RESIDUES AND TRACE ELEMENTS

# Validation of a Method for the Determination of Multiclass Pesticide Residues in Fruit Juices by Liquid Chromatography/Tandem Mass Spectrometry after Extraction by Matrix Solid-Phase Dispersion

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**A multiresidue method was developed and validated for the determination of pesticide residues (omethoate, dimethoate, carbendazim, propoxur, thiabendazole, carbaryl, pirimicarb, azinphos-methyl, methidathion, and iprodione) in fruit juices. The samples were extracted by matrix solid-phase dispersion with diatomaceous earth and analyzed by liquid chromatography/tandem mass spectrometry. The method detection limits were <0.2 ppb for all pesticides; the relative standard deviations for analyses of samples fortified over the range of 2–50 ng/g were <9%, and the recoveries for each pesticide were all between 77 and 102%. The proposed method was used to analyze 21 commercial fruit juices; pesticide residues were found in 71% of the samples.**

Interest is increasing in the detection and determination of residues of an ever-widening range of pesticides in agricultural products intended for human consumption. Strict control is necessary to protect the consumer from the harmful impact of pesticide residues. This concern has been reflected by the European Union in the maximum residue limits (MRL) for pesticide residues in a variety of agricultural products. Significant traces of pesticides were found in fruit juices by using strong chemical and physical treatment; monitoring by the U.S. Food and Drug Administration (FDA) in 1999 showed that 60% of the analyzed samples were positive for pesticide residues (1). Because children are the principal consumers of fruit juices, there has been much interest in the determination of pesticide levels in juices, even at very low concentrations.

Multiresidue methods are preferable because many pesticides can be determined in a single analysis, reducing time and costs. However, most known screening protocols involve tissue preparation and several extraction, purification, and concentration steps, which make them expensive to perform when many samples must be analyzed. To eliminate some of the difficulties associated with solvent extraction and solid-phase extraction (SPE) of pesticide residues, matrix solid-phase dispersion (MSPD) has been used. It is possible by this technique to decrease the requirement for solvents, cartridges, and analysis time. Kadenczki et al. (2) demonstrated the applicability of MSPD to a large number of fruit and vegetable matrixes and pesticides residues; various matrixes and several solvents have been used for extraction by MSPD (3–6). Mechanisms and applications of MSPD have been reviewed by Barker (7).

Analytical methodologies for the determination of pesticides in fruit juices are based mostly on gas chromatography, liquid chromatography (LC), and immunoassay techniques (8–13). Therefore, the aim of the work described in this paper was to develop an analytical method, based on MSPD with diatomaceous earth, for the determination of 4 chemical classes of pesticides (organophosphorus compounds, carbamates, benzimidazoles, and dichloroanilides) and to establish a method of food analysis by using a liquid chromatography/tandem mass spectrometry (LC/MS/MS) system. Figure 1 shows the structures of the selected analytes (omethoate, dimethoate, methidathion, azinphos-methyl, propoxur, carbaryl, pirimicarb, carbendazim, thiabendazole, and iprodione). The choice of the pesticides to investigate was based on 2 parallel considerations: the individual chemicals used to protect the cultures related to the most common fruit juice production (pear, peach, apricot, pineapple, and apple) were listed; from these were selected the pesticides most frequently detected in the monitoring of the fresh fruits (14).

## Experimental

### *Reagents*

(**a**) *Pesticide analytical standards*.—Omethoate, dimethoate, carbendazim, propoxur, thiabendazole, carbaryl, pirimicarb, azinphos-methyl, methidathion, and iprodione were purchased from LabService (Bologna, Italy).

(**b**) *Analyte standard stock solutions*.—Individual standard solutions were prepared at 1 mg/mL in methanol, for all the pesticides except carbendazim, for which the standard solution was prepared at 0.05 mg/mL, because of its low solubility. Composite working standard solutions were prepared by mixing an appropriate amount of each standard solution and

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diluting with methanol. All standard solutions were stored at 4°C before use.

(**c**) *LC mobile phase*.—For the LC/MS/MS analysis, deionized water, obtained from Milli-Q Plus apparatus (Millipore, Bedford, MA), and Plus methanol, supplied by Carlo Erba (Milan, Italy), were used. Formic acid was supplied by Merck (Darmstadt, Germany).

