Suitability of Microwave-Assisted Extraction for Multiresidue Pesticide Analysis of Produce[†]

Harry M. Pylypiw, Jr.,* Terri L. Arsenault, Christine M. Thetford, and
Mary Jane Incorvia Mattina

The Connecticut Agricultural Experiment Station, Department of Analytical Chemistry,
123 Huntington Street, New Haven, Connecticut 06511

A systematic study of the microwave-assisted extraction of field-incurred pesticide residues from several crop matrices was conducted. Five crops consisting of beets, cucumbers, lettuce, peppers, and tomatoes were grown and treated in the field with seven pesticides, dacthal, chlorpyrifos, chlorothalonil, diazinon, permethrin, methoxychlor, and azinphos-methyl. Values were determined for the microwave extraction parameters, time and temperature, which resulted in efficient recovery over the selected pesticides and crops. The microwave settings were shown to be dependent on both crop matrix and pesticide. Recovery of the fungicide chlorothalonil was highly dependent on temperature, while the remaining pesticides tested were not so demanding. Using the selected microwave time and temperature values, pesticide recoveries from the microwave method were then compared with those of the conventional method. Statistical comparison of pesticide recoveries and method reproducibility of the microwave method versus the conventional blender extraction indicated that microwave extraction data compare favorably with conventional extraction data.

Keywords: *Microwave-assisted extraction; pesticide residues; multiresidue pesticide analysis in produce; field-incurred pesticide residues*

INTRODUCTION

Pesticide residues are present in foods as a result of their application to agricultural crops to prevent losses from weeds, insects, and plant pathogens. A variety of multiresidue analytical methods have been developed to analyze crops for these agrochemicals. A major drawback with many of these methods is their requirement for large quantities of petroleum based solvents (Cairns *et al.*, 1993; Hsu *et al.*, 1991; Luke *et al.*, 1981; Okumura *et al.*, 1991; Pylypiw, 1993). Thus, large quantities of solvent waste are generated as a result of the determination of trace amounts of contaminants in foods.

In recent years much effort has been directed toward reducing laboratory-generated waste while at the same time improving detection limits of analytical testing methods. Many conventional multiresidue methods begin with blending the crop with organic solvent. Typically, 50−100 g is subsampled from a larger quantity of homogenized produce to assure reproducible results. A typical initial extraction step in many multiresidue screening methods utilizes 200−500 mL of organic solvent. Only a small portion of the extracting solvent is carried through the entire procedure. Supercritical fluid extraction has been examined to reduce organic solvent usage associated with extraction of the target pesticide from the crop matrix (Pearce *et al.*, 1997; Lehotay and Eller, 1995). However, the cost of the equipment associated with analytical scale supercritical fluid extraction is considerable. Techniques such as solid phase extraction have been introduced to reduce solvent consumption during subsequent sample cleanup (Fillion *et al.*, 1995).

Microwave-assisted extraction (MAE) processes, which use microwave energy to heat samples and solvents in a closed, pressurized vessel, may achieve a 90% reduction in solvent consumption (Fish and Revesz, 1996; Lopez-Avila *et al.*, 1995). The equipment required for MAE is considerably lower in cost than commercial supercritical fluid extraction equipment. We report here our investigation of MAE to replace the conventional blender extraction portion of our multiresidue method. The conventional method in use in our laboratory requires 300 mL of organic solvent for the extraction of 100 g of sample (Pylypiw, 1993) in a laboratory blender. A much smaller sample size and much less organic solvent are incorporated into the microwave method discussed in this paper. All crops used in our study were grown and treated with pesticides in the field. It has been acknowledged that maximization of recoveries of field-incurred analytes from environmental matrices is far more realistic for the assessment of analytical methodologies under development than recoveries based on laboratory spiking into the matrix (Fish and Revesz, 1996; Lehotay and Ibrahim, 1995; Lopez-Avila *et al.*, 1995). We concluded that for this study recovery results of field-incurred pesticides are far more comparable to analysis of market-basket produce than recoveries from crop matrices spiked in the laboratory.

The studies reported here were designed to answer several questions. First, what are the appropriate microwave settings of time and temperature for adequate recoveries across all selected pesticides and matrices? Second, how do recoveries from the microwave extraction compare with those from the conventional blender extraction? And finally, how reproducible are the data from the microwave method? This final aspect of the study is important to establish since the subsample size in the microwave method is considerably smaller than that in the conventional method.

* Author to whom correspondence should be addressed (e-mail pestman@caes.state.ct.us).

MATERIALS AND METHODS

Apparatus. *Microwave Extraction Apparatus.* We used an MSP-1000, 12-sample capacity, instrument from CEM Corp., Matthews, NC. Operating conditions were as follows: power, 50%; P_{max}, 160 psi; ramp time, 3 min; hold time, 7 min. Teflon PFA lined extraction vessels with 100 mL capacity were used. Specific details regarding the operation of this microwave system have been published elsewhere (Fish and Revesz, 1996).

