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ORIGINAL ARTICLE

# Monitoring of pesticide residues in Riyadh dates by SFE, MSE, SFC, and GC techniques

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**Abstract** In the present work, simple and rapid extraction and analysis techniques of insecticide (OCPs, OPPs, pyrethroids), fungicide, acaricide, and herbicide residues in three cultivars' of date fruits viz., Khalas, Sukkari, Nabout Seif and their seeds have been applied. The date cultivars were collected from eight local markets of Riyadh, KSA. The extraction of pesticide residues from the three varieties of date samples was conducted by rapid and new extraction techniques, Supercritical Fluid Extraction (SFE) and Microwave Solvent Extraction (MSE). The analysis was performed, without clean-up, by Supercritical Fluid Chromatography (SFC) and Gas Chromatography (GC) using different detectors. The results showed that the SFE, MSE, SFC and GC techniques are clearly faster, more sensitive and more cost effective than conventional methods. The recovery efficiency of SFE and MSE was 99% and 97%, respectively. The recoveries, MDL (Minimum Detection Limit) and repeatability achieved in this study meet the standards set for tolerance level monitoring of these pesticides. The mean levels of some tested residues of pyrethroids, herbicides, and fungicides in dates and their seeds are below the MRL (Maximum Residue Level). However, lindane (BHC gamma isomer), dieldrin, dimethoate, chlorpyrifos and all tested acaricide residues in date fruit samples exceeded the MRLs indicating a hazardous trend in the date palm cultivation. The data also showed a higher concentration of OP dimethoate in the date seeds, which is sometimes, used as animal feed. The present results provide important information on the current contamination status of the date fruits in Riyadh markets and point to the action needed for controlling

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the excessive application of pesticides. This study is the first monitoring and screening of pesticide residues of 6 groups in Saudi Arabian dates.



## 1. Introduction

Dates have full nutritive value and it is considered as principal food in Arab peninsula. It has been mentioned in the Holy Qura'n. The total production of dates was 884,000,00 tons, harvested from about 21 millions palm trees, distributed in 140,000,00 hectare, in year 2003, in the Kingdom of Saudi Arabia. Of this production 34,000 tons (9%) were exported with safety tags such as pesticide residue-free (Ministry of Agriculture, 2005).

Based on statistical data for 19 countries, the WHO working group estimated that worldwide, there have been as many as 50,000 cases annually of pesticide poisoning. The mortality rate has been 1% in countries where medical treatment is readily available, so deaths are estimated to be about 5000 a year.

However, it is reckoned that the real number of poisonings is considerably greater at about 2 million. About 40,000 persons die and admittedly 70% of the lethal cases occur in developing countries. This shows that every 17 min a person dies due to pesticide poisoning, and every 10 min 28 subjects are poisoned by pesticide (Roy et al., 1995; Ekstrom et al., 1996; Neidert and Saschenbrecker, 1996).

Insecticides, fungicides, acaricides and herbicides have been excessively used in agriculture including date palm farms, which put the health of the consumers at risk with adverse effects (Blanco et al., 2002a,b; Colume et al., 2000; Fernandez et al., 2000, 2001; Polzhofer, 1977; Akiyama et al., 2002; Pico et al., 2000; Torres et al., 1996; Ripley et al., 2003; FDA, 1993). It is quite apparent that such state of affairs calls for the need of more accurate, cost-effective and rapid analytical techniques capable of detecting the minimum concentrations of multi pesticide residues (EL-Saeid and Shaht, 2000; Valenzuela et al., 2000; Chen and Wang, 1996; Navarro et al., 2000; Nishikawa, 1993; Anastassiades and Schwack, 1998; Khan, 1982; Okihashi et al., 2005).

Supercritical Fluid Extractor (SFE) and Microwave Solvent Extractor (MSE) were recommended and applied as rapid, efficient, and sensitive techniques for the extraction of different groups of pesticides from fruits, vegetables, soils, and water (France and Voorhees, 1988; Ahmed et al., 1998; Christer et al., 2004; Sannino, 1995; Muccio et al., 1999; Stejnbaher et al., 2003).

