*World Journal of Analytical Chemistry, 2025, Vol. 10, No. 2, 48-57*
Available online at http://pubs.sciepub.com/wjac/10/2/2
Published by Science and Education Publishing
DOI:10.12691/wjac-10-2-2

# Detection and Quantification of 12 Multiclass Pesticides in Dates Fruit Consumed in the UAE

**Afnan Wael Ibrahim Alanqar, Mohammed A. Meetani***

Department of Chemistry, United Arab Emirates University, AlAin, UAE
*Corresponding author: mmeetani@uaeu.ac.ae

*Received October 10, 2025; Revised November 12, 2025; Accepted November 20, 2025*

**Abstract** Date palms (Phoenix dactylifera) are among the top trees cultivated in the UAE, and dates are one of the most consumed fruits. Due to the high demand and to secure production, dates farmers depend on the application of various types of chemicals, including pesticides, insecticides, fungicides, and herbicides. These chemicals find their way into water, soil, and air,ultimately affecting the plant parts, including date fruits. Contamination of date fruit with levels higher than the threshold (Maximum Residue Levels (MRL)) poses a risk to the consumers' health. In this work, a new method was developed for quantifying the levels of 12 multiclass pesticides in 26 date samples using QuEChERS sample preparation technique followed by LC-(+ESI)-MS/MS. The presence of carbosulfan pesticide was evident in all samples and was determined at levels exceeding the MRL value (10 µg/kg) in 15 out of 26 samples. Azoxystrobin and EPN were also detected above their MRL (10 µg/kg) in two and one sample, respectively. Metalaxyl was found at a concentration which is almost 5 times its MRL (50 µg/kg) in one sample. Chlorpyrifos and Phenthoate, each in a different sample, reached high concentrations of 9.1136 µg/kg, and 7.8062 µg/kg respectively, but did not reach the threshold limit of 10 µg/kg. All the other six pesticides (Thiophanate-methyl, Tribnuron-methyl, Fluazip-p-butyl, Dimethoate, Pirimiphos-methyl, and Triazophos) were found to be at low concentration levels, much below their MRLs. This study indicates the need for increasing awareness among farmers on safer practices regarding the application of agricultural chemicals and more stringent monitoring and enforcement of the relevant laws.

***Keywords:*** *LC –ESI (+) –MS/MS, Multi-class Pesticides, Dates, QuEChERS*

**Cite This Article:** Afnan Wael Ibrahim Alanqar and Mohammed A. Meetani, "Detection and Quantification of 12 Multiclass Pesticides in Dates Fruit Consumed in the UAE." *World Journal of Analytical Chemistry*, vol. 10, no. 2 (2025): 48-57. doi: 10.12691/wjac-10-2-2.

## 1. Introduction

In the UAE, date fruits are among the most important crops, providing substantial economic advantages. The UAE is a leading global exporter and importer of dates in both quantity and value. In 2010, the UAE topped the world in date exports with 237,898 metric tons and imports with 227,726 metric tons [1]. Also, a pilot study conducted in 2010 -that concerned UAE Al Ain citizens' consumption patterns of dates revealed that the average consumption of dates is 8 dates daily per person [2]. The increase in demand due to population growth led to dependence on various pesticides to safeguard date produce.

A key issue with extensive pesticide application is the potential contamination of dates with their residues, which poses a risk to human health. Adverse health effects of exposure to pesticides include, but are not limited to, cancer, diabetes, endocrine disruption [3] neurological deficits, and respiratory disorders [4].

In the UAE, a federal law for setting the maximum residue limits (MRL) of pesticides allowed in food products and animal feed was established [5]. MRL is defined as the maximum allowable limits below which pesticide residue in food products does not pose a concern to human health [6]. Second, the Ministry of Environment and Water, also, Abu Dhabi Food Control Authority (ADFCA) together assume the responsibility of controlling the pesticide residues in all imported and locally produced food products [7].

Due to the advantages of specific, high sensitivity, and accurate measurements of levels that satisfy regulatory requirements, chromatography coupled to mass spectrometric methods is, most of the time [3,4,6,8,9] [10,11,12,13] the technique of choice for the detection and quantification of pesticides in dates. While LC-MS/MS was used for polar pesticides in most studies, GC-MS/MS proved superior when volatile, low boiling point, and non-polar pesticides were studied, as it offered higher sensitivity.

QuEChERS is a modern and well-established sample preparation method originally developed by Anastassiades and Lehotay for the extraction of pesticides from fruits and vegetables [14]. It involves two key steps: the first step utilizes salting-out partitioning for extraction, while the second step is a clean-up step. In the clean-up step, dispersive solid-phase extraction (dSPE) is applied with

an appropriate sorbent for further purification. This sample preparation technique has several advantages over other techniques, especially when used for pesticide analysis, including high recovery over a broad range of pesticides with different polarities, robustness, high accuracy and precision, the need for readily available lab sample preparation equipment (centrifuge and vortex) in addition to being a relatively cheap and environmentally friendly technique [6].

Two studies were conducted in the UAE for the determination of pesticides in dates. A study by Abdul Majeed and his team analyzed the levels of 343 pesticides in imported dates to the UAE using (LC–ESI (+)-MS/MS) and (QuEChERS) sample preparation technique [8]. The other study was conducted by R. Morsi et al., where both UHPLC-MS/MS method and the QuEChERS sample preparation technique were used. In Morsi's work, 14 different carbamates were measured in 55 samples, and carbamate residue levels were compared to their respective MRLs [9]. In the first study, samples were collected from date imports only. In the second study, samples were collected both from supermarkets and farms within the UAE; however, only one group of pesticides was considered [9]. A multi-residue LC-MS/MS method is needed to determine the concentration of the commonly applied pesticides within the UAE in dates available both in local farms and supermarkets. To the author's knowledge, no multi-class pesticide determination work has been done on the dates of the UAE from both markets and date farms.