Gas Chromatograph. A Hewlett-Packard Co., Avondale, PA, Model 5890, equipped with the following detectors was used: (1) ^{63}Ni electron capture detector; (2) flame photometric detector, operating in P mode; (3) electrolytic conductivity detector, Model 4420, OI Analytical Corp., College Station, TX, reactor temperature, 900 °C; vent time, 3.5 min, operating in the halogen mode. General operating conditions were as follows: initial temperature, 175 °C; no initial hold time; ramp rate, 1 °C/min; final temperature, 250 °C; final hold time, 10 min; total run time, 85 min; carrier gas, He; injector temperature, 225 °C; operated in the splitless mode; purge off time, 0.50 min. The autoinjector was a HP-7673, and a 2–4 μL injection volume was used.

Chromatographic Column. The capillary column, 30 m × 0.53 mm, 0.5 μm film, SPB-1, was from Supelco Inc., Bellefonte, PA. Alternative columns included 30 m × 0.53 mm or 15 m × 0.53 mm, 0.5 μm film, SPB-5, SPB-608, and SPB-20 columns.

Data Collection. All GC data were collected on a HP Vectra PC using HP 3365 ChemStation software.

Reagents. *Chemicals.* Petroleum ether (30–60 °C), 2-propanol, 2,2,4-trimethylpentane, and sodium sulfate (anhydrous, granular), Resi-Analyzed grade, were from J. T. Baker Chemical Inc., Phillipsburg, NJ. Saturated sodium sulfate was prepared by adding approximately 250 g of sodium sulfate to 800 mL of distilled water and warming on a steam bath until the sodium sulfate crystals dissolved. The solution was cooled overnight at room temperature to allow the excess sodium sulfate crystals to precipitate.

Analytical Standards and Formulated Pesticides. All pesticide compounds were obtained from commercial sources or from pesticide manufacturers. All analytical standards were diluted with 2,2,4-trimethylpentane to give a 10 μg/mL intermediate standard from which individual and mixed standard solutions were prepared. For field application pesticide formulations were diluted with water as indicated on the manufacturer's label.

Production of Crops with Field-Incurred Residues. Beets (Early Wonder), two varieties of lettuce (Parris Island Romaine and Salad-bowl loose leaf), cucumbers (Marketmore), tomatoes (Red Cherry), and peppers (open pollinated) were grown at the Connecticut Agricultural Experiment Station's Lockwood Farm, Hamden, CT, in a 90 ft × 30 ft plot. Two weeks after seeding and/or transplanting, the soil was treated with dacthal 75%, 110 g/gal of distilled water. Beginning 6 weeks after seeding/transplanting and continuing at 1 week intervals, the crops were sprayed with chlorothalonil, diazinon, permethrin, methoxychlor, and azinphos-methyl. At 9 weeks after seeding or transplanting, chlorpyrifos was substituted for azinphos-methyl in the five-pesticide mix. All insecticides and fungicides were applied at the rate of 5 g/0.5 gal of distilled water for active ingredients with a label concentration of 25% in the formulation. Application rates were chosen to achieve incurred residues at levels ranging from 0.1 to 5.0 μg/g. Over a period of 6 weeks various crops were harvested for residue testing 3 days after a spraying. Crops were harvested when ripe so as to produce crops similar to those offered for sale to the consumer.

Sample Preparation. Samples were prepared for testing unpeeled and raw. Samples (usually 3–4 kg) were placed in a food cutter (Hobart Model 84145, Hobart, Corp., Troy, OH) and chopped for 2–3 min or until homogeneous, and a 0.3–0.5 kg subsample was removed for immediate testing. The remaining chopped sample was placed in 1-L glass jars and frozen at −15 °C for further analysis.

Subsamples were prepared for pesticide analysis using a conventional multiresidue procedure (Pylypiw, 1993). In this conventional method, a 100 g portion of the chopped sample was combined with 100 mL of 2-propanol and 200 mL of petroleum ether and then blended (explosion resistant, Waring 14-509-53; blender containers, 1 qt, Fisher 14-509-11A, Fisher Scientific Co., Pittsburgh, PA) for 3–4 min. After blending, the sample was decanted through a filtering funnel into a 1-L separatory funnel. The filtered sample solution was gently agitated with three 350-mL portions of distilled water. After the last water wash was drained off, a final wash with 50 mL of distilled water and 10 mL of saturated sodium sulfate solution was done to break any emulsions formed from the previous water washes. After these cleanup steps, the remaining organic extract was dried over sodium sulfate and analyzed by gas chromatography. The average limit of detection for the pesticides determined in this study was 10 ng/g (Pylypiw, 1993).