Recently, few studies in the KSA focused on estimation of a single pesticide residues in dates (Suleiman and Osman, 2005; Suloiman and Osman, 2003), and residue of three pesticides were analyzed in Saudi dates cultivars (Kamel et al., 2007). Therefore, this study was undertaken for multi-residue analysis of six pesticide groups in date samples, collected from local markets in Riyadh city, using different extraction and analytical techniques: SFE, MSE and SFC, and GC techniques.

## 2. Materials and methods

### 2.1. Date samples collection and preparation

Three cultivars of date palm samples (Khalas, Sukkari, and Nabout Seif) were collected from 8 local markets in Riyadh. The each sample were first separated from their seeds then cut into slices divided into two portions. One portion was used as a blank or control sample for quality control and determination the current pesticide residues. The other portion was used for spiking with each single pesticide in each group of investigated pesticides to calculate the recovery percentage. Both date samples were taken for the extraction and analysis.

### 2.2. Recovery assays

Untreated samples of the three varieties (Khalas, Sukkari, Nabout Seif) were spiked with each pesticide at levels ranging from 1.0 to 2.0 μg/g. The spiked samples were allowed to equilibrate for one hour prior to extraction. Three replicates were analyzed to calculate the Recovery and Relative Standard Deviation (RSD%).

### 2.3. Pesticide standard

Pesticides standard were obtained from Chem. Service, Inc. (West Chester, PA, USA) and EPA (Research Triangle Park, NC, USA). Tested pesticides represented 4 pesticide groups, namely, insecticides (OPPs, OCPs, pyrethroids), fungicides, acaricides, and herbicides. Each single pesticide was prepared at concentrations ranging from 0.001 to 2.00 ppm dissolved in pesticide grade methanol to be used for spiking, injection, MDLs, recovery, and residue analysis.

### 2.4. Extractions procedures

#### 2.4.1. Supercritical Fluid Extraction (SFE) method

The pesticide extraction method of France and Voorhees (1988), was modified by EL-Saeid (1999) for multi-residue extraction, and used in the present investigation. At SFE model 7680T (Hewlett–Packard), which included a solid phase sorbing trap with 30 mm of Hypersil ODS which the $CO_2$ extraction solvent was decompressed during collections.

Ten grams of dry date samples were transferred into the extraction thimble. The extraction process was carried out in three steps; in the first step $CO_2$ density was 0.25 g/ml, extraction pressure was 77 bars (1117 psi), chamber temperature was 40 °C, and $CO_2$ flow rate was 1.0 ml/min. In the second step, $CO_2$ density was 0.67 g/ml, extraction pressure was 239 bars (3469 psi). The chamber temperature was 80 °C, and $CO_2$ flow rate was 2.5 ml/min. The nozzle temperature was set at 45 °C in both steps.

The sample extract was collected on the ODS sorbing trap at 10 °C. The extracted sample was eluted from the trap with 1.5 ml of methanol at a flow rate of 0.4 ml/min and a trap temperature of 40 °C and collected in auto sampler vials placed in a fraction collector. The ODS trap was regenerated between extractions by rinsing with 2 ml of methylene chloride followed by 2 ml of methanol at 1 ml/min to the waste. The same conditions were applied in the third step as to the second step except that a 30% modifier was used. The time of extraction per sample was 45 min (step 1, 5 min, step 2, 40 min, and step

3, 10 min). The first step was performed to eliminate hydrocarbons and non-polar compounds, the second step was performed to extract the insecticides, and the third step was performed to wash the thimble and ODS trap and to insure that no pesticides escaped in step 2.

*2.4.2. Microwave Solvent Extraction (MSE) method*

The USEPA application note no. E009 and CEM application notes no. E003 (CEM Corporation, 1994) were modified (EL-Saeid, 1999) for multi-residue extraction and were used during the present study. MSE system model MES-1000 with lined extraction vessels (LEV), was involved. This system consists of a 950-W microwave instrument, which has been specifically designed for use with organic solvents.