(**d**) *Sorbent*.—Diatomaceous earth Spe-ed Matrix was purchased from LabService.

(**e**) *Solvents*.—Ethyl acetate and the other chemicals were purchased from Carlo Erba.

### Apparatus

(**a**) *Liquid chromatograph*.—A Perkin-Elmer Series 200 binary pump (Perkin-Elmer, Norwalk, CT), equipped with a Rheodyne 7125 injector with a 50 µL loop and a Perkin-Elmer Series 200 vacuum degasser, was used for LC. Post-column addition was performed by a Model 2510 isocratic LC pump (Varian, Walnut Creek, CA).

(**b**) *Analytical column*.—Alltima column, 25 cm × 4.6 mm id, filled with 5 µm $C_{18}$ reversed-phase packing (Alltech, Deerfeld, IL).

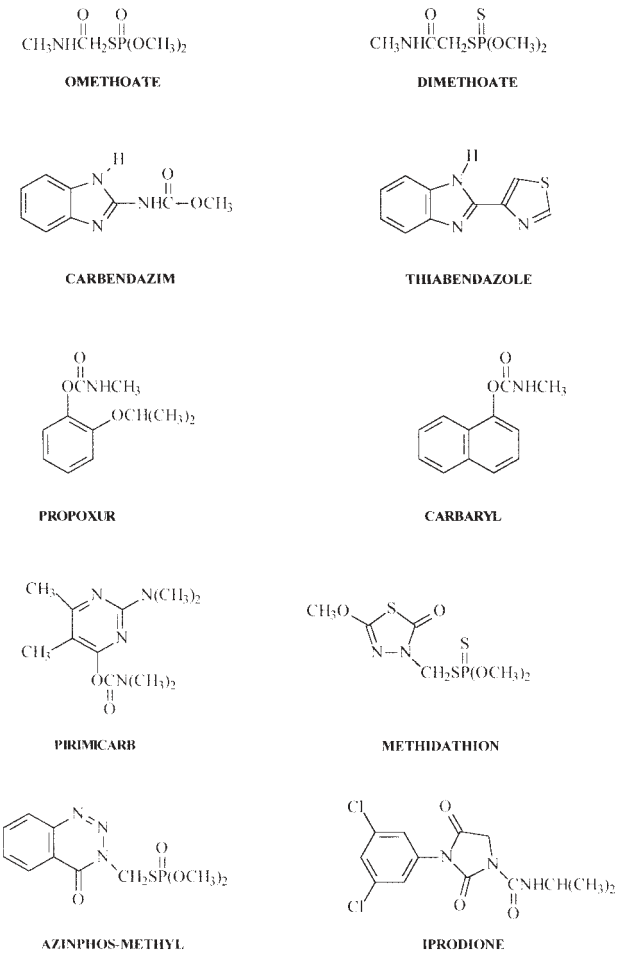


**Figure 1. Structures and common names of the selected pesticides.**

(**c**) *Mass spectrometer*.—PE Sciex API 2000 tandem triple-quadrupole mass spectrometer (Perkin-Elmer) equipped with a TurboIonSpray interface. This is a new high-flow atmospheric pressure interface developed by Sciex: pneumatically assisted electrospray ionization is called Ionspray in the PE Sciex LC/MS interface device.

### MSPD Procedure

A 1 g portion of Spe-ed Matrix diatomaceous earth was mixed with 1 g fruit juice (a representative portion of the sample) until the sample was completely adsorbed into the solid phase. A 6 mL cartridge was filled with the powdery sample mixture, with 2 polyethylene fritted disks to keep the packing in place; the elution was performed with 10 mL ethyl acetate at 1 mL/min. The effluent was collected in a conical tube and dried with a gentle nitrogen stream in a thermostatic bath at 30°C. The residue was reconstituted with 500 µL methanol–water (50 + 50, v/v), and 50 µL was injected into the LC/MS/MS apparatus.

Fortified samples, for recovery studies, were prepared by spiking 1 g fruit juice with a known volume of working standard solution to obtain, for each pesticide, concentrations of 2, 5, 10, and 50 ng/g. The samples were kept for 12 h in the dark at room temperature before the MSPD procedure. Unspiked samples were used as blanks.