Modification of the conventional extraction was necessary for microwave extraction. After initial chopping, a 10-g subsample was placed into the microwave vessel together with 10 mL of 2-propanol and 20 mL of petroleum ether. The vessel was sealed and heated for appropriate times, 10 or 20 min, at temperatures of 80, 100, or 120 °C. After heating, the vessel was cooled to room temperature and the solvent transferred to a 250-mL separatory funnel. The cleanup steps and pesticide detection limits in this procedure were identical to those used in the conventional extraction, except for solvent quantity. Specifically, to the separatory funnel were added 35 mL of distilled water. The separatory funnel was capped, vented, and gently swirled for 1 min. The funnel was then allowed to stand for 5–10 min, to allow the water and organic solvent layers to separate. After separation, the water layer was drained off and discarded. The organic layer was washed, with gentle agitation of the separatory funnel, two more times, each time with 35 mL of distilled water without added sodium sulfate. After the third water wash was drained, 10 mL of distilled water and 1 mL of saturated sodium sulfate solution were added to the funnel and the separatory funnel was swirled for a few seconds. This final wash served to break any emulsions formed from the previous water washes. The final wash was discarded, and the organic solvent extract was transferred to a 40-mL vial that contained 2–3 g of anhydrous sodium sulfate. The vial was sealed with a Teflon-lined cap, shaken for 1 min, and allowed to settle for 10 min. This step was repeated two additional times. Prior to analysis of the extract by GC, the extract was allowed to stand undisturbed over the sodium sulfate a minimum of 1 h, to allow any particulates to settle.

RESULTS AND DISCUSSION

The first experiments were designed to determine suitable values for the microwave parameters, time and temperature. The settings were selected such that the pesticide recoveries from the microwave method were comparable with those from the conventional method and thus provided an alternative to the conventional method for multiresidue analysis. Second, since the mass of the subsample used in the microwave extraction was $^1/_{10}$ that used in the conventional method, it was essential for us to demonstrate whether or not the microwave method produced consistent results.

Determination of Microwave Parameters. To determine suitable values of the microwave extraction time and temperature parameters, samples of Romaine and Salad-bowl lettuce were analyzed that contained field-incurred residues of six pesticides: chlorothalonil, diazinon, dacthal, methoxychlor, permethrin, and azinphos-methyl. The microwave extraction was performed for 10 and 20 min at each of the following temperatures: 80, 100, and 120 °C at 50% power. The power setting of 50% was chosen to provide more even heating when fewer than 12 vessels were in the oven. At each
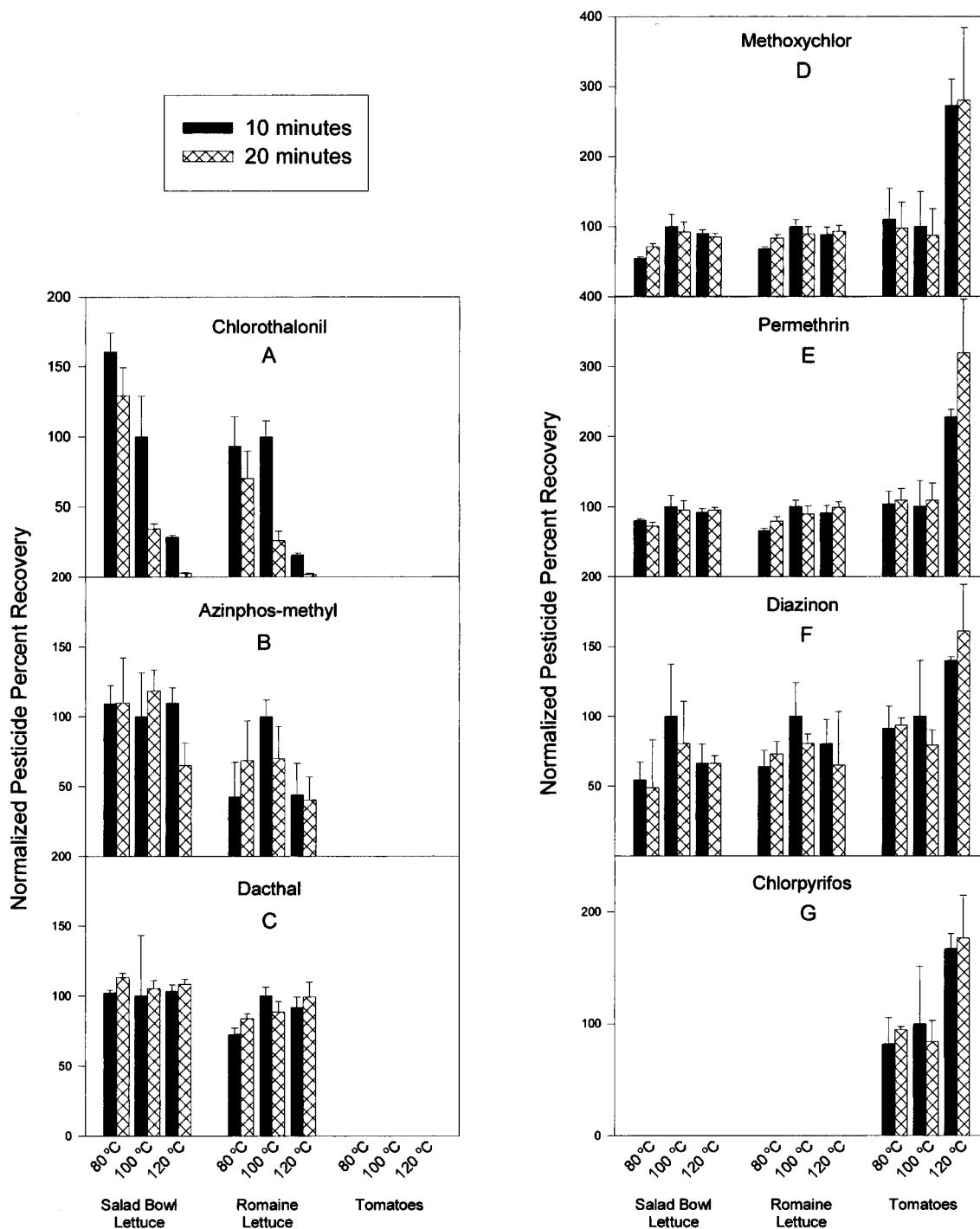
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Figure 1. Pesticide residues recovered in field-incurred crops at three extraction temperatures and two extraction times. The percent of each pesticide recovered is normalized to 100 °C at 10 min of extraction time. Error bars represent 1 SD of the mean.