Extraction conditions are controlled by temperature using an inboard fiber optic system, which allows extraction temperatures to be selected from 20 to 200 °C in 1 °C increments. Temperature and pressure data can be copied to an external printer or downloaded to a PC; a maximum of 12 samples can be extracted simultaneously. Safety features of this system are intended to prevent ignition of flammable and explosive extraction solvents. All ignition sources have been eliminated from the microwave cavity, the cavity is Teflon lined, and additional Teflon has been added to the cavity ceiling.

Other safety features include a solvent vapor detector in the system air exhaust, which turns off the microwave magnetron if solvent vapors are detected in the microwave cavity. An exhaust blower continually moves air through the cavity. All extraction vessels are connected to a sealed center collection vessel so that in the event of vessel safety membrane rupture, solvent vapors will be contained, directed from the cavity through a venture exhaust tube, and routed to the external exhaust. The venture in the cavity exhaust creates a slight vacuum that helps to remove solvent vapors.

The extraction vessel is a double-walled vessel specifically adapted for use with organic solvents. The vessel consists of an inner Teflon PFA liner and liner cover and outer bode that gives mechanical strength to the vessel is a special grade of Ultempolyetherimide that is resistant to attack by organic solvents. Extraction conditions were conducted with 20 g date sample, extraction solvent was 40 ml of acetone:hexane (3:2), pressure was 125 psi, microwave power was 85%, temperature was110 °C and time of extraction was 15 min for all pesticide groups in the same run.

*2.4.3. Pesticide residue analysis*

*2.4.3.1. Supercritical Fluid Chromatography*. All pesticide residues in date samples were analyzed by Supercritical Fluid Chromatography (SFC/UVD) at 220 nm and extracted by SFE. Determination methods for pyrethroids herbicides, acaricides, and fungicides (France and Voorhees, 1988; Muccio et al., 1999; Ashraf et al., 1991) were modified (EL-Saeid, 1999) to meet the needs of the present work. A Hewlett–Packard SFC model G 1205A attached to an HP 1050 diode array detector, modifier pump G 1205A, and a silica column (Alltec Hypersil APS 25 μm, length 205 mm, ID 4.6 mm) was used.

Pyrethroids were run at an oven temperature of 60 °C at a pressure of 130–200 bars (5 bar/min), flow rate was 1–3 ml/min at (2 ml/min), and 2% methanol was used as modifier, peaks were detected at 220 nm. Herbicides and fungicides were run at an oven temperature of 30 °C, at a pressure of 80–150 bars (30 bar/min), flow rate of 1–2 ml/min, and the modifier, 2–3% methanol (5%/min). Carbamates were run at an oven temperature of 32 °C, at a pressure of 80 bars, flow rate of 1–2 ml/min (5 ml/min), and the modifier, 2–4% methanol (5%/min).

Herbicides were detected at 220 nm, while fungicides were detected at 210 nm. The overall methods were elaborated and verified by trials of several injections to obtain the best separation. To calculate relative standard deviation (RSD%), three replicates spikes were analyzed. The total number of investigated data was 72 samples.

*2.4.3.2. GC/NPD/ECD methods*. Both of EPA 608 and EPA 525 methods for determining organochlorine (OCPs) and organophosphorus (OPPs) respectively, (Bai et al., 2005) were modified (Dogheim et al., 2002) to increase the number of analyzed pesticides were used. The (OCPs) insecticides were determined using a Hewlett–Packard 5980 series II gas chromatography fitted with ECD DB 608 (30 m × 0.53 μm × 0.33 μm film) column. Helium was used as the carrier gas at a pressure of 10 psi, flow rate 3.2 ml/min.

The injector was operated in the split mode with the split ratio 32:1 and its temperature was maintained at 220 °C connected to an auto sampler (Hewlett–Packard 7673). The oven was temperature programmed from an initial temperature of 140 °C (0.5 min hold) to 250 °C at a rate of 6 °C/min, then to 250 °C at 10 °C/min. The oven was held at this temperature for 5 min. The compounds were detected with an electron-capture detector (ECD) at 330 °C.

