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Research Article

# DETERMINATION OF RESIDUAL DIMETHOATE IN TOMATO USING CAPILLARY GAS CHROMATOGRAPHIC ANALYSIS WITH ELECTRON CAPTURE DETECTION

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**ABSTRACT**

Pesticide Dimethoate (Di) residue from tomato samples with acetone followed by ethylacetate:hexane (90:10,v/v) were extracted. Analytical screening was by GC-ECD using capillary column type Trb-1. The effect of spraying time on residual Di in tomato samples was studied as the follows: *I- Morning spraying at 08.00; II- Afternoon spraying at 17.00; III- Night spraying at 21.00.* The samples were accumulated after 2 h, 12 h, 24 h (1 day), 2, 3, 4, 5, 6, 8 and 10 days (Di was extracted after well washing tomato fruits). Fortification times, (when $m_{Di} \leq 500$ ppb in tomato), were 105, 116 and 132 h after spraying for I, II and III, respectively. It was found that, the morning spraying is the best. Linearity for determination of pesticide Di from tomato samples was at levels of 25-1500 ng.mL$^{-1}$ (ppb in tomato), with relative standard deviations (RSD) does not exceed 4.8%. The average recoveries were 94.0 to 97.5%. Detection and quantification limits were 3.72 and 11.28 ng.mL$^{-1}$ (ppb in tomato), respectively. The method proved to be selective, sensitive, and with good precision and recovery rates. The method was accredited according to UNE-EN ISO/IEC 17025:2005 international standard.

**Keywords:** Tomato, Pesticide residues Dimethoate, Spraying time, GC– ECD.

## INTRODUCTION

Dimethoate is phosphorous pesticide, mol. mass 229.3 g/mol, molecular formula $(CH_3O)_2P(S)SCH_2C(O)NHCH_3$; $C_5H_{12}NO_3PS_2$, storage temperature +4$^oC$ [1].

Pesticide residues were determined by gas chromatography with mass selective detector (GC–MSD) in 240 samples of fresh fruit and vegetables. Sample extract was cleaned up using gel permeation chromatography (GPC). In 66.7% of the samples no residues were found, 25.8% of samples contained pesticide residues at or below MRL, and 7.5% of samples contained pesticide residues above MRL [2].

Pesticide residues from crop samples with acetone followed by dichloromethane partitioning were extracted. Crop extracts were cleaned-up by gel permeation chromatography equipped. Analytical screening was by gas chromatography using long, narrow-bore fused-silica open-tubular columns equipped with electron-capture detection (ECD). Recoveries of majority of pesticides from spiked samples of carrot, melon and tomato at fortification levels of 0.04-0.10 mg/kg ranged from 70 to 108% [3].

Tomato plants were subjected to a single chemical treatment, when fruits were close to ripeness, by applying pesticides at the doses recommended by the manufacturers. The pesticide residues were extracted using acetone and dichloromethane as solvents and determined by gas (benalaxyl and chlorothalonil) and liquid (methomyl) chromatography. This finding indicates the need for careful control of the spraying doses of this fungicide, in particular on varieties of tomato which are used fresh [4].

The various stages in the determination of pesticide residues in fruit and vegetables were discussed. The merits of the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) technique and two-dimensional gas chromatography were determined [5].

The single-drop microextraction (SDME) technique coupled with GC-NPD and GC-ECD was evaluated for the determination of multi-class pesticides in vegetables. The optimum sample preparation was achieved with the use of a mixture of acetone:$H_2O$ (10:90, v/v) in donor sample solution preparation and the consequent SDME using a toluene drop under mild stirring for 25 min. The efficiency of the extraction process was studied in fortified tomato and courgette samples and matrix effects were further estimated [6].

A simple and low cost method, based on solid–liquid extraction with low temperature purification (SLE–LTP), was optimized and validated for the determination of some pesticides in tomato samples. The analyses were performed by the GC–ECD and confirmed by the GC–MS. The method requires 4 g of tomato and an extraction mixture (8.0 mL acetonitrile, 0.5 mL water and 1.5 mL ethyl acetate), which was established by mixture experimental design. After optimization, pesticide recovery rates ranged from 79% to 97%, with a standard deviation of less than 5% [7].