# 2. Material and Methods

## 2.1. Sample collection

The total number of samples collected is 26. 17 out of 26 date fruit samples (samples No. 2,4,5,12,13,14, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26) were collected from farms and local date markets in different locations within the UAE. The remaining 9 samples (samples No. 1,3,6,7,8,9,10,11,15) were branded date fruit samples collected from supermarkets. Out of the branded samples, two are produced in the KSA and consumed in the UAE. The remaining 7 market samples are produced locally. Sample 11 served as a blank for recovery studies since the number and quantity of pesticides detected in the sample were considerably low.

## 2.2. Chemicals and Reagents

HPLC grade acetonitrile and methanol procured from Honeywell (Seelze, Germany) were used. Ultrapure water was produced using the Milli-Q Plus system (MilliporeSigma, USA). Ammonium formate, sodium chloride (NaCl), anhydrous magnesium sulfate (MgSO4) and acetic acid were supplied by Sigma-Aldrich (St. Louis, MO, USA). Millex® PTFE syringe filters were purchased from Merck Millipore (Carrigtwohill, Ireland). pesticide standards and internal standards (IS) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Bond Elute® 15 ml QuEChERS dispersive solid-phase extraction (d-SPE) kits (Pig and Fats, AOAC, W/CH) provided by Agilent Technologies Inc. (Wilmington, DE, USA).

## 2.3. Standards

The selected pesticides are among the commonly imported pesticides to the UAE, as identified by Kaakeh and coworkers [15]. These pesticides are Pirimiphos-methyl, Triazophos, Phenthoate, Dimethoate, Chlorpyrifos, carbosulfan, Metalaxyl, Thiophanate-methyl, Azoxystrobin, Fluazifop-P-butyl, Tribenuron-methyl, and EPN. In addition, a list of isotopically labeled internal standards (Chlorpyriphos-d10, Dimethoate-d6, Carbofuran-D3, Etofenprox-d5, Triphenyl phosphate (TPP)) was selected such that for each pesticide family, one internal standard belonging to the same family is selected. Table 1 shows the selected internal standard against the corresponding pesticide.

**Table 1. The list of pesticides that were studied, their family, their use, and the internal standard belonging to the same family**

| Pesticides Name | Family | Pesticide Description | Internal Standard |
|---|---|---|---|
| pirimiphos-methyl | Organophosphorus | Insecticide | TPP |
| Triazophos | Organophosphate | | TPP |
| phenthoate | Organothiophosphate | Insecticides | Chlorpyriphos-d10 |
| Dimethoate | Organophosphate | | Dimethoate-d6 |
| chlorpyrifos | Organophosphate | | Chlorpyriphos-d10 |
| carbosulfan | Carbamate | | Carbofuran-D3 |
| Metalaxyl | Depsipeptides | fungicide | Chlorpyriphos-d10 |
| Thiophanate-methyl | Carbamate | | Carbofuran-D3 |
| Azoxystrobin | Strobin, Strobilurins | | Etofenprox-d5 |
| Fluazifop-p-butyl | Aryloxyphenoxy propionate | Herbicides | TPP |
| Tribenuron-methyl | sulfonylurea | | Tebuconazole-d5 |
| EPN | Organophosphorus | Insecticide | Dimethoate-d6 |

## 2.4. Instrumentation

LC-MS/MS (Shimadzu HPLC instrument (Nexera-i LC-2040C 3D, Kyoto, Japan) coupled to an 8045 Shimadzu triple-quadrupole LCMS (Kyoto, Japan) ) and Zorbax Extended-C18 4.6x250 mm 5µm columns were used. A centrifuge (HERMLE Benchmark Z 326K model from Labortechnik GmbH, Germany), a sample concentrator system (Stuart Cole Parmer, UK) fitted with a block heater (Stuart Cole Parmer, UK), and a single-tube vortex (JISICO, Korea) were also used.

## 2.5. Calibration Curves

Each pesticide was prepared by weighing the exact mass of individual pesticide standards in the range of 10-50 mg into a 10.0 mL dark vial. The weighted powder of pesticide was dissolved in a suitable solvent. A fresh working solution was prepared by proper dilution of the stock solutions using methanol to get 100 ppm. The 100 ppm solution was also diluted with methanol to reach 10 and 1 ppm for each pesticide. Second, six mixtures were prepared. MIX1 was prepared such that only pesticides were mixed to obtain 1.0 ppm for each pesticide in the

final mixture of all pesticides. Then, MIX1 was serially diluted to obtain the other five MIXs (MIX2, MIX3, MIX4, MIX5 and MIX6). Third, from each mixture, two levels of concentration are prepared, where internal standards are also included in fixed concentrations to obtain12 standards. The standards cover a calibration range from 0.000005 to 0.1 ppm with levels (0.000005, 0.000001, 0.00005, 0.00001, 0.0005, 0.0001, 0.005, 0.001, 0.05, 0.01, 0.5, 0.1) ppm (Please check Figure 1).

The twelve concentrations obtained from the six mixtures were analyzed on the LC-MS/MS and the calibration curves, one curve for each pesticide, were constructed by dividing the detected analyte signal by the signal of the internal standard and plotting against the standard concentrations. The calibration equations are summarized in Table 2 while Figure 2 demonstrates the calibration curve for one pesticide (chloropyrifos).

## 2.6. Sample Preparation (QuEChERS)

As for sample preparation, a similar QuEChERS procedure was employed by Morsi et al. First, date paste was formed by mixing 50 g of dates with 75 ml of deionized water and blending until it became homogeneous in a blender. Then, the blended material was divided and weighed into smaller portions of 10 g for each sample in a separate centrifuge tube. After that, extraction solvent (10 ml ACN with 10% acetic acid) and 100 µl internal standard were added. Each tube was vortexed and then left for one hour inside the fridge. After the incubation period, salts were added to each centrifuge tube (4 g MgSO4 and 1g NaCl) then each tube was vortexed for 3 minutes and centrifuged for 10 minutes at 4500 rpm and -5°C. The supernatant was collected and inserted into a QuEChERS dispersive kit centrifuge tube and gently inverted until the date pigment disappeared. The kit tubes were centrifuged for 10 minutes, and the supernatant was collected and dried in a stream of air. Finally, the dry samples were reconstituted with the mobile phase and filtered through PTFE syringe disks before analysis on the LC-MS/MS.