temperature, six vessels, each containing a 10-g lettuce sample, were heated at 50% power to the selected temperature using a 3-min ramp and held at that temperature for 7 min, for a total run of 10 min. When this step was completed, three vessels were removed, and the remaining vessels were heated at 50% power for an additional 10 min for a total of 20 min.

The results from both lettuce matrices for the six pesticides were analyzed using a two-factor factorial design analysis of variance (Montgomery, 1984). For both lettuce samples, time was significant only for the extraction of chlorothalonil, shown in Figure 1A. It can be easily seen that a 10-min extraction resulted in higher recovery than a 20-min extraction at all three temperatures examined. Temperature was also signifi-

cant for chlorothalonil in both lettuce matrices, with 80 °C yielding the best recovery. However, this trend was not observed with other pesticides. For example, with the Romaine lettuce matrix, it was found that analyte recovery at 100 °C was significantly better for azinphos-methyl, dacthal, methoxychlor, and permethrin. However, with the Salad-bowl lettuce matrix, there was no significant difference in recoveries for these pesticides with regard to extraction temperature. The time and temperature data for these four pesticides are shown in Figure 1B–E. For diazinon, there was no significant difference between time or temperature for either matrix as shown in Figure 1F. Thus, although 10 min and 80 °C were optimal for chlorothalonil, we concluded

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Table 1. Summary Data for Optimization of Microwave Parameters[a]

pesticide	temp (°C)	Salad-bowl lettuce		Romaine lettuce		tomatoes	
		10 min	20 min	10 min	20 min	10 min	20 min
chlorothal-	80	3.78	3.05	1.10	0.83	b	b
onil	100	2.35	0.80	1.18	0.30	b	b
	120	0.67	0.60	0.18	0.02	b	b
dacthal	80	0.57	0.63	0.49	0.56	0.02	0.02
	100	0.56	0.62	0.67	0.59	0.00	0.01
	120	0.58	0.60	0.62	0.67	0.02	0.02
diazinon	80	0.08	0.07	0.14	0.16	0.35	0.36
	100	0.14	0.11	0.22	0.18	0.39	0.31
	120	0.09	0.09	0.18	0.14	0.54	0.62
chlorpyrifos	80	c	c	c	c	0.52	0.60
	100	c	c	c	c	0.63	0.53
	120	c	c	c	c	1.05	1.11
methoxychlor	80	3.62	3.89	2.69	3.30	0.40	0.35
	100	4.24	3.92	3.97	3.54	0.36	0.31
	120	3.80	3.60	3.51	3.70	0.98	1.01
permethrin	80	9.14	11.2	7.28	8.81	0.64	0.67
	100	11.3	10.8	11.2	10.0	0.62	0.67
	120	10.4	10.8	10.1	11.0	1.40	1.97
azinphos-	80	6.44	6.47	2.39	3.84	c	c
methyl	100	5.90	6.98	5.63	3.94	c	c
	120	6.48	3.83	2.46	2.26	c	c

[a] Values are average concentrations in μg/g of pesticide residues based on three replicates. [b] Degraded in storage. [c] Not sprayed on this crop.