### LC/MS/MS Analysis

The analytes were separated by LC with gradient elution by using methanol as phase A and water as phase B as follows: methanol was increased from 35 to 100% in 26 min, at a 1 mL/min flow rate. Formic acid (20mM, freshly prepared each day) was added post-column to the LC column effluent at a flow rate of 0.10 mL/min for 24 min and stopped before the elution time of iprodione. A total of 200 µL LC column effluent mixture was diverted into the ion spray ionization (ISI) source. All pesticides except iprodione were detected in the positive ionization (PI) mode; iprodione was detected in the negative ionization (NI) mode. The capillary voltages were 4500 and –4500 V in the PI and NI modes, respectively. Nitrogen was used as the nebulizer gas, curtain gas (both 1.2 L/min), turbo gas (1 L/min), and collision gas (3 mtorr). The TurboIonSpray probe temperature was maintained at 350°C. For each analyte, selected reaction monitoring (SRM) was chosen for quantitation after the collision-induced dissociation spectra, obtained by full-scan product-ion experiments, were examined. Mass axis calibration of each of the mass-resolving quadrupoles, $Q_1$ and $Q_3$, was performed by infusion of a polypropylene glycol solution at 10 µL/min. Unit mass resolution was established and maintained in each mass-resolving quadrupole by keeping a full width at half maximum of ca 0.7 Da. Data acquisition was divided into 4 periods (Table 1), and in each period individual ion optics and MS/MS tuning parameters were optimized for each SRM transition in order to enhance the sensitivity. For recovery studies, the concentrations of the analytes were calculated by measuring peak areas from extracted-ion current profiles and comparing them with those obtained from standard solutions.

**Table 1. Experimental conditions for the SRM LC/MS determination of selected analytes**

| Analyte | SRM transition, *m/z* | Declustering potential, V | Collision potential, V | Retention window, min | Dwell time, ms |
|---|---|---|---|---|---|
| Omethoate | 214→183 | 51 | 15 | 0–7 | 1500 |
| Dimethoate | 230→199 | 46 | 18 | 7–13 | 1500 |
| Carbendazim | 192→160 | 66 | 25 | 13–24 | 300 |
| Propoxur | 210→111 | 41 | 19 | 13–24 | 300 |
| Thiabendazole | 202→175 | 106 | 37 | 13–24 | 300 |
| Carbaryl | 202→145 | 56 | 13 | 13–24 | 300 |
| Pirimicarb | 239→182 | 61 | 39 | 13–24 | 300 |
| Azinphos-methyl | 318→132 | 51 | 21 | 13–24 | 300 |
| Methidathion | 302→145 | 46 | 13 | 13–24 | 300 |
| Iprodione | 328→141 | –51 | 19 | 24–30 | 1500 |

The peak area ratio for selected ions was determined using the PE Sciex package Multiview 1.4.

## Results and Discussion

### *Development of the MSPD Procedure*

MSPD with diatomaceous earth is a very fast and simple technique for food extraction. This procedure needs no preliminary treatment, as is needed for SPE. The first step in the method setup was the evaluation of a suitable matrix/diatomaceous earth ratio to allow complete adsorption of the fruit juice and to facilitate the transfer into the cartridge. A ratio of 1:1 was shown to be satisfactory; enhancing the diatomaceous earth ratio gave no improvement.

The cartridge packing has to be as homogeneous as possible to minimize errors, and the flow rate of the extracting solution should be set at approximately 1 mL/min by a flow control valve.

For the recoveries of the selected pesticides, several solvents with different polarities were tested. Methanol and acetonitrile gave good results in the recovery tests, but they had the drawback of coextracting the organic matter of the fruit juice. With methylene chloride, the recovery of omethoate (very polar analyte) was unsatisfactory (60%); moreover, during the solvent evaporation step, a persistent methylene chloride–water double layer was formed that impeded the evaporation step. Ethyl acetate was found to be the most efficient and selective solvent that provided very clear extracts.

The required solvent volume for MSPD extraction with ethyl acetate was determined by analyzing 5 mL eluate fractions from different spiked samples (5 and 50 ng/g). The results showed that increasing the volume of the extraction solvent from 10 to 20 mL had no significant effect on recovery. Consequently, 10 mL solvent (solvent/sample ratio of 10:1) was considered sufficient for quantitative extraction.