## 2.7. HPLC-MS Instrument Conditions

Positive (ESI) mode was employed for the detection and quantification of pesticide residues. The summary of operating parameters for electrospray method is depicted in Table 3.

The quantification method used was the internal standard calibration method utilizing isotopically labeled internal standard (ILIS) pesticides. For the analysis of all pesticides, a method was developed on the mass spectrometer using the multiple reaction monitoring mode (MRM). Table 4 summarizes MRM parameters, while Table 5 summarizes the LC parameters.

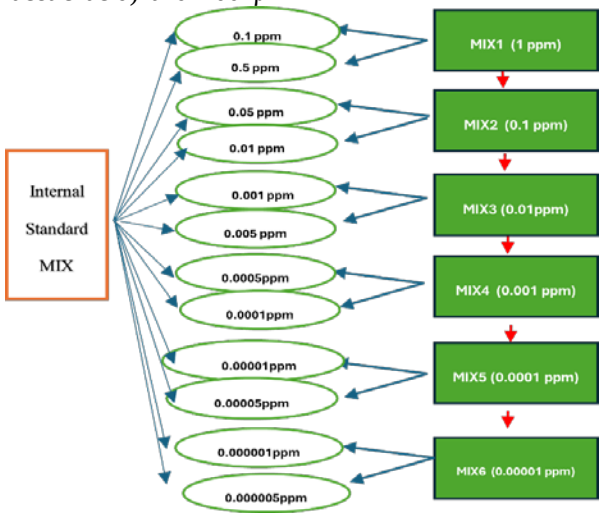


**Figure 1.** Illustration of sample preparation for constructing the calibration curves

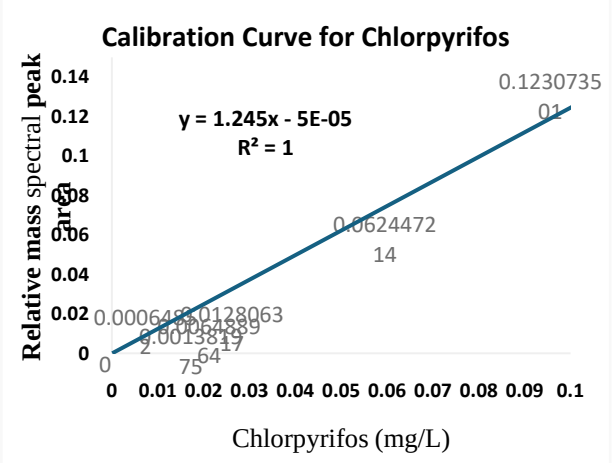


**Figure 2.** Calibration curve for chlorpyrifos

**Table 2. Summary of the equations for the calibration curves constructed for the 12 pesticides**

| # | Pesticid Name | Internal Standard | Calibration Equation | $R^2$ Value |
|---|---|---|---|---|
| 1 | Chlorpyrifos | Chlorpyrifos-D10 | y = 1.245x - 6E-05 | 1 |
| 2 | Phenthoate | Chlorpyrifos-D10 | y = 4.9892x + 0.0109 | 0.9997 |
| 3 | Dimethoate | Dimethoate-D6 | y = 1.2035x + 0.0019 | 0.9998 |
| 4 | Carbosulfan | Carbofuran-D3 | y = 0.1064x - 0.0004 | 0.9989 |
| 5 | Thiophanate-methyl | Carbofuran-D3 | y = 3.5133x - 0.0153 | 0.9992 |
| 6 | Azoxystrobin | Etofenprox-D5 | y = 10.718x + 0.0029 | 0.9995 |
| 7 | Metalaxyl | Chloropyrifos D10 | y = 13.177x + 0.0965 | 0.9922 |
| 8 | Fluazip-p-butyl | TPP | y = 2.9178x - 0.0008 | 0.9993 |
| 9 | Pirimiphos-methyl | TPP | y = 4.0538x - 0.0004 | 0.9992 |
| 10 | Triazophos | TPP | y = 3.2328x + 0.0015 | 0.9998 |
| # | Pesticid Name | Internal Standard | Calibration Equation | $R^2$ Value |
| 11 | EPN | Dimethoate-D6 | y = 0.7099x - 0.0039 | 0.9982 |
| 12 | Tribenuron-methyl | TPP | y = 1.0103x - 0.0009 | 0.9961 |

**Table 3. Summary of LC and MS operating parameters for electrospray method**

| LC Conditions | | | |
|---|---|---|---|
| Mobile Phase | B: ACN:MeOH (2:1) | Flowrate | 0.3 ml/min |
| | C: 10 mM ammonium formate in $H_2O$ | | |
| | D: MeOH | | |
| LC Conditions | | | |
| Sample injection Vol. | 10 µl | | |
| MS Conditions | | | |
| Interface | ESI | | |
| Nebulizer Gas | 3.0 (L/min) | DL Temperature | 250 $^0$C |
| Heating Gas Flow | 10 (L/min) | Block Temperature | 400 $^0$C |
| Interface Temperature | 300 $^0$C | Drying Gas | 10.0 (L/min) |
| Interface HV | 4.0 (KV) | Focus HV | 4.0 KV |
| Optimization Time | | | |
| Analysis Time | LC stop time, LC acquisition time, MS acquisition time: All 1 min | | |