An appropriate control of Pesticides residues in food samples has to be operated. In this study 105 pesticides with GC/SQ-MS and 46 pesticides with HPLC/IT-MS after extraction in four matrices (grape, lemon, onion and tomatoes) were analysed [8].

An alternative to conventional capillary gas chromatography (GC) is evaluated as a new approach to determine pesticide residues in vegetables. Low-pressure gas chromatography–tandem mass spectrometry (LP-GC–MS–MS) is proposed after a fast and simple extraction of the vegetable samples with dichloromethane and without clean up. The use of the above-mentioned GC technique reduced the total time required to determine 72 pesticides to less than half the present time (31 min), increasing the capability of a monitoring routine laboratory [9].

A new extraction and purification method for high sensitive determination four pesticides, Dimethoate (Di), Chlorpyrifos-ethyl (CPE), Deltamethrin (Del) and Cypermethrin (Cyp) from vegetables was developed. The method involves the extraction of samples with acetone and ethylacetate:hexane (95:5,v/v) mixture, purification using Florisil cartridges at optimum eluting ratio of 5% acetone in hexane, then followed by gas chromatography using electron capture detection (ECD). Under the optimized condition, the recovery of the pesticides from vegetables reach the range of (80–112%) with RSD of 6.5% (n= 3), the limit of detection for Di, CPE, Cyp, and Del, were 1.00, 0.96, 1.30, and 1.90 ng.mL$^{-1}$, and the limit of quantification was 3.3, 2.9, 3.9, and 5.8 ng.mL$^{-1}$, respectively. The method was applied successfully for the determination of pesticides in some local vegetable contamination [10].

A special attention is given to the substances that can compromise food safety, such as pesticide [11]. The analytical method involves several steps, such as sampling, sample preparation, separation, detection and data analysis [12].

Some methods involve the use of solid-phase extraction cartridges when using acetonitrile for the extraction of pesticide residues from fruits and vegetables [13]. Twenty-eight phosphorous insecticides utilizing a gas chromatography analysis technique after acetone and

benzene mixture extraction and silica catridges cleaning up were determined [14].

Forty-eight phosphorous insecticides were extracted with methanol:dichloromethane (1:9), followed by cleaned up step using solid phase excretion with gel permeation chromatography and silica gel mini columns [15]. Direct injection of food extract into an online solid phase excretion using a strong cation-exchange resin for determination of some pesticides was applied [16]. The main methods for the determination of pesticides in nonfatty food samples have been employed recently [17-20].

The aim of the present work was to develop a rapid and accurate method to determine Di pesticide in trial testing of tomato samples using GC-ECD analysis and actual definition fortification times of pesticide after spraying. The paper describes a simple and effective procedure for sample extraction using acetone followed by ethylacetate:hexane (90:10,v/v).

## MATERIALS AND METHODS

### Apparatus

A Shimadzu GC version 2010 gas chromatography with an electron capture detector (ECD) was used. Capillary column (30 m, 0.32 mm i.d. with a 0.25 µm film thickness) type Trb-1 was performed on Teknokroma Co. The injector and the detector temperature were at 250°C and 300°C, respectively. The carrier gas was Nitrogen (99.999%), with rate 6 mL/min. Programmed column temperature: 100°C one min, then to 300°C with increasing temperature rate 10°C/min. The injection volume of samples was 1 µL.

### Reagents and chemicals

Reagent-grade chemicals were of the highest purity available from their sources. Acetone, ethylacetate, hexane, anhydrous sodium sulfate and sodium chloride were purchased from the Merck Company. The pesticide standard of Dimethoate (Di) was of 99.4% purity supplied from Riedel-de Haen. A stock solution of Dimethoate (1000 µg.mL$^{-1}$) was prepared in acetone. Working solutions of Di were prepared daily by diluting the stock solution within the concentration range of 25-1500 ng.mL$^{-1}$. An internal standard of 1-Chloro-4-fluorobenzene (98.0%) from the Aldrich was used.