The organophosphorus (OPPs) pesticides were determined using the same model gas chromatograph fitted with both a flame photometric detector (FPD) with 526 nm phosphorus filter and a nitrogen phosphorus detector (NPD) attached to a DB 1701 column (30 m × 530 μm × 1.0 μm film) with a split end (1:1) for both detectors. The injector was operated in the split mode, temperature was 250 °C, using auto injector. Helium was used as the carrier gas at a pressure of 10 psi. The detectors temperature were maintained at 250 °C, and the oven was programmed from

**Table 1** Pyrethroid residues (ppm) and RSD in date samples extracted by SFE/MSE and determined by SFC/UVD at 220 nm.

| Date samples | Pyrethroid residues (ppm ± RSD) | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Cypermethrin | Deltamethrin | Cypermethrin | Deltamethrin |
| Khalas | 0.02 ± 0.01 | 0.03 ± 0.02 | ND | 0.02 ± 0.01 |
| Sukkari | ND | ND | ND | ND |
| NaboutSeif | 0.03 ± 0.02 | ND | 0.02 ± 0.01 | ND |

ND: not detected, RSD: relative standard deviation.

**Table 2** Pyrethroids recovery and RSD percentages of spiked date samples extracted by SFE/MSE and determined by SFC/UVD at 220 nm.

| Date samples | Recovery and RSD% of pyrethroids | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Cypermethrin | Deltamethrin | Cypermethrin | Deltamethrin |
| Khalas | 94.4 ± 2.3 | 97.5 ± 1.8 | 94.5 ± 1.4 | 91.1 ± 1.5 |
| Sukkari | 95.6 ± 1.1 | 97.6 ± 1.7 | 95.7 ± 1.9 | 94.2 ± 1.3 |
| Nabout Seif | 97.8 ± 2.4 | 98.3 ± 1.4 | 95.2 ± 2.2 | 93.8 ± 1.7 |

RSD: relative standard deviation.

**Table 3** Herbicide residues (ppm) and RSD in date samples extracted by SFE/MSE and determined by SFC/UVD at 220 nm.

| Date samples | Herbicide residues (ppm ± RSD) | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Glyphosate | Atrazine | Glyphosate | Atrazine |
| Khalas | ND | ND | ND | 0.02 ± 0.01 |
| Sukkari | 0.02 ± 0.01 | 0.02 ± 0.01 | ND | ND |
| Nabout Seif | 0.03 ± 0.02 | ND | 0.03 ± 0.02 | ND |

ND: not detected, RSD: relative standard deviation.

**Table 4** Herbicide recovery and RSD percentages of spiked date samples extracted by SFE/MSE and determined by SFC/UVD at 220 nm.

| Date samples | Recovery and RSD% of herbicide | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Glyphosate | Atrazine | Glyphosate | Atrazine |
| Khalas | 96.3 ± 1.3 | 96.5 ± 1.2 | 95.7 ± 1.4 | 95.1 ± 3.5 |
| Sukkari | 98.6 ± 1.3 | 97.6 ± 1.5 | 97.1 ± 1.9 | 96.2 ± 2.3 |
| Nabout Seif | 98.3 ± 2.6 | 98.3 ± 1.8 | 96.6 ± 2.7 | 97.8 ± 2.7 |

RSD: Relative standard deviation.

**Table 5** Fungicide residues (ppm) and RSD in date samples extracted by SFE/MSE and determined by SFC/UVD at 220 nm.

| Date samples | Fungicide residues (ppm ± RSD) | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Benomyl | Carbendazim | Benomyl | Carbendazim |
| Khalas | 0.04 ± 0.02 | 0.05 ± 0.02 | 0.02 ± 0.01 | 0.05 ± 0.03 |
| Sukkari | ND | 0.05 ± 0.01 | ND | 0.04 ± 0. 02 |
| Nabout Seif | ND | 0.03 ± 0.02 | ND | 0.03 ± 0.01 |

ND: not detected, RSD: relative standard deviation.

an initial temperature of 100 °C (0.5 min hold) to 250 °C at 3 °C/min, and held for 20 min.