**Table 4. Values for multi-reaction monitoring (MRM) mode for the 12 pesticides and the five internal standards**

| # | Chemical Name | Retention Time (min) | Precursor m/z | Product m/z | Collision Energy (V) |
|---|---|---|---|---|---|
| 1 | Dimethoate D6 | 14.124 | 236 | 131.05 | -21 |
| | | | 236 | 205.05 | -9 |
| | | | 236 | 131.05 | -21 |
| 2 | Dimethoate | 14.155 | 230.1 | 199.1 | -9 |
| | | | 230.1 | 125.05 | -21 |
| | | | 230.1 | 171 | -14 |
| 3 | Thiophanate-methyl | 14.963 | 343.1 | 151.1 | -19 |
| | | | 343.1 | 311.05 | -10 |
| | | | 343.1 | 268.15 | -11 |
| 4 | Carbofuran-D3 | 15.584 | 225.2 | 123.2 | -21 |
| | | | 225.2 | 165.25 | -13 |
| | | | 225.2 | 55.2 | -27 |
| 5 | Tribnuron-methyl | 16.112 | 396.2 | 155.3 | -14 |
| | | | 396.2 | 181.2 | -21 |
| | | | 396.2 | 364.15 | -11 |
| 6 | Azoxystrobin | 16.588 | 404.3 | 372.05 | -15 |
| | | | 404.3 | 344.15 | -25 |
| | | | 404.3 | 329.1 | -30 |
| 7 | Metalaxyl | 16.73 | 280.2 | 220.15 | -13 |
| | | | 280.2 | 192.25 | -17 |
| | | | 280.2 | 248.15 | -9 |
| 8 | Triazophos | 17.427 | 314.1 | 162.2 | -18 |
| | | | 314.1 | 119.1 | -34 |
| | | | 314.1 | 97 | -34 |
| 9 | Phenthoate | 18.156 | 321 | 247.05 | -10 |
| | | | 321 | 135.3 | -20 |
| | | | 321 | 79.15 | -43 |

| | | | | | |
|---|---|---|---|---|---|
| 10 | TPP | 18.393 | 327 | 77.2 | -40 |
| | | | 327 | 152.1 | -40 |
| | | | 327 | 215.05 | -26 |
| 11 | Pirimiphos-methyl | 18.972 | 306.1 | 108.1 | -31 |
| | | | 306.1 | 164.25 | -22 |
| | | | 306.1 | 67.15 | -43 |
| 12 | EPN | 19.150 | 324.2 | 296.05 | -13 |
| | | | 324.2 | 86.2 | -31 |
| | | | 324.2 | 157.05 | -21 |
| # | Chemical name | Retention time (min) | Precursor m/z | Product m/z | Collision Energy (V) |
| 13 | Fluazip-p-butyl | 19.539 | 384.2 | 282.15 | -20 |
| | | | 384.2 | 328.1 | -16 |
| | | | 384.2 | 91.15 | -35 |
| 14 | Chloropyrifos D10 | 21.331 | 362.1 | 99 | -33 |
| | | | 362.1 | 200.95 | -20 |
| | | | 362.1 | 131.1 | -21 |
| 15 | Chlorpyrifos | 21.471 | 351.9 | 200.05 | -18 |
| | | | 351.9 | 97 | -32 |
| | | | 351.9 | 125.1 | -20 |
| 16 | Etofenprox D5 | 24.845 | 399.35 | 182.4 | -15 |
| | | | 399.35 | 364.2 | -11 |
| | | | 399.35 | 140.2 | -27 |
| 17 | Carbosulfan | 25.055 | 381.3 | 118.15 | -20 |
| | | | 381.3 | 160.2 | -14 |
| | | | 381.3 | 76.2 | -36 |

**Table 5. Summary of method parameters**

| | | | |
|---|---|---|---|
| Column | Zorbax Extended-C18 4.6x250 mm 5µm | | |
| Mobile phase | -A: Washing Solution (IP, ACN, MeOH, Acetone)<br>-B: 10 mM Ammonium Formate in H2O (pH3)<br>-C: ACN : MeOH (2:1)<br>-D: pure MeOH | | |
| Mobile Phase flow rate | 0.3 ml/min | | |
| Oven Temperature | 45 $^{0}$C | | |
| Gradient | Time | Mobile Phase | Value (%) |
| | 0.1 | Solvent B Conc. | 80 |
| | 0.1 | Solvent C Conc. | 10 |
| | 0.1 | Solvent D Conc. | 10 |
| Gradient | 2.5 | Solvent B Conc. | 80 |
| | 2.5 | Solvent C Conc. | 10 |
| | 2.5 | Solvent D Conc. | 10 |
| | 5.0 | Solvent B Conc. | 20 |
| | 5.0 | Solvent C Conc. | 30 |
| | 5.0 | Solvent D Conc. | 50 |
| | 7.0 | Solvent B Conc. | 20 |
| | 7.0 | Solvent C Conc. | 30 |
| | 7.0 | Solvent D Conc. | 50 |
| | 7.0 | Solvent B Conc. | 20 |
| | 8.0 | Solvent B Conc. | 5 |
| | 8.0 | Solvent C Conc. | 25 |
| | 8.0 | Solvent D Conc. | 70 |
| | 10 | Solvent B Conc. | 5 |
| Gradient | 10 | Solvent C Conc. | 25 |
| | 10 | Solvent D Conc. | 70 |
| | 11.5 | Solvent B Conc. | 60 |
| | 11.5 | Solvent C Conc. | 35 |
| | 11.5 | Solvent D Conc. | 5 |
| | 14.0 | Solvent B Conc. | 60 |
| | 14.0 | Solvent C Conc. | 35 |
| | 14.0 | Solvent D Conc. | 5 |
| | 15.0 | Solvent B Conc. | 0 |
| | 15.0 | Solvent C Conc. | 90 |

| Column | Zorbax Extended-C18 4.6x250 mm 5µm | | |
|---|---|---|---|
| | 15.0 | Solvent D Conc. | 10 |
| | 17.0 | Solvent B Conc. | 0 |
| | 17.0 | Solvent C Conc. | 90 |
| | 17.0 | Solvent D Conc. | 10 |
| | 17.5 | Solvent B Conc. | 0 |
| Gradient | 17.5 | Solvent C Conc. | 98 |
| | 17.5 | Solvent D Conc. | 2 |
| | 27.0 | Solvent B Conc. | 0 |
| | 27.0 | Solvent C Conc. | 98 |
| | 27.0 | Solvent D Conc. | 2 |
| | 30.0 | Solvent B Conc. | 80 |
| | 30.0 | Solvent C Conc. | 10 |
| | 30.0 | Solvent D Conc. | 10 |
| | 32.5 | controller | stop |

### 2.8. Limit of Detection (LOD) & Limit of Quantification (LOQ)

The Limit of Detection (LOD) and the Limit of Quantification (LOQ) were also investigated and were calculated from the obtained calibration curves using the equations below:

$$LOD = \frac{3.3\sigma}{S}$$

$$LOQ = \frac{10\sigma}{S}$$

Where σ is the standard deviation of the response,

S is the slope of the calibration curve.

