05 ppm) onion extract, (B and E) standard solution (0.05 ppm), and (C and F) blank onion extract.

Table I. Influence of Modifiers on the Recovery of Fluazifop-P and Fluazifop-P-butyl at 80 °C and 350 atm and 0.6 ppm Fortification Level

			recovery,[a] %			
			acid		ester	
modifier	vol, mL	sample wt, g	mean	SD[b]	mean	SD
water	0.1	0.1	64.8	3.6	68.8	6.2
methanol	1.0	1.0	64.2[c]	4.4	59.3	6.6
	0.1	0.1	69.3[d]		61.8	
ethanol	1.0	1.0	76.4	12.4	64.1	2.3

[a] Mean of duplicates. [b] Standard deviation. [c] Mean of triplicates. [d] Single extraction.

Table II. Influence of Extraction Pressure on the Recovery of Fluazifop-P and Fluazifop-P-butyl at 80 °C and 0.6 ppm Fortification Level

		recovery, %				
		acid		ester		
pressure, atm	density, g/mL	mean	SD	mean	SD	n[a]
350	0.784	64.2	4.4	59.3	6.6	3
400	0.823	90.4	6.3	81.4	5.1	5

[a] Number of extractions.

Table III. Influence of Extraction Temperature on the Recovery of Fluazifop-P and Fluazifop-P-butyl at 400 atm and 2.4 ppm Fortification Level

		recovery, %				
		acid		ester		
temp, °C	density, g/mL	mean	SD	mean	SD	n
90	0.790	81.4	6.3	84.0	7.0	3
80	0.823	80.2	2.7	83.6	5.4	7
60	0.891	80.2	1.6	84.1	16.5	4[a]
50	0.924	70.7	1.9	74.8	0.8	2

[a] Two extractions at 0.5 ppm and two at 1.0 ppm.

Table IV. Influence of Temperature on the Recovery of Fluazifop-P and Fluazifop-P-butyl at a Constant Density of 0.824 g/mL and 2.4 ppm Fortification Level

		recovery, %				
		acid		ester		
temp, °C	pressure, atm	mean	SD	mean	SD	n
80	400	80.2	2.7	83.6	5.4	7
70	347	73.4	4.9	67.4	1.2	2
50	238	76.9	0.5	71.0	4.5	2

system with CO_2 for 5-min static and 10-min dynamic extractions at 450 atm and 80 °C. The restrictor thus treated could be used for 13–15 sample extractions without posing any problems.

The extraction recoveries were determined by fortifying the freeze-dried sample (1 g) with 0.6, 1.2, 2.4, and 6 ppm of the two analytes and were above 80% for both analytes in most cases (see Table V). At fortification levels of 0.06 and 0.6 ppm and using GC/MSD, the recoveries were over 89% (see Table VI). The recoveries from the four identical extracts, determined separately using HPLC/UV and GC/MSD detection, were comparable (see Table VII). Figures 3 and 4 show the absence of chromatographic interferences. The lower recovery data, especially at higher fortification levels, did not suggest that the extraction was incomplete; rather, they suggested that the analytes were strongly bound to sample matrix (Clegg, 1987). This explanation was further supported by the quantitative recovery obtained when the analytes were fortified onto the glass wool, which was then extracted under the same conditions. The binding effect appeared to be immediate since the

Table V. Recoveries (Percent) of Fluazifop-P and Fluazifop-P-butyl at 80 °C and 400 atm Using 10-min Static followed by 60-min Dynamic Extractions and HPLC/UV Determination

	fortifn,	acid, %			fortifn,	ester, %			
	ppm	mean	SD	CV	ppm	mean	SD	CV	n
	0.6	94.4	12.3	13.0	0.6	92.8	13.3	14.3	7
LOD	0.2				0.2				
LOQ	0.7				0.7				
	1.2	81.0	0.5	0.6	1.3	89.8	3.8	4.3	4
	2.4	80.2	2.7	3.4	2.6	83.6	5.4	6.4	7
	6.2	78.3	4.4	5.6	6.4	77.8	2.8	3.6	5
overall		84.3	9.7	11.6		86.2	9.7	11.2	23
range		75.0–119				75.2–112			

Table VI. Recoveries (Percent) of Fluazifop-P and Fluazifop-P-butyl at 80 °C and 400 atm Using 10-min Static followed by 60-min Dynamic Extractions and GC/MSD Determination

	fortifn,	acid, %			fortifn,	ester, %			
	ppm	mean	SD	CV	ppm	mean	SD	CV	n
	0.06	89.1	8.4	9.4	0.06	96.9	9.4	9.7	7
LOD	0.01				0.02				
LOQ	0.04				0.05				
	0.6	101.2	2.7	2.7	0.6	100.6	5.9	5.9	4
overall		93.5				89.2			
range		80.2–104				82.2–110			

Table VII. Comparison of Recoveries (Percent) Using GC/MSD[a] at 0.6 ppm Fortification Level

	acid		ester	
extract no.	HPLC/UV	GC/MSD	HPLC/UV	GC/MSD
1	91.8	100.8	97.7	105.8
2	94.5	97.6	92.8	95.2
3	99.6	104.0	112.0	95.8
4	83.2	102.3	93.6	105.7
mean	92.3	101.2	99.0	100.6
SD	6.8	2.7	8.9	5.9
CV	7.4	2.7	9.0	5.8

[a] All other extraction conditions were identical to those of Table V.

recoveries of fortified sample left for 15 min and 24 h were comparable.

Using LC/UV, the limit of detection (LOD), defined as 3 × SD, at the lowest fortification level of acid and ester (0.6 ppm) was 0.2 ppm for both and the limits of quantitation (LOQs), defined as 10 × SD, were 0.7 ppm for both acid and ester (see Table V). Using the same criteria, the LODs were 0.01 ppm for the acid and 0.02 ppm for the ester and the LOQs were 0.04 and 0.05 ppm, respectively, when determined by GC/MSD at the lowest fortification level (0.06 ppm) (see Table VI).

Conclusions. The developed SFE procedure may be a viable alternative to existing solvent extraction methodologies for fluazifop-P-butyl and fluazifop-P in onions. It is considered faster and less labor-intensive and requires much smaller sample size [1 g of dry weight, i.e., 8.3 g of net weight, instead of 30–100 g (Clegg, 1987)]. This paper, as well as others (Wheeler and McNally, 1989; Lopez-Avila et al., 1990; Alexandrou and Pawliszyn, 1989; Anderson et al., 1989), shows that SFE has great potential in isolating pesticide residues from crops and environmental samples, in particular for those residues which involve long and cumbersome cleanup methods. Multi-extraction instruments have been developed recently to extract a maximum of four or eight samples simultaneously. If these instruments are used, it will further cut down the sample cleanup time for a large number of samples. The smaller sample size is important on special

occasions, such as for determining the misuse of pesticides when consumers experience adverse effects after injesting the produce. However, each new analyte and matrix combination will require slightly different conditions, and optimization experiments should be performed.

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