Figure 2. Comparison of methoxychlor residues (μg/g) in 11 crop matrices extracted with conventional blender extraction and MAE for 10 min. SB, Salad-bowl lettuce; RM, Romaine lettuce; BR, beet roots; TM, tomatoes; PE, peppers; CU, cucumbers; 1, harvest 1; 2, harvest 2; F, fresh matrix; Z, frozen matrix. Error bars represent 1 SD of the mean.

that 100 °C was the optimum temperature and 10 min was the optimum time for a multiresidue screen.

To confirm this conclusion, the experiment was repeated on previously frozen tomato matrix. This matrix contained four pesticides: diazinon, chlorpyrifos, methoxychlor, and permethrin. The matrix was extracted by varying the parameters of time and temperature as described previously. Similar to the lettuce matrices, we noted that variation of the extraction time did not produce statistically different recoveries. However, with the tomato matrix statistically improved recoveries of these four pesticides were noted at 120 °C. This is shown in Figure 1D−G. The recovery averages for all three matrices are summarized in Table 1. The data indicate that optimum microwave extraction recoveries are dependent on the extraction temperature along with the sample matrix and pesticides for the crops and analytes included in this study.

The behavior of the field-incurred chlorothalonil in all of the matrices examined merits comment. In the lettuce samples, the behavior of chlorothalonil during the microwave extraction appeared to be consistent with its being a thermally labile compound probably undergoing hydrolysis in the crop matrix. Similar thermal lability of the pesticides endrin aldehyde and dichlorvos has been reported when using supercritical fluid extraction (Snyder *et al.*, 1993). In the freshly harvested tomatoes chlorothalonil was initially detected at 0.03 μg/g as determined by the conventional extraction method. When the frozen tomato matrix was tested at a later time, no chlorothalonil was detected using either the conventional or microwave extraction methods. Further examination of our data revealed that chlorothalonil degraded by about half on lettuce samples that were refrigerated for as brief a time as 2 days (data not shown). These observations contrast with the accepted thermal stability of chlorothalonil in aqueous medium under both acidic and alkaline conditions (*Farm Chemicals Handbook '97*, 1997). It is apparent that the analysis for chlorothalonil must be conducted as rapidly
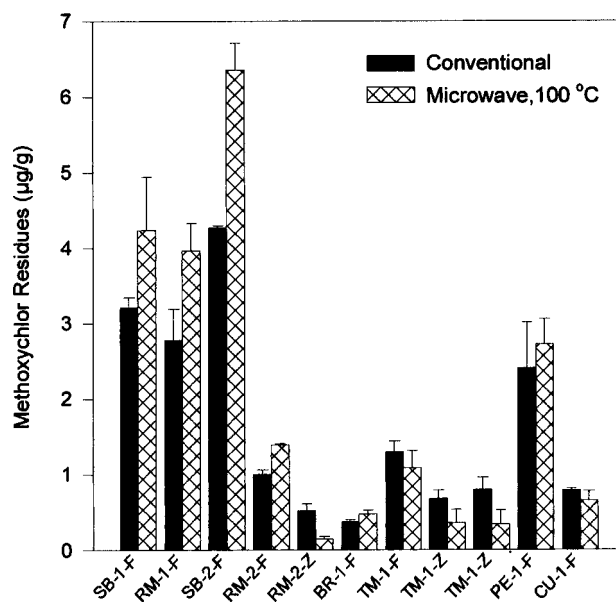
as possible following harvest. In addition, the comparison of chlorothalonil recovery data from both techniques is valid only on samples harvested and extracted simultaneously.

To provide suitable recoveries for a multiresidue method, we selected microwave time and temperature settings of 10 min and 100 °C for our comparison study of microwave with the conventional method discussed below. It is apparent from the preceding that these must be considered compromise values.