The extract was then dried with a gentle nitrogen stream in a thermostatic bath at 30°C and reconstituted before the LC/MS/MS analysis. Losses of iprodione were noted at water bath temperatures of >30°C.

The recovery studies were conducted with fruit juice samples obtained from biological agriculture, purchased at local bio-shops. The absence of the monitored pesticides in the juice matrix was verified by analyzing the blanks under the reported experimental conditions. Recoveries of selected pesticides obtained by using various solvents are summarized in Table 2.

The recovery results and the relative standard deviations (RSDs) obtained from analyses of apple juice and peach juice fortified at 2, 5, 10, 20, and 50 ng/g, using ethyl acetate as the extractant, are shown in Table 3. The recoveries of all the monitored pesticides are very good (>80% in most cases) and

**Table 2. Preliminary evaluation of extractants from peach juice samples spiked at 20 ng/g**

| | Recovery ± RSD, %[a] | | |
|---|---|---|---|
| Analyte | Methanol | Acetonitrile | Methylene chloride |
| Omethoate | 97 ± 5 | 103 ± 5 | 60 ± 9 |
| Dimethoate | 95 ± 4 | 96 ± 3 | 86 ± 7 |
| Carbendazim | 98 ± 4 | 99 ± 4 | 104 ± 5 |
| Propoxur | 91 ± 6 | 104 ± 4 | 108 ± 5 |
| Thiabendazole | 105 ± 3 | 96 ± 6 | 99 ± 4 |
| Carbaryl | 91 ± 6 | 97 ± 3 | 100 ± 4 |
| Pirimicarb | 89 ± 4 | 91 ± 4 | 88 ± 5 |
| Azinphos-methyl | 91 ± 5 | 83 ± 5 | 78 ± 8 |
| Methidathion | 93 ± 4 | 87 ± 6 | 95 ± 7 |
| Iprodione | 89 ± 5 | 93 ± 7 | 86 ± 8 |

[a] Each value is the mean of 4 determinations; RSD = relative standard deviation.

**Table 3. Recovery (%)[a] and RSD[b] of pesticides added to fruit juice sample at 5 different spiking levels, with ethyl acetate as the extractant**

| Pesticide | Spiking level, ng/g | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | | 5 | | 10 | | 20 | | 50 | |
| | Peach juice | Apple juice | Peach juice | Apple juice | Peach juice | Apple juice | Peach juice | Apple juice | Peach juice | Apple juice |
| Omethoate | 78 ± 9 | 91 ± 9 | 83 ± 7 | 82 ± 5 | 89 ± 4 | 85 ± 4 | 90 ± 5 | 89 ± 4 | 90 ± 4 | 91 ± 4 |
| Dimethoate | 91 ± 4 | 102 ± 5 | 88 ± 5 | 89 ± 5 | 95 ± 3 | 96 ± 3 | 97 ± 3 | 98 ± 3 | 93 ± 5 | 94 ± 5 |
| Carbendazim | 96 ± 8 | 95 ± 8 | 96 ± 7 | 96 ± 6 | 93 ± 2 | 94 ± 2 | 84 ± 3 | 95 ± 3 | 96 ± 3 | 96 ± 3 |
| Propoxur | 97 ± 5 | 96 ± 4 | 85 ± 4 | 89 ± 4 | 96 ± 2 | 95 ± 3 | 92 ± 3 | 93 ± 3 | 100 ± 4 | 100 ± 4 |
| Thiabendazole | 89 ± 9 | 90 ± 8 | 90 ± 9 | 90 ± 9 | 94 ± 5 | 94 ± 5 | 92 ± 2 | 93 ± 2 | 94 ± 3 | 94 ± 3 |
| Carbaryl | 100 ± 4 | 99 ± 4 | 79 ± 5 | 82 ± 5 | 92 ± 6 | 91 ± 6 | 86 ± 4 | 91 ± 5 | 99 ± 4 | 98 ± 4 |
| Pirimicarb | 98 ± 3 | 97 ± 4 | 93 ± 4 | 95 ± 4 | 102 ± 4 | 101 ± 4 | 98 ± 3 | 99 ± 3 | 89 ± 4 | 96 ± 4 |
| Azinphos-methyl | 82 ± 6 | 84 ± 5 | 91 ± 8 | 92 ± 7 | 89 ± 2 | 91 ± 3 | 92 ± 5 | 94 ± 5 | 96 ± 5 | 97 ± 5 |
| Methidathion | 77 ± 5 | 86 ± 4 | 95 ± 3 | 92 ± 3 | 93 ± 5 | 92 ± 5 | 89 ± 4 | 90 ± 4 | 88 ± 6 | 91 ± 4 |
| Iprodione | 79 ± 9 | 82 ± 8 | 75 ± 8 | 79 ± 6 | 81 ± 7 | 82 ± 7 | 78 ± 7 | 81 ± 6 | 83 ± 6 | 84 ± 6 |