The value of σ when conducting the calculations based on the calibration curve is equivalent to the root mean square error or the standard deviation of the y-intercept, while S is the slope of the regression line.

### 2.9. Recovery

For the recovery experiments, date samples were spiked with the 12 pesticides at 3 concentration levels (25 µg/kg, 125 µg/kg and 250 µg/kg) before extraction. By reading from the solvent-based calibration curves the concentration corresponding to the obtained signal, then dividing by the spiked concentration and multiplying the ratio by 100, the recovery value was obtained.

This experiment was then expanded to cover 10 concentration levels (1.25,0.25,0.125, 0.025, 0.0125, 0.0025 , 0.00125 , 0.00025, 0.000125, 0.000025) mg/kg.

## 3. Results & Discussion

In 2007 Kaakeh et al. identified top five commonly used insecticides, fungicides, and herbicides formulas in the UAE [15]. The formulas comprise 18 active components (pesticides) belonging to different pesticide families [15]. From these identified pesticides, 12 (Pirimiphos-methyl, Triazophos, Phenthoate, Dimethoate, chlorpyrifos, carbosulfan, Metalaxyl, Thiophanate-methyl, Azoxystrobin, Fluazifop-p-butyl, Tribenuron-methyl, EPN) were selected and studied in date fruits.

To enhance the chromatographic separation, mobile phases acetonitrile, methanol, and water with ammonium formate were used. Acetonitrile with methanol at different ratios for different analytes was a suitable mobile phase with water. EPN, Oxadiazon, Etofenprox-d5, carbofuran-d3, and TPP preferred ACN: MeOH (2:1) while the rest of the compounds preferred ACN: MeOH (1:2). Therefore, a gradient elution of pure methanol, acetonitrile:methanol (2:1) and an aqueous solution containing 10mM ammonium formate was used to achieve the optimal separation of 12 analytes and 5 internal standards in 32.5 min at a flow rate of 0.3 ml/min as indicated in Table 5.

The QuEChERS method (Quick, Easy, Cheap, Effective, Rugged, and Safe), introduced in 2003, has gained widespread recognition as a simplified and effective sample preparation alternative to classical Liquid- Liquid Extraction (LLE) and Solid Phase Extraction (SPE). In fact, most reports [3,4,6,8,9,11,13,16] in the literature concerned with pesticide detection and determination in dates reported using QuEChERS as a sample preparation technique. Two studies [12,17] reported using Ultrasonic Assisted Extraction and Supercritical Fluid Extraction, respectively. Using QuEChERS as suggested by Morsi et al. [9], a successful extraction was achieved for the selected pesticides in this work.

The 26 date fruit samples were randomly collected from different local markets and farms in both Al Ain city and the northern emirates and were analyzed for measuring the levels of the 12 pesticides considered in this study. For this purpose, LC-MS/MS method was developed. Using the solvent-based calibration curves, the determination of pesticide levels was obtained and compared to European Commission MRLs. All the samples had detectable levels of carbosulfan residues, with varying amounts ranging from 4.4 µg/kg to 42.8 µg/kg. Also, carbosulfan exceeded the MRL (10 µg/kg) in 16 out of 26 (61.5%) of the samples. Triazophos is the second most frequently determined pesticide in the 26 date samples. It was detected in all but two samples; however, all concentrations of this compound were below the MRL (10 µg/kg). In addition to carbosulfan, three pesticides-EPN, Azoxystrobin, and Metalaxyl- were detected above their MRLs of 10 µg/kg for the first two and 50 µg/kg for Metalaxyl. The detected concentration was 17.3 µg/kg for EPN in one sample and 13.4 µg/kg and 21.7 µg/kg for Azoxystrobin, each in a different sample. Azoxystrobin and EPN were therefore detected in concentrations almost twice above their MRL

(10 µg/kg). Pesticide concentration levels reached 234.8 µg/kg for Metalaxyl in one sample, reaching almost 5 times its MRL concentration (MRL 50 µg/kg). However, Metalaxyl was the least detectable (11.5%) pesticide in the 26 samples, followed by chlorpyrifos (15.4 %) which was detected in concentrations ranging from 0.5 to 9.11 µg/kg therefore at levels just below the 10 µg/kg MRL in one sample. All the other five pesticides were found to be low in concentration levels, much below their MRLs. Table 6 summarizes the pesticides against the detected concentrations in µg/kg for all 26 samples.

It is worth noting that this study agree with those reported by Morsi et al. [9]. The two projects report a similar range of concentrations for the pesticide carbosulfan.

The LOD and LOQ values in µg/kg for the 12 pesticides were calculated and are summarized in Table 7.

The concentrations detected lower than the calculated LOQ values are highlighted in red in Table 6 for the pesticides chlorpyrifos, phenthoate, dimethoate, azoxystrobin, fluazifop-butyl, pirimiphos-methyl, and triazophos. As for the remaining five pesticides, the calculated LOQ values (carbosulfan, thiophanate-methyl, metalaxyl, EPN, and tribenuron-methyl) are above their respective MRL values. Therefore, this approach can't be used as far as solvent-based calibration curves for these five pesticides are concerned.

The results obtained from analyzing the area of spiked before extraction samples for obtaining recovery values are summarized in Table 8.