### A stock solution of Dimethoate (Di)

An accurately weighed 25.15 mg standard sample of Di (99.4%) was dissolved in acetone, transferred into a 25 mL standard flask and diluted to the mark with acetone to obtain 1000 µg.mL$^{-1}$ of Di, 0.250 mL from this solution diluted with acetone to 100 mL ( 2500 ng.mL$^{-1}$ of Di) stock solutions of Di.

### A stock solution of internal standard

An accurately weighed 25.51 mg standard sample of internal standard (1-Chloro-4-fluorobenzene, 98.0%) was dissolved in acetone, transferred into a 25 mL standard flask and diluted to the mark with acetone to obtain 1000 µg.mL$^{-1}$ of internal standard, then 0.100 mL from this solution diluted with acetone to 100 mL (1000 ng.mL$^{-1}$ of internal standard) stock solutions of internal standard.

### Standard solutions

Volumes 0.100, 0.200, 0.400, 0.600, 0.800, 1.000, 2.000, 3.000, 4.000, 5.000 and 6.000 mL from stock solution Di and 0.500 mL from stock solution of internal standard (for each one) were transferred into volumetric flasks (10 mL), respectively, then completed to the mark with acetone (these solutions content: 25, 50, 100, 150, 200, 250, 500, 750, 1000, 1250 and 1500 ng.mL$^{-1}$ of Di with 50 ng.mL$^{-1}$ of internal standard, respectively).

### Procedure (Pesticide extraction from tomato)

Tomato samples of 20 pieces of grown fruits (from different places of tomato open field trials) were well washed and cut each one and well stirred, then accumulated and mixed, finally taken 10 g (as sample). The samples or standard average recovery solutions of indicated pesticide were prepared with adding 0.0 (blank), 0.100, 0.200, 0.400, 0.600, 0.800, 1.000, 2.000, 3.000, 4.000, 5.000 and 6.000 mL from stock solution Di (0.0, 0.25, 0.50, 1.00, 1.50, 2.00, 2.50, 5.00, 7.50, 10.00, 12.50 and 15.00 µg of Di) to 10 g sample, then adding 100 mL acetone and stirred to homogenize for 5 min, filtrated using 5A (541) filter paper, after that the resulting filtrates were then mixed with 100 mL NaCl 20% (w/v) and subjected to purification extraction process with 50 mLx2 batches (100 mL the final volume) of ethylacetate:hexane 90:10, v/v. The organic extracted phase was then filtered on 5A (541) filter paper after moisture absorption using 10 g of anhydrous sodium sulfate. The filtrate was then evaporated using rotary evaporator with a temperature less than 40°C to dryness and the residue dissolved again with acetone and transferred into volumetric flasks (10 mL), added internal standard of 1-Chloro-4-fluorobenzene 500 ng (0.500 mL from stock solutions of internal standard) for each flask, then the volume was made to 10 mL using the same solvent to give the pesticide extract (measure solutions).

## RESULTS AND DISCUSSION

### Optimum parameters for determination of residual Di in tomato

The optimum parameters established for determination of residual Di in tomato using capillary GC- ECD showed in Table 1.

**Table 1: The optimum parameters established for determination of residual Di in tomato using capillary GC- ECD.**

| Parameters | Operating modes |
|---|---|
| Capillary column, type Trb-1 | 30 m 0.32 mm i.d. with a 0.25 µm film thickness |
| Solvent for Di and internal standard | Acetone |
| Extraction solvent | Acetone followed by ethylacetate:hexane (90:10,v/v) |
| Carrier gas | Pure $N_2$ (99.999%) |
| Rate of carrier gas | 6 mL/min |
| Detector temperature | 300°C |
| Injector temperature | 250°C |
| Programmed column temperature | 100°C one min, then to 300°C with increasing temperature rate 10°C/min |
| Injection volume of samples | 1 µL |
| Detector | Electron capture detector (ECD) |
| Extraction solvent | First step: 100 mL acetone<br>Second step: 50 mLx2 batches ethylacetate:hexane 90:10, v/v |
| Solvent for working sample | Acetone |
| Linearity range of Di concentration after extraction from tomato | 25-1500 ng.mL$^{-1}$ (25-1500 ppb in tomato) |
| Regression equation: | *y=0.00490x+0.0008 |
| Slope | 0.00490 |
| Intercept | 0.0008 |
| Correlation coefficient ( $R^2$) | 0.9997 |
| RSD% | 4.8% |
| LOD ( 3.3SD) | 3.72 ng.mL$^{-1}$ (ppb in tomato) |
| LOQ (10SD) | 11.28 ng.mL$^{-1}$ (ppb in tomato) |