[a] Each value is the mean of 6 determinations.
[b] RSD = relative standard deviation.

are independent of the sample matrix and the fortification level. Also the RSD is <10% for all analytes.

### *Optimization of the LC/MS/MS Analysis*

Preliminary experiments were conducted to find the best instrumental conditions, those that allowed unequivocal identification of the analytes in real samples at trace levels. It was necessary to operate first in the MS mode: the ISI spectra showed as the base peak the pseudo-molecular ion ($[M + H]^+$ or $[M - H]^-$) that was chosen as the precursor ion in the MS/MS experiments. The most abundant product ion transition for each analyte was monitored to obtain the highest quantitative sensitivity possible. To further optimize MS/MS conditions and sensitivity for individual compounds, SRM analysis was performed by using 10 different settings of the ion optics and MS/MS tuning conditions (Table 1) to achieve the lowest level of quantitation for the pesticides in fruit juices. The fragmentation study for the optimization of the




**Figure 2. SRM/LC/MS chromatogram obtained by injecting 50 μL peach juice extract spiked with each pesticide at 10 ng/g. Peak identity: 1 = omethoate; 2 = dimethoate; 3 = carbendazim; 4 = propoxur; 5 = thiabendazole; 6 = carbaryl; 7 = pirimicarb; 8 = azinphos-methyl; 9 = methidathion; and 10 = iprodione.**

SRM parameters was conducted with standard solutions of each pesticide, at concentrations of 100 pg/μL in methanol–water (50 + 50, v/v), and with syringe pump infusion at a flow rate of 10 μL/min.

The chromatographic run was divided into 4 time intervals to establish individually defined regions in which to optimize ion optics and MS/MS tuning parameters.

To increase signal stability and intensity in the PI mode, we assisted the molecular ionization in the interface by adding formic acid post-column. The presence of $H^+$ ions inhibited iprodione ionization, and the addition of formic acid was stopped 24 min after the beginning of the run by an automatic switching system. This procedure allowed a 3-fold increase in the signal intensity of this analyte. For all the pesticides analyzed in the PI mode, it was necessary to study the variation in signal intensity as the post-column concentration of formic acid was varied from 1 to 100mM. Good results were obtained with the addition of 20mM formic acid; a general enhancement of the ion signal was achieved by increasing the formic acid concentration from 1 to 20mM post-column. Further additions of formic acid resulted in a gradual weakening of the ion signal.

The use of a TurboIonSpray interface, instead of the normal IonSpray, accelerates the solvent vaporization and increases the ionization yield, by a hot gas flow, orthogonal to the ionic spray. Because too high a temperature can lead to partial or total degradation of the molecules, it was necessary to regulate the gas temperature and flow to obtain maximum ionization with minimum loss of analyte. Setting the Turbo gas at 350°C produced the highest signal for all the pesticides monitored.

Figure 2 shows an SRM/LC/MS chromatogram for an extract of peach juice fortified with each pesticide at 10 ng/g.