**Table 6. Pesticide Levels (ppb) in Real Dates Fruits Samples as Determined by LC-MS/MS Method**

| | EPN | Thiophanate-methyl | Tribnuron-methyl | Fluazip-p-butyl | Azoxystrobin | Metalaxyl | Chlorpyrifos | Phenthoate | Dimethoate | Pirimiphos-methyl | Triazophos | Carbosulfan |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ND | ND | 0.35 | 0.11 | 0.01 | ND | ND | ND | 0.69 | 0.04 | 1.81 | **14.39** |
| 2 | ND | 1.48 | ND | 0.07 | ND | ND | ND | ND | ND | 0.64 | 0.14 | **14** |
| 3 | ND | 1.46 | ND | 0.1 | ND | ND | ND | ND | ND | 1.48 | 1.71 | **24.18** |
| 4 | 4.16 | 1.6 | ND | ND | 1.27 | 0.07 | ND | 0.95 | 2.32 | 0.2 | 0.86 | **22.47** |
| 5 | 2.39 | 1.19 | 0.38 | ND | 0.12 | ND | 1.82 | 0.37 | 0.94 | ND | 0.79 | **24.02** |
| 6 | 2.64 | 1.2 | 0.83 | ND | 0.06 | ND | ND | 0.22 | 1.14 | 0.09 | 0.72 | **12.2** |
| 7 | 3.41 | 1.26 | ND | ND | 0.71 | ND | ND | ND | 0.63 | ND | 0.89 | **13.63** |
| 8 | 2.68 | 1.25 | ND | ND | 0.29 | ND | ND | ND | 0.14 | ND | 0.21 | **10.11** |
| 9 | 1.62 | 1.33 | ND | ND | 0.96 | ND | ND | ND | 0 | ND | 0.1 | 9.56 |
| 10 | 2.33 | 1.2 | ND | ND | 5 | ND | ND | ND | 0.54 | ND | 0.99 | 4.59 |
| 11 | 2.34 | 1.36 | ND | ND | **13.38** | 7.95 | ND | 7.81 | 2.38 | ND | 3.63 | 1.85 |
| 12 | ND | 1.23 | ND | ND | **21.66** | ND | ND | ND | 1.05 | ND | 0.86 | 2.72 |
| 13 | ND | 1.65 | 0.22 | 0.07 | 0.22 | ND | ND | 0.23 | 2.42 | ND | 2.28 | 5.84 |
| 14 | 2.91 | 1.5 | 0.58 | 0.13 | 0.22 | ND | ND | 0.95 | 3.24 | ND | 1.73 | **42.89** |
| 15 | 2.7 | 1.37 | 0.53 | ND | 0.06 | ND | ND | 0.11 | 1.68 | ND | 1.16 | **31.58** |
| 16 | ND | 1.37 | ND | ND | 0.13 | ND | ND | ND | 0.42 | ND | 0.71 | **27.86** |
| 17 | ND | ND | ND | ND | 0.03 | ND | ND | ND | 0.58 | ND | 0.18 | **11.97** |
| 18 | ND | 1.26 | ND | ND | ND | ND | 0.5033 | ND | ND | ND | 0.01 | 4.42 |
| 19 | ND | 1.41 | ND | ND | 0.93 | ND | 9.1136 | ND | ND | 0.63 | 0.65 | **10.08** |
| 20 | **17.39** | ND | 1.27 | ND | ND | ND | 2.6444 | ND | 3.56 | 0.12 | 0.57 | **30.34** |
| 21 | ND | 1.4 | ND | ND | 0.81 | ND | ND | ND | ND | ND | 0.6 | 9.91 |
| 22 | ND | ND | 0.47 | ND | 0.01 | ND | ND | ND | ND | 0.06 | ND | 4.68 |
| 23 | 2.69 | 1.23 | ND | ND | 0.05 | **234.86** | | ND | 1.74 | ND | 0.52 | **15.43** |
| 24 | ND | ND | 0.27 | ND | 0.07 | ND | ND | ND | ND | ND | 0.26 | 6.64 |
| 25 | ND | 1.11 | ND | ND | ND | ND | ND | ND | ND | ND | 0.67 | 7.19 |
| 26 | ND | ND | ND | ND | ND | ND | ND | ND | ND | ND | 0.6 | 7.73 |
| | Concentration < LOD | | | | | | | | | | | |

ND:Not Detected

**Table 7. LOD and LOQ calculated values for the 12 pesticides**

| Pesticide | LOD (µg/kg) | LOQ (µg/kg) |
|---|---|---|
| Chlorpyrifos | 1.426114309 | 4.321558513 |
| Phenthoate | 8.834451533 | 26.77106525 |
| Dimethoate | 9.137291367 | 27.68876172 |
| Carbosulfan | 17.88574234 | 54.1992192 |
| Thiophanate | 16.07109852 | 48.70029854 |
| Azoxystrobin | 2.358313148 | 7.146403478 |
| Metalaxyl | 45.08297385 | 136.6150723 |
| Fluazip-p-butyl | 3.157190491 | 9.567243911 |
| Pirimiphos-methyl | 3.373199616 | 10.22181702 |
| Triazophos | 1.693526618 | 5.131898841 |
| EPN | 23.74032448 | 71.94037722 |
| Tribnuron-methyl | 7.257608926 | 21.99275432 |