Comparison of Extraction Techniques. Eight crop samples, including two harvests of Romaine and Salad-bowl lettuce, beet roots, tomatoes, peppers, and cucumbers were extracted by the two techniques side-by-side. Samples of all crop matrices were prepared in duplicate, several in triplicate, extracted using both extraction techniques, and pesticide residue recoveries were determined. Comparisons of the two extraction methods were made for six pesticides: chlorothalonil, dacthal, methoxychlor, permethrin, diazinon, and chlorpyrifos. Not all crops contained all six pesticides. Statistical comparisons were made between the two extraction techniques using a paired *t*-test by pesticide and by crop matrix. This test improves precision by making comparisons within matched pairs of data (Montgomery, 1984). Initially, one harvest of fresh Salad-bowl lettuce and one harvest of Romaine lettuce were used for this comparison. The results from these two samples (SB-1-F, RM-1-F), shown to the left in Figure 2 for the pesticide methoxychlor, implied that the MAE was better at extracting these pesticides from a crop matrix than a conventional blender extraction. These observations shown for methoxychlor were similar for other pesticides in the lettuce matrices with the exception of chlorothalonil. To confirm these findings, we tested additional crop samples. These samples were fresh Salad-bowl and Romaine lettuce from a second harvest (SB-2-F, RM-2-F), beet roots (BR-1-F), tomatoes (TM-1-F), cucumbers (CU-1-F), and peppers (PE-1-F), analyzed at harvest time, followed by samples of Romaine lettuce (RM-2-Z) and tomatoes (TM-1-Z) that
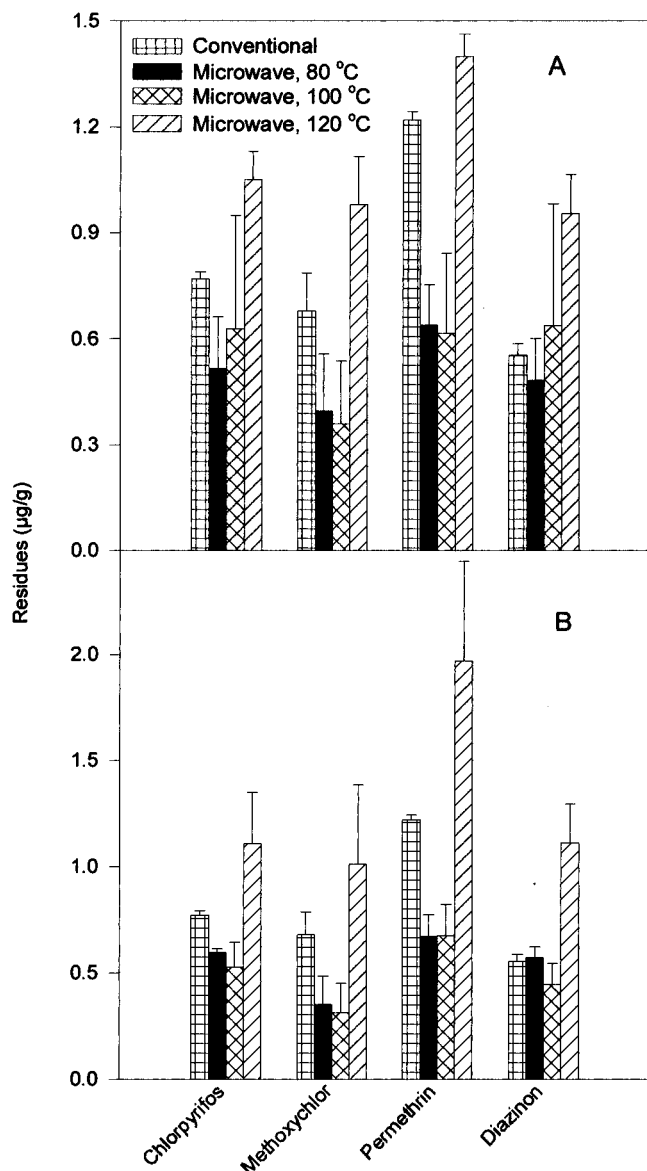
Figure 3. Comparison of four pesticide residues (μg/g) in tomato matrix extracted with conventional blender extraction and MAE at three extraction temperatures and extraction times of (A) 10 min and (B) 20 min. Error bars represent 1 SD of the mean.

Table 2. Mean Values (in Micrograms per Gram) and Variances for Each Extraction Method[a]

		conventional		microwave	
matrix	pesticide	mean	variance	mean	variance
Romaine	chlorpyrifos	0.316	0.000418	0.318	0.000827
lettuce	dacthal	0.0765	0.0000280	0.0734	0.0000490
	methoxychlor	0.517	0.00884	0.145	0.00100
	permethrin	0.700	0.00299	0.743	0.00423
	diazinon	0.117	0.000106	0.113	0.000108
tomatoes	chlorpyrifos	0.649	0.00800	0.382	0.0250
	dacthal	0.0106	0.0000110	0.0125	0.0000460
	methoxychlor	0.796	0.0274	0.342	0.0335
	permethrin	1.10	0.0250	0.303	0.0140
	diazinon	0.294	0.00100	0.218	0.00300

[a] Each mean represents six replicates.

other pesticides in the tomato matrix, however, 120 °C is preferable. The data presented in Figure 3A suggest that the recoveries of the four pesticides using MAE for 10 min are actually larger than those from the conventional method when the temperature is increased to 120 °C. This trend is also true using MAE for 20 min as shown in Figure 3B. Temperatures above 120 °C were not sustainable in the microwave due to pressure overruns. If this observation is borne out for additional crops and pesticides, it implies that conventional solvent extraction methods (Luke *et al.,* 1981), when compared to more rigerous extraction methods (Paquet and Khan, 1995), may be underestimating some pesticide residues in some crops by 10–100%.