## 3. Results

### 3.1. Residues of pyrethroid insecticides

The result of pyrethroids and their recovery% are shown in Table 1. The residue of all three insecticides was under the MRLs level. The residue level of cypermethrin in Khalas cultivars was 0.02 ppm (MRL 0.1 ppm). Cypermethrin was not detected in Sukkari cultivar. Cypermethrin was detected in Nabout Seif at 0.03 ppm (MRL 0.01 ppm). Deltarmethrin was detected in cultivars of Khalas and Sukkari (0.03 and 0.01 ppm, respectively), but was not detected in Nabout Seif cultivar (MRLs of deltamethrin 0.2 ppm). Recovery% ranged from 91.1 ± 1.5 to 98.3 ± 1.4, as shown in Table 2.

### 3.2. Herbicide residues

Herbicide residues in date samples ranged from 0.01 ± 0.01 to 0.03 ± 0.03 ppm (Table 3). Glyphosate was detected in all three cultivars Khalas, Sukkari, and Nabout Seif. The residues in the three cultivars were 0.02, 0.02, and 0.03 ppm, respectively. The data showed that SFE technique is more efficient than MSE technique.

The recovery% ranged from 95.1 ± 3.5 to 98.6 ± 1.3. Atrazine was detected in Khalas and Sukkari and the residue levels were 0.03 and 0.02 ppm, respectively. By using MSE, glyphosate was detected in Sukkari and Nabout Seif (0.01 and 0.03 ppm, respectively), but was not detected in Khalas cultivar.

### 3.3. Fungicide residues

Two fungicides were detected in some date samples of the three cultivars (Table 5). The fungicide benomyl was detected in Khalas date samples only, and the residue level was 0.04 ppm by (SFE). Carbendazim was detected in the three cultivars Khalas, Sukkari, and Nabout Seif (0.05, 0.05, and 0.03 ppm, respectively. Uing MSE, benomyl was detected in Khalas date samples (0.02 ppm). Carbendazim was detected in samples of the three cultivars at 0.05, 0.04, and 0.03 ppm, respectively.

The main recovery% of benomyl and carbendazim ranged from 91.1 ± 1.8 to 93.8 ± 1.8, respectively (Table 6).

### 3.4. Acaricide residues in dates

Acaricide residues results are shown in Table 7. Using SFE method, the residue level of amitraz in Khalas and Nabout Seif

**Table 6** Fungicide recovery and RSD percentages of spiked date samples extracted by SFE/MSE and determined by SFC/UVD at 220 nm.

| Date samples | Recovery and RSD% of fungicides | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Benomyl | Carbendazim | Benomyl | Carbendazim |
| Khalas | 91.1 ± 2.2 | 90.5 ± 1.3 | 91.5 ± 2.4 | 91.1 ± 1.8 |
| Sukkari | 92.3 ± 1.9 | 91.0 ± 1.2 | 91.7 ± 2.9 | 92.2 ± 1.6 |
| Nabout Seif | 93 ± 2.1 | 90.3 ± 1.9 | 93.2 ± 2.4 | 93.8 ± 1.8 |

RSD: relative standard deviation.

was 0.08 ppm, whereas not detected in Sukkari samples. The residue level of dicofol was detected in Khalas and Nabout Seif at 0.06 and 0.08 ppm, respectively. The acaricide Tourk was detected in all of the three sample date cultivars, Khalas, Sukkari, and Nabout Seif at 0.04, 0.07, and 0.08 ppm, respectively.

Also, abamectin was detected in two date cultivars samples, Khalas and Nabout Seif, at 0.04 and 0.07 ppm, respectively. By using MSE technique, three acaricides were detected in all three cultivars, the residue level ranged from 0.04 to 0.08 ppm. The acaricide recovery ± RSD% ranged from 94.5 ± 1.0 to 99.4 ± 1.2 (Table 8). All detected acaricide residues were higher than the MRL permissible by official organizations (Table 7).