**Table 8. Recovery values calculations**

| Spiked Conc. (µg/kg) | Pesticide | Conc. (mg/kg) | Conc. µg/kg | Recovery % |
|---|---|---|---|---|
| 25 | EPN | | | |
| 125 | EPN | 0.00617669 | 6.176686 | 4.94 |
| 250 | EPN | 0.00669134 | 6.691344 | 2.68 |
| | | | | |
| 25 | Thiophanate-methyl | 0.0053739 | 5.373903 | 21.50 |
| 125 | Thiophanate-methyl | 0.00563402 | 5.634021 | 4.51 |
| 250 | Thiophanate-methyl | | | |
| | | | | |
| 25 | Tribnuron-methyl | 0.00180324 | 1.803236 | 7.21 |
| 125 | Tribnuron-methyl | 0.00528585 | 5.285851 | 4.23 |
| 250 | Tribnuron-methyl | 0.01585415 | 15.85415 | 6.34 |
| | | | | |
| 25 | Fluazip-p-butyl | 0.024 | 23.624 | 94.50 |
| 125 | Fluazip-p-butyl | 0.113 | 113.095 | 90.48 |
| 250 | Fluazip-p-butyl | 0.217 | 216.614 | 86.65 |
| | | | | |
| 25 | Azoxystrobin | 0.022 | 21.653 | 86.61 |
| 125 | Azoxystrobin | 0.104 | 104.433 | 83.55 |
| 250 | Azoxystrobin | 0.227 | 226.578 | 90.63 |
| | | | | |
| 25 | Metalaxyl | 0.011 | 11.252 | 45.01 |
| 125 | Metalaxyl | 0.106 | 106.483 | 85.19 |
| 250 | Metalaxyl | 0.272 | 272.385 | 108.95 |
| | | | | |
| 25 | Chlorpyrifos | 0.014 | 13.805 | 55.22 |
| 125 | Chlorpyrifos | 0.063 | 62.515 | 50.01 |
| 250 | Chlorpyrifos | 0.097 | 96.583 | 38.63 |
| | | | | |
| 25 | Phenthoate | 0.012 | 12.331 | 49.32 |
| 125 | Phenthoate | 0.159 | 159.251 | 127.40 |
| 250 | Phenthoate | 0.292 | 291.859 | 116.74 |
| | | | | |
| 25 | Dimethoate | 0.001 | 1.138 | 4.55 |
| 125 | Dimethoate | 0.011 | 11.311 | 9.05 |
| 250 | Dimethoate | 0.023 | 23.179 | 9.27 |
| | | | | |
| 25 | Pirimiphos-methyl | 0.005 | 5.301 | 21.20 |
| 125 | Pirimiphos-methyl | 0.026 | 26.178 | 20.94 |
| 250 | Pirimiphos-methyl | 0.050 | 49.569 | 19.83 |
| | | | | |
| 25 | Triazophos | 0.008 | 8.374 | 33.50 |
| 125 | Triazophos | 0.044 | 44.179 | 35.34 |
| 250 | Triazophos | 0.066 | 65.504 | 26.20 |

| Spiked Conc. (µg/kg) | Pesticide | Conc. (mg/kg) | Conc. µg/kg | Recovery % |
|---|---|---|---|---|
| | | | | |
| 25 | Carbosulfan | 0.058 | 57.566 | 230.26 |
| 125 | Carbosulfan | 0.206 | 206.063 | 164.85 |
| 250 | Carbosulfan | 0.497 | 496.646 | 198.66 |

**Table 9. Linearity of Regression for Spiked Before Extraction Samples**

| Pesticide | Regression Equation | $R^2$ |
|---|---|---|
| Chlorpyrifos | y = 0.4355x + 0.0056 | 0.9999 |
| Phenthoate | y = 5.4042x - 0.018 | 0.9996 |
| Dimethoate | y = 0.1196x + 1E-05 | 0.9993 |
| Carbosulfan | y = 0.1711x + 0.0007 | 0.9959 |
| Thiophanate | Not Determined | |
| Azoxystrobin | y = 7.6243x + 0.0449 | 0.998 |
| Metalaxyl | y = 11.931x + 0.0204 | 0.9972 |
| Fluazip-p-butyl | y = 2.1961x + 0.0001 | 0.9998 |
| Pirimiphos-methyl | y = 0.6802x + 0.0012 | 0.9997 |
| Triazophos | y = 0.7631x + 0.0054 | 0.9966 |
| EPN | Not Determined | |
| Tribnuron-methyl | Not Determined | |

Only for two pesticides (Fluazip-P-butyl and Azoxystrobin) the calculated recovery values fall within the acceptable range of 70-120%. This might incorrectly be attributed to unsuccessful extraction. However, when expanding the experiment to include 10 spiked samples, a pattern is observed. The linear systematic suppression and enhancement of the signal obtained for the spiked before extraction samples suggest the presence of a significant matrix effect. This is true since, in the absence of a matrix effect, the recovery values and corresponding areas need not follow a pattern but are rather random in values. Therefore, to obtain the actual recovery values, matrix-matched calibration curves should be constructed and used for the calculations. Linear regression equations of signal ratio (pesticide signal/internal standard) versus spiked before concentrations of the 12 pesticides were constructed and are available in Table 9.

For 3 pesticides (EPN, Thiophanate-methyl, and Trebnuron-methyl), obtaining a regression line was not possible due to the absence of signal for most spiked samples because of the signal suppression caused by the matrix.

## 4. Conclusion

In this study, 12 pesticide residues in date fruits consumed in the UAE, both imported and locally produced, were investigated. The detection and quantification of those pesticides are important steps in ensuring food safety and public health.

This study highlights the misalignment of some dates fruit producers with regard to maintaining pesticide levels in the date fruit products below the maximum residue limits (MRL) adopted by regulatory authorities in the UAE. The preliminary results of the persistent presence of carbosulfan at levels exceeding twice the MRL (10 µg/kg) in 57.7% and Metalaxyl at levels 5 times exceeding the MRL value (10 µg/kg) in one sample (3.8%) indicate a possible negative health risk impact on consumers. Although less frequent, Azoxystrobin also exceeded its MRL in two samples, reaching 133.8% and 216.6% its residue limit (10 µg/kg). EPN was detected in one sample at a concentration of 17.39 µg/kg therefore reaching 173.9% its MRL (10 µg/kg).

A study on the levels of the most applied pesticides in date fruits consumed in the UAE was not available in the literature and needed to be addressed. Also, the results indicate the necessity of raising awareness among date palm farmers and applicators about the possible adverse health impacts associated with the over application of pesticides on consumers' health. Furthermore, measures must also be in place for more stringent application of the relevant laws. Also, due to the limited studies on date fruits in the UAE, this work can be considered a starting point for quality control entities to conduct more research on date fruits of this type. On the other hand, the successful method developed for multi-class pesticide analysis can serve as an example for future studies.