| | |
|---|---|
| Linearity range of Di standard concentration in acetone | 25-1500 ng.mL$^{-1}$ |
| Regression equation: | *y=0.00521x+0.0003 |
| Slope | 0.00521 |
| Intercept | 0.0003 |
| Correlation coefficient ( $R^2$) | 0.9997 |
| RSD% | 3.20 |
| LOD (3.3SD) | 2.64 ng.mL$^{-1}$ |
| LOQ (10SD) | 8.00 ng.mL$^{-1}$ |

* y= Intensity, x= concentration of Di (ng.mL$^{-1}$ or ppb).

**Calibration curves**

The standard concentrations in acetone were in the range of 25–1500 ng.mL$^{-1}$. Fig. 1 show the chromatograms of standard solutions with internal standard of 1-Chloro-4-fluorobenzene 50 ng.mL$^{-1}$. The calibration curves were plotted by the ratio (S/Sa) of the peak area of Di (S) to the peak area of the internal standard (Sa), see Fig. 2, curve 1 and Table 2. The standard calibration curve after extraction Di from tomato samples showed in Fig. 2, curve 2 and Table 3, which were used for quantification of Di in subsequent experiments for different samples.

**Average recovery**

The solutions content 0.0 (blank), 25, 50, 100, 150, 200, 250, 500, 750, 1000, 1250 and 1500 ng.mL$^{-1}$ of Di in 10 g of tomato were extracted (as procedure **2.6.**). Di with internal standard 50 ng.mL$^{-1}$ was measured. The results indicate that, the average recovery was vary between 94.0-97.5%, see Table 4.

**Effect of spraying time**

The effect of spraying time on residual Dimethoate in tomato samples was studied as the follows: *I- Morning spraying at 08.00; II- Afternoon spraying at 17.00; III- Night spraying at 21.00.* The samples were accumulated after 2 h, 12 h, 24 h, 2 days, 3 days, 4 days, 5 days, 6 days, 8 days and 10 days. The pesticides were extracted using acetone followed by ethylacetate:hexane (90:10,v/v) as (**2.6.**) and measured by calibration curve after extraction (Fig. 2, curve 2) according the equation y=0.00490x+0.0008; where y: $S/S_a$ and x: concentration of Di ng.mL$^{-1}$ or ppb in tomato.

- **Morning spraying at 08.00:** Quantity of pesticide (Di) increase to 1142 ng.mL$^{-1}$ until 24 h after spraying (from 960 to 1142 ng.mL$^{-1}$), then sharply decrease to 445 ng.mL$^{-1}$ until 120 h (5 days), after that slowly decrease to 252 ng.mL$^{-1}$ after 10 days, see Fig. 3 and Table 5.
- **Afternoon spraying at 17.00:** Quantity of pesticide (Di) increase to 1100 ng.mL$^{-1}$ until 36 h after spraying (from 910 to 1100 ng.mL$^{-1}$), then sharply decrease to 483 ng.mL$^{-1}$ until 120 h (5 days), after that slowly decrease to 304 ng.mL$^{-1}$ after 10 days, see Fig. 3 and Table 5.
- **Night spraying at 21.00:** Quantity of pesticide (Di) increase to 960 ng.mL$^{-1}$ until 48 h (2 days) after spraying (from 640 to 960 ng.mL$^{-1}$), then sharply decrease to 530 ng.mL$^{-1}$ until 148 h (≈6 days), after that slowly decrease to 252 ng.mL$^{-1}$ after 10 days, see Fig. 3 and Table 5.