### *3.5. Organophosphorus (OP) residue in dates*

The residue levels of dimethoate and chlorpyrifos of the three cultivars are shown in Table 9. The residue levels of dimethoate in Sukkari and Nabout Seif were 0.2 and 0.24 ppm (MRL of dimethoate is 0.05 ppm). The residue level of dimethoate in Sukkari was 3 times higher than the MRLs. The residue levels of chlorpyrifos in the three date samples of Khalas, Sukkari, and Nabout Seif were 0.16, 0.18, and 0.15 ppm, respectively (SFE method). The MRLs of chlorpyrifos is 0.02 ppm and the residue level of chlorpyrifos was 6 times higher the MRL SFE method.

Dimethoate was detected in all three cultivars when the MSE was used. The residue levels in all three cultivars were 0.24, 0.27, and 0.28 ppm, respectively, whereas, the MRLs of dimethoate was 0.05 ppm. The residue level detected in Khalas

**Table 9** OPPs residues (ppm) and RSD in date samples extracted by SFE/MSE and determined by GC/NPD.

| Date samples | OPPs residues ± RSD% | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Dimethoate | Chlorpyrifos | Dimethoate | Chlorpyrifos |
| Khalas | ND | 0.16 ± 0.04 | 0.24 ± 0.03 | 0.18 ± 0.01 |
| Sukkari | 0.26 ± 0.08 | 0.18 ± 0.02 | 0.27 ± 0.04 | ND |
| Nabout Seif | 0.24 ± 0.03 | 0.15 ± 0.05 | 0.28 ± 0.02 | 0.17 ± 0.08 |

ND: not detected, RSD: relative standard deviation.

**Table 10** OPPs recovery and RSD percentages of spiked date samples extracted by SFE/MSE and determined by GC/NPD.

| Date samples | Recovery and RSD% of OPPs | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Dimethoate | Chlorpyrifos | Dimethoate | Chlorpyrifos |
| Khalas | 95.4 ± 2.3 | 96.5 ± 1.8 | 95.5 ± 1.4 | 95.1 ± 1.5 |
| Sukkari | 97.6 ± 1.1 | 98.6 ± 1.7 | 97.7 ± 1.9 | 98.2 ± 1.3 |
| Nabout Seif | 97.8 ± 2.4 | 98.3 ± 1.4 | 97.2 ± 2.2 | 97.8 ± 1.7 |

RSD: relative standard deviation.

**Table 7** Acaricide residues (ppm) and RSD in date samples extracted by SFE/MSE and determined by SFC/UVD at 220 nm.

| Date sample | Acaricide residues (ppm) ± RSD | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | SFE | | | | MSE | | | |
| | Amitraz | Dicofol | Tourk | Abamectin | Amitraz | Dicofol | Tourk | Abamectin |
| Khalas | 0.08 ± 0.03 | 0.06 ± 0.04 | 0.04 ± 0.03 | 0.04 ± 0.01 | 0.08 ± 0.03 | 0.05 ± 0.04 | 0.04 ± 0.02 | 0.03 ± 0.02 |
| Sukkari | ND | ND | 0.07 ± 0.04 | ND | 0.06 ± 0.04 | 0.08 ± 0.05 | 0.05 ± 0.04 | 0.06 ± 0.03 |
| Nabout Seif | 0.08 ± 0.03 | 0.08 ± 0.05 | 0.08 ± 0.02 | 0.07 ± 0.02 | 0.07 ± 0.02 | ND | 0.07 ± 0.04 | 0.06 ± 0.04 |

ND: not detected, RSD: relative standard deviation.