### *Linearity and Calibration*

The linear dynamic range of the method was evaluated for the selected analytes under the conditions reported in the *Ex-*

**Table 4. Calibration data and method detection limits (MDLs) for the analytes**

| Analyte | Calibration equation | *r* | MDL, ng/g |
|---|---|---|---|
| Omethoate | $y = (2.08x - 0.36)\ 10^4$ | 0.9987 | 0.14 |
| Dimethoate | $y = (4.09x - 0.27)\ 10^4$ | 0.9998 | 0.9 |
| Carbendazim | $y = (1.80x + 0.22)\ 10^5$ | 0.9999 | 0.6 |
| Propoxur | $y = (5.51x + 1.21)\ 10^4$ | 0.9993 | 0.13 |
| Thiabendazole | $y = (6.92x - 3.66)\ 10^4$ | 0.9934 | 0.15 |
| Carbaryl | $y = (1.81x + 0.24)\ 10^4$ | 0.9996 | 0.10 |
| Pirimicarb | $y = (9.45x + 0.85)\ 10^3$ | 0.9999 | 0.19 |
| Azinphos-methyl | $y = (2.54x + 0.34)\ 10^4$ | 0.9999 | 0.07 |
| Methidathion | $y = (9.99x + 1.84)\ 10^3$ | 0.9997 | 0.16 |
| Iprodione | $y = (1.22x + 0.80)\ 10^4$ | 0.9999 | 0.20 |

**Table 5. Results of analysis of commercial samples of different brands (A–E)**

| | Residue found, ng/g[a] | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Peach juice | | | | Apricot juice | | | | Pear juice | | | | Apple juice | | | | Pineapple juice | | | |
| Pesticide | A | B | C | D[b] | A | B | C | D[b] | E[b] | A | B | C | D[b] | A | B | C | D[b] | E[b] | A | B | E[b] |
| Omethoate | ND[c] | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | <EQL[d] | ND | ND | ND | ND | ND | <EQL | 6.5 | ND |
| Dimethoate | ND | ND | 0.8 | 0.9 | ND | 0.5 | 0.7 | 1.2 | ND | ND | ND | ND | 1.1 | ND | ND | 1.5 | 2.0 | ND | 0.5 | 0.5 | ND |
| Carbendazim | 12.1 | 43.2 | 25.6 | ND | 6.9 | 19.3 | 15.1 | 0.7 | <EQL | 0.8 | 1.9 | 2.1 | <EQL | 24.9 | 37.3 | 48.1 | 1.6 | ND | ND | 3.3 | ND |
| Propoxur | ND | ND | ND | 1.3 | ND | ND | ND | 0.7 | ND | ND | ND | ND | <EQL | ND | ND | ND | 1.9 | ND | 0.8 | 0.7 | ND |
| Thiabendazole | 1.8 | 1.3 | 2.1 | 3.3 | ND | 0.9 | 2.2 | 14.3 | <EQL | 4.7 | 1.3 | 2.1 | <EQL | 81.3 | 113.2 | 131.2 | 1.1 | <EQL | 1.9 | 39.2 | <EQL |
| Carbaryl | 23.4 | 15.3 | 11.2 | 1.1 | ND | 4.1 | 3.4 | 4.1 | ND | 5.2 | 3.9 | 13.1 | 0.9 | ND | ND | ND | 1.2 | ND | ND | 3.6 | ND |
| Pirimicarb | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | 15.1 | ND | ND | ND | ND |
| Azinphos-methyl | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | 11.8 | ND | ND | ND | ND |
| Methidathion | 1.5 | ND | 4.3 | ND | ND | 1.1 | ND | 0.9 | ND | 2.1 | 4.5 | 7.2 | 1.0 | ND | ND | ND | 1.4 | ND | 0.9 | ND | ND |
| Iprodione | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND |

[a] Each value is the mean of 2 determinations.
[b] Product of biological agriculture.
[c] ND = not detected.
[d] EQL = estimated quantitation limit.

*perimental* section. This set of measurements was obtained by injecting into the LC column various known amounts of a composite working standard solution. Measurements were obtained in triplicate for each amount injected. The average peak area of each set of injections was plotted versus the amount injected, and the resulting plot indicated a good linear response from 0.1 to 20 ng injected.

Matrix-matched and solvent-based calibration solutions were prepared for several sample types (apple, peach, and apricot juices) for comparison in accordance with European Union guidelines for pesticide residue monitoring (15). Matrix-matched calibration solutions were prepared by adding suitable amounts of working standard solution to blank extracts over the analyte concentration range of interest, equivalent to 1–100 ng/g. Solvent-based calibration solutions were prepared by serial dilution of working standard solution with methanol–water (50 + 50, v/v).