Reproducibility of Extraction Technique. After selecting 10 min and 100 °C as the most suitable microwave extraction conditions, we examined the method for sample to sample reproducibility. Confirmation of method reproducibility is relevant since the sample size has been reduced from 100 g in the conventional method to 10 g in the microwave method. To determine reproducibility, we extracted six samples each of tomatoes and Romaine lettuce, on the same day, using conventional and microwave extraction. These two crops each contained five pesticide residues— chlorpyrifos, dacthal, methoxychlor, permethrin, and diazinon. For nine of the pesticide recoveries there were no differences in the variance between the two extraction techniques. However, the variance of methoxychlor on Romaine lettuce extracted with the microwave technique was found to be lower than the variance for the conventional extraction (see Table 2). To evaluate if this variance was significant, all of the variances for each pesticide and each matrix were examined statistically using Bartlett's test, and the residuals of these variances were plotted to examine visually the difference between the individual values for an extraction technique and the average value for that technique (Montgomery, 1984). Figure 4A shows the residue levels for five pesticides in the Romaine lettuce matrix, and Figure 4B shows the plot of the residuals for each of those pesticides. These data indicated that both techniques had similar variabilities about the means with the exception of methoxychlor. The pesticide residue data for the tomato matrix all had similar variabilities about their means. These are shown in Figure 5. Thus, we felt that even though there was a reduction in sample size when using microwave extraction, the smaller sample size did not significantly effect the variance of the result.

Conclusions. The data from this study of the suitability of microwave extraction for multiresidue pesticide screening of produce indicate that the tech-
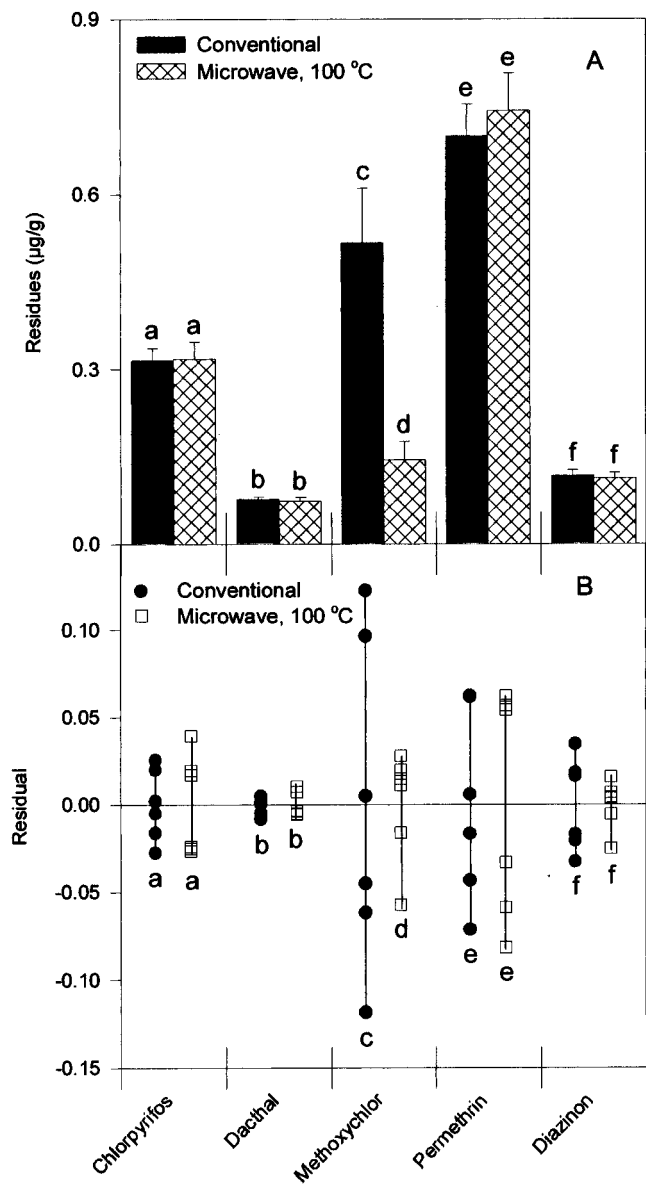
were frozen at harvest time and analyzed approximately 4 months later. The methoxychlor residue results from these samples are shown in Figure 2.