**Table 8** Acaricides recovery and RSD% of spiked date samples extracted by SFE/MSE and determined by SFC/UVD at 220 nm.

| Date sample | Recovery and RSD% of acaricides | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | SFE | | | | MSE | | | |
| | Amitraz | Dicofol | Tourk | Abamectin | Amitraz | Dicofol | Tourk | Abamectin |
| Khalas | 99.4 ± 1.2 | 98.8 ± 2.7 | 95.8 ± 1.8 | 97.8 ± 3.8 | 98.0 ± 2.8 | 97.8 ± 2. | 96.0 ± 2.8 | 99.8 ± 2.6 |
| Sukkari | 98.8 ± 3.7 | 96.6 ± 1.6 | 96.6 ± 3.1 | 97.6 ± 1.4 | 96.6 ± 1.3 | 95.5 ± 1.8 | 96.0 ± 1.6 | 96.6 ± 5.1 |
| Nabout Seif | 98.3 ± 4.5 | 96.5 ± 1.9 | 95.5 ± 2.4 | 96.5 ± 3.4 | 97.5 ± 1.7 | 96.5 ± 1.6 | 94.5 ± 1.1 | 96.5 ± 4.4 |

RSD: relative standard deviation.

**Table 11** OCPs residues (ppm) and relative standard deviation (RSD) in date samples extracted by SFE/MSE and determined by GC/ECD.

| Date samples | OCPs residues ± RSD% | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Lindane | Dieldrin | Lindane | Dieldrin |
| Khalas | 0.11 ± 0.06 | ND | 0.12 ± 0.07 | 0.15 ± 0.08 |
| Sukkari | ND | 0.16 ± 0.08 | 0.18 ± 0.07 | ND |
| Nabout Seif | 0.14 ± 0.08 | 0.15 ± 0.03 | ND | 0.16 ± 0.05 |

ND: not detected, RSD: relative standard deviation.

**Table 12** OCPs recovery and RSD percentages of spiked date samples extracted by SFE/MSE and determined by GC/ECD.

| Date samples | Recovery and RSD% of OCPs | | | |
|---|---|---|---|---|
| | SFE | | MSE | |
| | Lindane | Dieldrin | Lindane | Dieldrin |
| Khalas | 99.4 ± 2.7 | 97.5 ± 1.8 | 98.5 ± 2.4 | 99.1 ± 1.6 |
| Sukkari | 99.6 ± 4.1 | 98.6 ± 1.3 | 99.7 ± 3.9 | 99.2 ± 1.8 |
| Nabout Seif | 99.8 ± 4.4 | 98.3 ± 2.8 | 98.2 ± 3.2 | 98.8 ± 1.9 |

RSD: relative standard deviation.

and Nabiut Seif was at 0.18 and 0.17 ppm, respectively by using MSE method. The organophosphorous recovery ± RSD% ranged from 95.1 ± 1.5 to 98.6 ± 1.7.

### 3.6. Organochlorine (OC) residues

The residue levels of lindane and dieldrin are shown in Table 11. Lindane was detected in Khalas and Nabout Seif at 0.11 and 0.14 ppm, respectively (The MRLs of lindane is 0.01 ppm). Deildrin was detected in Sukkari and Nabout Seif samples 0.16 and 0.15 ppm, respectively (SFE method), (the MRLs of deildrin is 0.01 ppm). By using MSE, residue levels of lindane were 0.12 and 0.18 ppm in Khalas and Nabout Seif samples, respectively.

Also, dieldrin residue levels were 0.15 and 0.16 ppm in Khalas and Nabout Seif samples. The individual OCPs recovery ± RSD% ranged from 97.5 ± 1.8 to 99.8 ± 4.4.

The residue level of OCPs detected in date samples were ten times higher than the MRLs.

### 3.7. Pesticide residues in date seeds

As shown in Table 13, the only compound detected in the date seeds was dimethoate. The residue was detected in all of the three date cultivars. The residue levels were 0.089, 0.103, and 0.125 ppm in Khalas, Sukkari, and Nabout Seif, respectively by using SFE and MSE techniques meanwhile, the dimethoate residue level was 0.077, 0.099, and 0.125 ppm by using MSE.

## 4. Discussion

The levels of pesticide residues investigated in the three cultivars of dates were extracted by using modified Supercritical Fluid Extraction (SFE) and Microwave Solvent Extractor (MSE) techniques and determined by SFE and GC, ECD/NPD. Six groups of pesticides viz., pyrethroids and their metabolites, OPPs, OCPs, acaricides, fungicides and herbicides were studied. The extraction method by SFE was fast, safe with high recovery percentage and inexpensive for all four groups of pesticide residues.