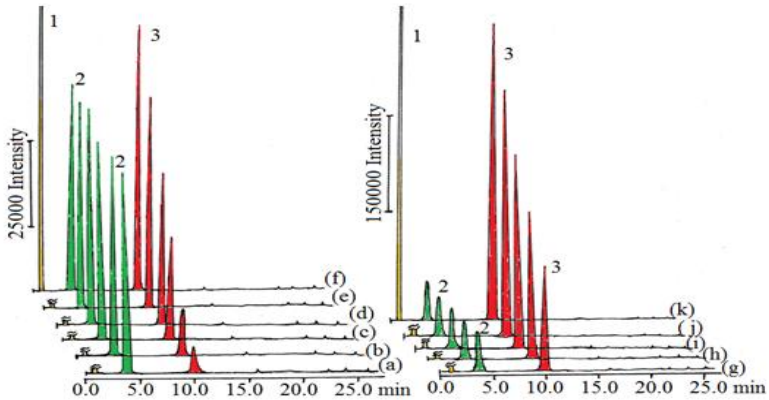


**Fig. 1: Chromatograms of Dimethoate (3) in standard solutions in acetone for standard concentrations: a- 25, b- 50, c- 100, d- 150, e- 200, f- 250, g- 500, h- 750, 1000, j- 1250 and k- 1500 ng.mL$^{-1}$(1- Acetone, 2- Internal standard of 1-Chloro-4-fluorobenzene 50 ng.mL$^{-1}$).**

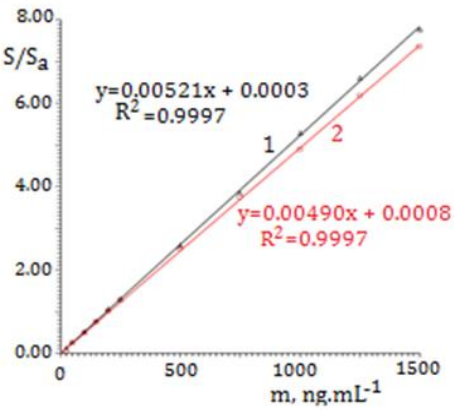


**Fig. 2: Calibration curves of GC- ECD determination Di in standard solutions (1) and standard solutions in tomato samples after extraction (2) by the ratio S/ $S_a$ (S- the peak area of Di and $S_a$ - the peak area of the internal standard).**

**Table 2: GC- ECD determination of Di in acetone standard solutions at various concentrations (n= 5, t=2.776)..**

| Taken standard m, ng.mL$^{-1}$ | Found $\overline{m} \pm$ SD, ng.mL$^{-1}$ | $\frac{SD}{\sqrt{n}}$, ng.mL$^{-1}$ | $\overline{m} \pm \frac{t.SD}{\sqrt{n}}$, ng.mL$^{-1}$ | RSD% |
|---|---|---|---|---|
| 25.0 | 25.1±0.80 | 0.36 | 25.1±0.99 | 3.20 |
| 50.0 | 49.6±1.49 | 0.67 | 49.6±1.85 | 3.01 |
| 100.0 | 101.3±2.93 | 1.31 | 101.3±3.64 | 2.90 |
| 150.0 | 147.5±4.13 | 1.85 | 147.5± 5.13 | 2.82 |
| 200.0 | 204.7±5.53 | 2.47 | 204.7±6.87 | 2.71 |
| 250.0 | 251.2±6.53 | 2.92 | 251.2±8.11 | 2.60 |
| 500.0 | 498.8±11.97 | 5.35 | 498.8±14.86 | 2.42 |
| 750.0 | 738.7±16.99 | 7.60 | 738.7±21.09 | 2.32 |
| 1000.0 | 1017.0±23.49 | 10.50 | 1017.0±29.16 | 2.31 |
| 1250.0 | 1270.4±29.73 | 13.29 | 1270.4±36.91 | 2.34 |
| 1500.0 | 1493.0±41.80 | 18.69 | 1493.0±51.89 | 2.80 |