Statistical comparison of all crops analyzed revealed that for all six pesticides examined, there was no difference between the conventional technique and MAE when the results were compared for each individual pesticide on all matrices containing the pesticide. When the *t*-test was done by crop matrix for all pesticides on the crop, it was also found that there was no statistical difference between the conventional and MAE methods. However, the microwave was slightly less efficient at extracting pesticides from the tomato matrix as shown in Figure 3. This suggests that microwave extraction is more matrix dependent than the conventional blender extraction.

Once again we emphasize that the choices of 10 min and 100 °C for the microwave extraction are compromise values with the intent of developing a multiresidue screening technique. For example, as shown in Figure 1A, 80 °C is preferable for chlorothalonil extraction. For

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Figure 4. Comparison of (A) five pesticide residues (μg/g) and (B) their residual variance in Romaine lettuce matrix extracted with conventional blender extraction and MAE for 10 min. Identical letters above each bar (A) indicate that the means for that pesticide were not statistically different. Error bars (A) represent 1 SD of the mean. Identical letters below each line (B) indicate that the variance for that pesticide was not statistically different.

Figure 5. Comparison of (A) four pesticide residues (μg/g) and (B) their residual variance in tomato matrix extracted with conventional blender extraction and MAE for 10 min. Identical letters above each bar (A) indicate that the means for that pesticide were not statistically different. Error bars (A) represent 1 SD of the mean. Identical letters below each line (B) indicate that the variance for that pesticide was not statistically different.

nique is dependent both on sample matrix and on pesticide. Chlorothalonil appears to degrade under microwave conditions. The optimum extraction temperature for a particular pesticide is also affected by the crop matrix. We selected 100 °C and 10 min as compromise MAE parameters for purposes of developing a multiresidue method on a variety of crop matrices. When using these parameters, the microwave extraction is comparable to our conventional extraction technique. The reduction in sample size and extraction solvent volume does not affect the reproducibility of the extraction procedure.

Our results suggest that microwave extraction parameters can be optimized for efficient extraction of individual pesticides and/or crop matrices. As additional pesticides and crops are examined with this technique, it may be possible to extract efficiently one set of pesticides at a lower temperature such as 80 °C and another set of pesticides at higher temperature.
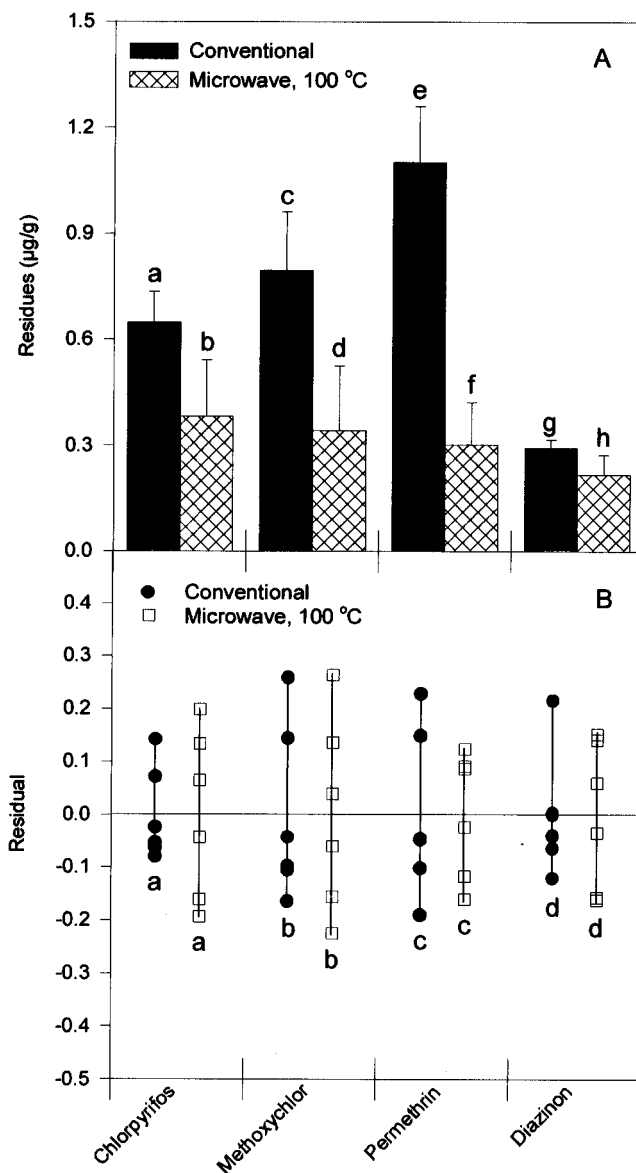
Under more robust conditions, pesticide recoveries for some pesticides may be improved over current solvent extraction methods, permitting a better assessment of the presence of pesticides in the food supply.

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