The resulting calibration curves (obtained by the determination of 5 levels in triplicate) were essentially superimposable, showing that neither matrix-enhancement effect nor suppression occurred. Table 4 shows the calibration data obtained from matrix-matched solutions for the analytes.

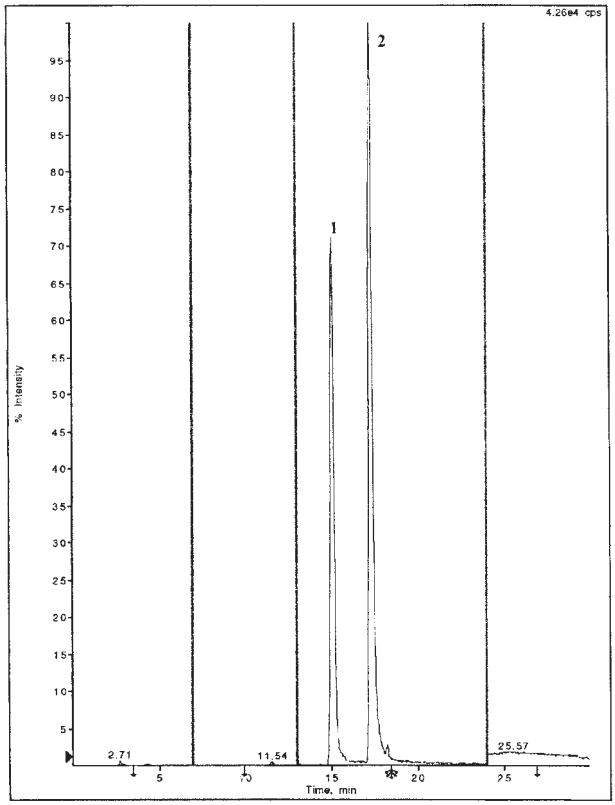


**Figure 3. SRM/LC/MS chromatogram obtained for an apple juice extract containing carbendazim at 24.2 ng/g (peak 1) and thiabendazole at 84.1 ng/g (peak 2).**

The slope, intercept, and correlation coefficient ($r$) were calculated by linear regression analysis.

### *Analytical Precision*

Intraday precision was determined by injecting into the LC column 50 μL composite working standard solution at 3 concentration levels (0.01, 0.05, and 0.2 ng/μL) in 5 replicates in 1 day. Interday precision was determined by measuring the same controls in duplicate for 5 days. Results from these measurements showed that the reproducibility of the method ranged between 5% (carbendazim) and 10% (iprodione).

### *Method Detection Limit*

For each analyte in each type of matrix, the method detection limit (MDL) was estimated in accordance with U.S. Environmental Protection Agency guidelines (16). The MDL was determined by multiplying the appropriate 1-sided 99% $t$-statistic by the standard deviation obtained by analysis of 3 matrix samples spiked at 1 ng/g. The estimated quantitation limit was defined as 5 times the MDL. Results are reported in Table 4, which shows that the method is suitable for determination of the analytes at very low concentrations.

### *Analysis of Samples*

The optimized analytical procedure was used to analyze fruit juices obtained from local markets. As shown in Table 5, residues of pesticides were found in 18 of the 21 sets of samples analyzed. Carbendazim, thiabendazole, carbaryl, and dimethoate were frequently present; omethoate, propoxur, azinphos-methyl, and methidathion were found occasionally. Pirimicarb was found in only one sample, and iprodione was always below the MDL. Figure 3 shows an SRM/LC/MS chromatogram for an apple juice sample in which carbendazim and thiabendazole were found.

## Conclusions

The MSPD extraction has been shown to be simple and very efficient in the determination of all the monitored pesticides; it is particularly suitable for routine analysis of many samples because of its rapidity and reproducibility. The time necessary for the extraction, including the evaporation step, is about 30 min. The LC/MS/MS analysis has shown very high sensitivity and confirmatory power, necessary requirements for trace quantitation of pesticide residues in complex matrixes. Moreover, the proposed analytical method, by the selectivity of tandem MS, is able to avoid a tedious and solvent-consuming cleanup step.

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