**Table 3: GC- ECD determination of Di in tomato samples at various standard concentrations with acetone followed by ethylacetate:hexane (90:10,v/v) as extraction solvent (n= 5, t=2.776).**

| Taken concentration, ng.mL$^{-1}$ (in solution) or ppb in tomato | Found concentration, ng.mL$^{-1}$ (in solution) or ppb in tomato | SD, ng.mL$^{-1}$ (or ppb) | $\frac{SD}{\sqrt{n}}$, ng.mL$^{-1}$ (or ppb) | $\overline{m} \pm \frac{t.SD}{\sqrt{n}}$, ng.mL$^{-1}$ (or ppb) | RSD% |
|---|---|---|---|---|---|
| 25.0 | 23.5 | 1.1 | 0.49 | 23.5±1.4 | 4.8 |
| 50.0 | 47.4 | 2.2 | 0.98 | 47.4±2.7 | 4.7 |
| 100.0 | 95.8 | 4.2 | 1.88 | 95.8±5.2 | 4.4 |
| 150.0 | 145.1 | 6.1 | 2.73 | 145.1± 7.6 | 4.2 |
| 200.0 | 194.2 | 8.0 | 3.58 | 194.2±9.9 | 4.1 |
| 250.0 | 243.8 | 9.0 | 4.02 | 243.8±11.2 | 3.7 |
| 500.0 | 479.8 | 17.3 | 7.74 | 479.8±21.5 | 3.6 |
| 750.0 | 719.7 | 25.9 | 11.58 | 719.7±32.2 | 3.6 |
| 1000.0 | 940.4 | 35.7 | 15.97 | 940.4±44.3 | 3.8 |
| 1250.0 | 1186.1 | 49.8 | 22.27 | 1186.1±61.8 | 4.2 |
| 1500.0 | 1412.6 | 66.4 | 29.69 | 1412.6±82.4 | 4.7 |

**Table 4: Average recovery of residual Dimethoate in tomato samples at various standard concentrations using capillary GC- ECD analysis with acetone followed by ethylacetate: hexane (90:10,v/v) as extraction solvent (n= 5).**

| Taken concentration, ng.mL$^{-1}$ (in solution) or ppb in tomato | Average recovery%, $\overline{x}$ ± SD | RSD% |
|---|---|---|
| 25.0 | 94.0±4.5 | 4.8 |
| 50.0 | 94.7±4.5 | 4.7 |
| 100.0 | 95.8±4.2 | 4.4 |
| 150.0 | 96.7±4.1 | 4.2 |
| 200.0 | 97.1±4.0 | 4.1 |
| 250.0 | 97.5±3.6 | 3.7 |
| 500.0 | 96.0±3.5 | 3.6 |
| 750.0 | 96.0±3.5 | 3.6 |
| 1000.0 | 94.0±3.6 | 3.8 |
| 1250.0 | 94.9±4.0 | 4.2 |
| 1500.0 | 94.2±4.4 | 4.7 |

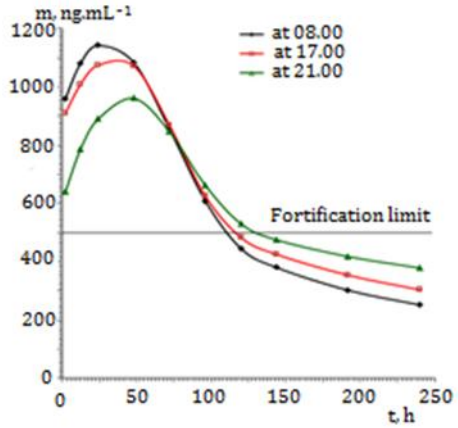


**Fig. 3: Effect of spraying time (at 08.00, 17.00 and 21.00 h) on quantity of residual Dimethoate in tomato samples using GC analysis (t,h- is sampling time after spraying by hour ).**

**Method validation**

Linear equations are presented in Table 4, showing high correlation coefficient with values more than 0.9997 (n = 5). The limit of detection (LOD) and the quantification limit (LOQ) for Di in standard solutions were 2.64. and 8.00 ng.mL$^{-1}$, respectively , and in extraction solution from tomato were 3.72 and 11.28 ng.mL$^{-1}$ or ppb, respectively. The recovery of the pesticide from tomato was within the range (94.0–97.5%) with RSD = 4.8% (n = 5). The average student's t-test values is 2.51 and the average student's F-test values is 1.51 [4, 10, 21] (the tabulated t-value and F-value are 2.776 and 6.39, respectively, for the 95% confidence level and n =5 [21]), The t-test and F-test could not detect any systematic error and proved accuracy of the proposed method. The method was accredited according to UNE-EN ISO/IEC 17025:2005 international standard [22].