Finally, the results suggest the need for conducting a health risk assessment study to evaluate the health impact of the presence of the pesticides at the levels mentioned above on consumers.

## References

[1] M. Siddiq and I. Greiby, "Overview of Date Fruit Production, Postharvest Handling, Processing, and Nutrition," Dates: Postharvest Science, Processing Technology and Health Benefits, pp. 1–28, Sep. 2013.

[2] H. S. Qazaq and N. Z. Al Adeeb, "The consumption pattern of Dates and its related food habits among UAE Citizens in Al-Ain City, UAE: A Pilot Study," Acta Hortic, vol. 882, pp. 1083–1089, Dec. 2010.

[3] O. I. Abdallah, S. S. Alamer, and A. M. Alrasheed, "Monitoring Pesticide Residues in Dates Marketed in Al-Qassim, Saudi Arabia Using a QuEChERS Methodology and Liquid Chromatography–tandem mass spectrometry," Biomedical Chromatography, vol. 32, no. 6, p. e4199, Jun. 2018.

[4] A. Khezri, M. Ansari, M. Amirahmadi, M. Shahidi, N. Mohamadi, and M. Kazemipour, "Pesticide Residues in Dates Using a Modified QuEChERS Method and GC-MS/MS," Food Additives & Contaminants: Part B, vol. 15, no. 3, pp. 168–176, Jul. 2022.

[5] UAE government, May. 2020, "Federal Law No. 10 of 2020

Concerning Pesticides," UAE Government, UAE legislation, the Palace of the Presidency in Abu Dhabi. Accessed: Jul. 29, 2025 [Online]. Available: https:// uaelegislation.gov.ae/ en/legislations/ 1463/download.

[6] Z. Eslami, V. Mahdavi, and B. Tajdar-Oranj, "Probabilistic health risk assessment based on Monte Carlo simulation for pesticide residues in date fruits of Iran," Environmental Science and Pollution Research, vol. 28, no. 31, pp. 42037–42050, Aug. 2021.

[7] Abu Dhabi Quality and Conformity Council, Dec. 2013, "Pesticide Management in the Emirate of Abu Dhabi-Part 1 (Regulatory Roles and Responsibilities)," Abu Dhabi Quality and Conformity Council, Abu Dhabi Specifications ADS 7. Accessed: Jul. 29, 2025 [Online]. Available: chrome-extension:// efaidnbmnnnibpcajpcglclefindmkaj/ https:// www.wkcgroup.com/ wp-content/uploads/2023/04/Pesticide-Management-in-the-Emirate-of-Abu-Dhabi.pdf.

[8] N. M. A. El-Mageed, I. I. Abu-Abdoun, K. A. H. Kayaf, and A. S. Janaan, "Monitoring of Pesticide Residues in Imported Datepalm Fruits in the United Arab Emirates," Eur J Nutr Food Saf, pp. 1–9, Nov. 2021.

[9] R. Morsi, K. Ghoudi, and M. A. Meetani, "Determination and health risk assessment of carbamate pesticide residues in date palm fruits (Phoenix dactylifera) using QuEChERS method and UHPLC-MS/MS," Scientific Reports 2024 14:1, vol. 14, no. 1, pp. 1–13, Jun. 2024.

[10] P. Jafarian Asl, R. Niazmand, B. M. Razavizadeh, M. A. Shakeri, and M. Jahani, "Monitoring of pesticide and some metal residues in Mazafati date fruit cultivar and risk assessment to health," Journal of Food Composition and Analysis, vol. 115, p. 104917, Jan. 2023.

[11] S. F. Taghizadeh, R. Rezaee, M. Azizi, A. W. Hayes, J. P. Giesy, and G. Karimi, "Pesticides, metals, and polycyclic aromatic hydrocarbons in date fruits: A probabilistic assessment of risk to the health of Iranian consumers," Journal of Food Composition and Analysis, vol. 98, p. 103815, May 2021.

[12] S. Mosallaei, Z. Tabatabaei, and A. Azhdarpoor, "Investigating organophosphorus pesticides in dates from Khesht City (Iran): Impact of washing and assessment of the health risks," Applied Food Research, vol. 4, no. 2, p. 100535, Dec. 2024.

[13] S. Attia , S. Zougari, H. Sahraoui, R. Aloui, S. Nsir, W. Hached, G. Nsir, K. Lebdi,"Pesticide residues surveillance of date palm (Phoenix dactylifera) in the south of Tunisia," Journal of Entomology and Zoology Study, vol. 7, no. 2,pp. 1085-1088, Feb. 2019, Accessed: Oct. 05, 2024. [Online]. Available: www.entomoljournal.com.

[14] M. González-Curbelo, B. Socas-Rodríguez, A. V. Herrera-Herrera, J. González-Sálamo, J. Hernández-Borges, and M. Rodríguez-Delgado, "Evolution and applications of the QuEChERS method," TrAC Trends in Analytical Chemistry, vol. 71, pp. 169–185, Sep. 2015.

[15] W. Kaakeh, M. Maraqa, M. Hasan, M. Almarzouqi, "Management of pesticides in the United Arab Emirates," J. Agric. Sci, vol. 16, pp15-31, Jan. 2004.

[16] S. B. Abdel Ghani, S. S. Alhewairini, and S. Hrouzková, "A Fast and Easy QuEChERS-DLLME Method Combined with GC-MS for Ethion and Bifenthrin Residues Determination and Study of Their Dissipation Dynamics in Palm Dates," Food Anal. Methods, vol. 11, no. 12, pp. 3542–3550, Dec. 2018.

[17] M. H. EL-Saeid and S. A. AL-Dosari, "Monitoring of pesticide residues in Riyadh dates by SFE, MSE, SFC, and GC techniques," Arabian Journal of Chemistry, vol. 3, no. 3, pp. 179–186, Jul. 2010.