We were able to obtain the optimum conditions that enabled us to extract a total of 14 pesticide residues in each date sample (control or spiked) in 55 min. The determinations were fast, no clean up exercise was needed, and lowest detection limit (ppb) was achieved for each pesticide residue (Tables 1–13). The application of Supercritical Fluid Chromatography (SFC) technique in the analysis of pesticide residues in all date

**Table 13** Pesticide residues (ppm) and RSD in date seeds extracted by SFE/MSE techniques and determined by SFC and GC/ECD/NPD.

| Pesticides | Dates seed type/pesticides residues (ppm) ± RSD | | | | | |
|---|---|---|---|---|---|---|
| | SF | | | MSE | | |
| | Khalas seeds | Sukkari seeds | Nabout Seif seeds | Khalas seeds | Sukkari seeds | Nabout Seif seeds |
| Cypermethrin | ND | ND | ND | ND | ND | ND |
| Deltamethrin | ND | ND | ND | ND | ND | ND |
| Glyphosate | ND | ND | ND | ND | ND | ND |
| Atrazine | ND | ND | ND | ND | ND | ND |
| Benomyl | ND | ND | ND | ND | ND | ND |
| Carbendazim | ND | ND | ND | ND | ND | ND |
| Amitraz | ND | ND | ND | ND | ND | ND |
| Dicofol | ND | ND | ND | ND | ND | ND |
| Tourk | ND | ND | ND | ND | ND | ND |
| Abamectin | ND | ND | ND | ND | ND | ND |
| Dimethoate | 0.089 ± 0.08 | 0.103 ± 0.08 | 0.125 ± 0.08 | 0.077 ± 0.05 | 0.099 ± 0.03 | 0.125 ± 0.09 |
| Chlorpyrifos | ND | ND | ND | ND | ND | ND |
| Lindane | ND | ND | ND | ND | ND | ND |
| Deildrin | ND | ND | ND | ND | ND | ND |

ND: not detected, RSD: relative standard deviation.

cultivars has been investigated. Pyrethroids recovery percentages of spiked samples group ranged from 91.1% to 98.3%, as found in Table 2. The residue levels of pyrethroids in all 3 cultivars ranged from 0.01 to 0.03 ppm. Meanwhile, herbicide residues in date samples using the same techniques were ranged from 0.01 to 0.03 ppm and their recovery percentages of spiked samples ranged from 95.1% to 98.6%.

Fungicide recoveries ranged from 91.1% to 93.8%. The average residues in spiked samples by same group were ranged from 0.02 to 0.05 ppm. The overall SFC run time was completely achieved within 10–30 min. On the other hand, the acaricide residues in all 3 cultivars ranged was exceeded the MRLs (Table 7).

By using modified techniques of SFE and MSE for residue extraction and GC/ECD/NPD for residues determination, the residue level of both insecticides dimethoate and chlorpyrifos found in all the three sample date cultivars Khalas, Sukkari, and Nabout Seif. The residue levels on both insecticides were higher three times compared with MRLs as shown in Table 9. The results of this study demonstrate that modified SFE, MSE, and GC methods are clearly faster for the determination of investigated OCPs in all date cultivars. OCPs, lindane, and dieldrine, found in date samples exceeded the MRLs as shown in Table 11. The cause of the increase of the residue level in date sample tested may have resulted from the use of insecticides by farmers without considering the time of the application of these insecticides.

## 5. Conclusion

The results of this study show the importance of detecting the residue levels of pesticides in samples of dates before being marketed. As shown in results, the residue level of certain insecticides and acaricides were higher than the maximum residue levels.

There is a need to educate farmers about the dangers posed by residues of these pesticides, which may lead to serious health problems in humans. Monitoring pesticide residues in date samples helps to assessing the potential risk of these products to consumers health and gives information on the pesticide treatments that have been used during the processes of harvesting, preservation, and distribution. The current techniques are more precise, cost-effective, and faster than the other techniques.

Laws and legislations are required as soon as possible to regulate pesticides application and residues in all food materials.

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