**CONCLUSION**

Analytical GC-ECD determination of pesticide Dimethoate (Di) residue from tomato samples witch extracted using acetone followed by ethylacetate:hexane (90:10,v/v) with capillary column type Trb-1 was applied. The effect of spraying time (*I- Morning spraying at 08.00; II- Afternoon spraying at 17.00; III- Night spraying at 21*.00) on residual Dimethoate in tomato samples was studied. It was found that, the best spraying time is *Morning spraying* and the fortification time is 105 h. . Linearity for determination of pesticide (Di) from tomato samples at levels of 25-1500 ng.mL$^{-1}$ (ppb in tomato), with relative standard deviations does not exceed 4.8%. The average recoveries (n = 5) were 94.0 to 97.5%. The method proved to be selective, sensitive, and with good precision and recovery rates. The method was accredited according to UNE-EN ISO/IEC 17025:2005 international standard.

**Table 5: Effect of spraying time on residual Dimethoate in tomato samples using capillary GC analysis (n= 5, t=2.776).**

| Spraying time | Measurement time after spraying, h | Found $\overline{m} \pm$ SD, ppb | $\frac{SD}{\sqrt{n}}$, ppb | $\overline{m} \pm \frac{t.SD}{\sqrt{n}}$, ppb | RSD% |
|---|---|---|---|---|---|
| Morning spraying at 08.00 | 2 | 960±30.5 | 13.7 | 960±37.9 | 3.18 |
| | 12 | 1090±34.3 | 15.4 | 1090±42.6 | 3.15 |
| | 24 | 1142±35.6 | 15.9 | 1142± 44.2 | 3.12 |
| | 48 | 1084±34.2 | 15.3 | 1084±42.4 | 3.15 |
| | 72 | 854±27.2 | 12.2 | 854±33.8 | 3.19 |
| | 96 | 608±19.5 | 8.7 | 608±24.2 | 3.21 |
| | 120 | 445±14.4 | 6.5 | 445±17.9 | 3.24 |
| | 144 | 390±12.7 | 5.7 | 390±15.7 | 3.25 |
| | 192 | 302±9.9 | 4.4 | 302±12.3 | 3.28 |
| | 240 | 252±8.3 | 3.7 | 252±10.4 | 3.31 |
| Afternoon spraying at 17.00 | 2 | 910±29.0 | 13.0 | 910±36.0 | 3.19 |
| | 12 | 1008±32.0 | 14.3 | 1008±39.7 | 3.17 |
| | 24 | 1075±33.9 | 15.1 | 1075±42.0 | 3.15 |
| | 48 | 1072±33.8 | 15.1 | 1072± 41.9 | 3.15 |
| | 72 | 868±27.7 | 12.4 | 868±34.4 | 3.19 |
| | 96 | 625±20.1 | 9.0 | 625±24.9 | 3.21 |
| | 120 | 483±15.7 | 7.0 | 483±19.4 | 3.24 |
| | 144 | 437±14.2 | 6.5 | 437±17.6 | 3.25 |
| | 192 | 354±11.5 | 5.2 | 354±14.3 | 3.26 |
| | 240 | 304±10.0 | 4.5 | 304±12.4 | 3.28 |
| Night spraying at 21.00 | 2 | 640±20.5 | 9.2 | 640±25.5 | 3.21 |
| | 12 | 760±24.3 | 10.9 | 760±30.2 | 3.20 |
| | 24 | 912±29.0 | 13.0 | 912±36.0 | 3.18 |
| | 48 | 961±30.4 | 13.9 | 961± 37.7 | 3.16 |
| | 72 | 846±27.0 | 12.1 | 846±33.5 | 3.19 |
| | 96 | 662±21.2 | 9.5 | 662±26.3 | 3.20 |
| | 120 | 530±17.1 | 7.6 | 530±21.2 | 3.22 |
| | 144 | 480±15.6 | 7.0 | 480±19.3 | 3.24 |
| | 192 | 418±9.5 | 4.2 | 418±11.7 | 2.26 |
| | 240 | 379±8.6 | 3.9 | 379±10.7 | 2.27 |

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