Detection of Pesticide Residues and Other Additives on Some Imported Fruits and Vegetables using Gas Chromatography - Mass Spectrometry

Eman M. Rasheed¹, Qais A. Ibrahim²

¹Ministry of Agriculture, Department Plant Protection, Iraq
²Division of Primaries Sciences, Collage of Agriculture, University of Baghdad, Iraq

Abstract: This paper presents a detection of pesticide residues and additives on imported fruits (Strawberry, Grapes, Peaches, and apples) using acetonitrile extraction method to determine the residual concentration during seasonal growth until it reaches the consumer. Extraction and purification processes conducted for crops in postgraduate Labs Faculty of Agriculture University of Baghdad. Different fresh fruits and vegetables include; Egyptian strawberries, African grapes, peaches, American Apple, potato, Iranian tomato, cucumber, Iranian red pepper and Turkish potatoes and cucumber were tested and analyzed using Gas Chromatography/Mass Spectrometry (GC/MS). QuEChERS method has been applied for extraction pesticide residues from targeted Vegetable and fruits. The GC/MS has been carried out for distinguish the Vegetable and fruits. Different factors were studied; retention time, elution time, relative abundance and molecular weight. The results showed that the pesticides with low molecular weight were eluted before the high molecular weight pesticides residues of pesticides. Different types of Pesticides were identified; pheromones, organic acids and solvents and anti-fungal to develop a comprehensive intervention measures and to reduce the potential health risk to consumers.

Keywords: pesticide residues, fruits, vegetables, acetonitrile, GC/MS, QUECHERS

1. Introduction

Pesticide is defined any substances or mixtures of substances intended to prevent, destroy, combat, repel, or mitigate the impact of a pest [1]. Therefore, a pesticide may be a chemical, biological agent or agent (such as a virus or bacteria), antimicrobial, disinfectant, bactericidal agent or even a tool used against any pest. Here the pest may be an insect. Pesticide residues define To pesticides that may remain on or after agricultural products. Regulatory bodies in many countries usually determine the maximum allowable percentage of those residues [2].

Food is the mainstay of life, and it is the key to the continuation of human life and safety. In order to achieve this, not only food is needed, but the most important thing is to provide balanced and fresh food free from all pollutants that harm human health, including pesticides residues [3].

Pesticide residues of fruits and vegetables after being treated with pesticides, which reach the surface of the plant or nearby water ways[4]. The residues are quantitatively estimated at one milligram per kilogram of food. Residues are shown in the exposed parts of the sprayed plant such as fruits, leaves, It can be said that pesticide residues are only a substance or a mixture of active ingredient and its decomposition products and other materials that help to be present in or on the crop used by humans as food or used as animal feed added to control the pests The crop is attacked[5]. Pesticide residues are classified according to the purpose of their use to their residues in vegetables and fruits. Studies have confirmed the presence of residues of the malathion herbicide Cucumber, cucumbers, tomatoes, potatoes, apples, French and American apples in a number of Arab countries, from which samples were collected, as well as chlorophosphate, spinach, cucumber, cucumber and tomatoes, as well as the detection of residues of dimethionite on cucumbers in these countries. The remaining residues ranged between 0.001 - 0.015 ppm [6]. Other studies have identified the rate of disappearance and destruction of insecticides (delta-methine and pyrimethrin) and four types of fungicides: minremol, tri-diminhon, quinothione, pyrazophos, and acaros dicofol and the remaining pesticides after repeated spraying on tomato fruits in the protected house. These fungicides were completely destroyed within three weeks and others showed an accumulation of residues with sprays [7]. In the results of other studies conducted in the Kingdom of Saudi Arabia, the presence of organic parathoroid insecticide (Permethrin) on green onions 0.207 ppm, while it is allowed to be present from this pesticide by 0.1 (ppm). In order to determine the permissible limits of pesticide residues on vegetables, studies have been conducted in a number of Arab countries where organic phosphorus residues, phosphamidone, methaditone, On potato plants in open fields or on cucumber plants in greenhouses where it was observed that pesticide residues were less than allowed after 16 days of pesticide spraying. [8]. Researchers have shown that increasing the concentration of the pesticide in the human body causes bad changes in humans Through TGA B was conducted on laboratory animals. The pesticide dichloro-diphenyl-trichloroethane (DDT)The human body is concentrated in the fatty layers of the human body. The risk of the pesticide is concentrated in its survival in agricultural soil for a long period without decomposition. The continuous intake of grains and the contaminated fruits and its consumption of meat. The birds that feed on the insects that are contaminated with these pesticides accumulate inside them. Eating these birds for insects and when eaten by humans cause slow poisoning leads to death, the greater the...
accumulation of quantity or the human being poisoned by eating the meat of animals that feed on contaminated plants [9]. The Daily Acceptable Daily Intake Limit (ADI) where the maximum residue of pesticide residues allowed for agricultural goods is found in marketing and in food, which can be identified as the amount of residual residues that humans consume without affecting their health. Eat daily with food and do no harm to human health. Most food products contain different concentrations of pesticides and these concentrations may be within the permissible limits or higher[10].This is called the maximum permissible limit (MRL).

These limits are determined by special organizations and laboratories that depend on the determination of these values based on, among other things, the type of pesticide, its method of effect and the way it is transmitted in the plant as well as the nutrition habits of the peoples which differ from one country to another[11]. Iraq is a member of the Codex Committee, IssuedThe countries of the world differ in determining the value of MRL and ADI according to the system adopted in each country. For example, the law in Scandinavia is the highest in terms of the permitted values for each pesticide, followed by Australia, New Zealand [12]. The Preharvest Interval (PHI) safety period, which is the period between the spraying of the plant with the pesticide until the crop is harvested, and the PHI, varies from one country to another. Crop to another that the residues of primary and final residues are dependent on the dynamic influencing factors. The initial residues on the leaves of treated plants are subject to dynamic processes due to climatic conditions such as heat, light and humidity. The pesticide is based on the chemical and physiological properties of the pesticide such as water solubility, vapor pressure, treatment method (air, ground spray) [13].

That there are many methods used to ensure the safety of food pesticides residues where they took wide space in different countries of the world for the preservation of human health and the fact that the principle of chemical control is the most used method. Food preparation, such as washing, peeling, cooking, canning and cooking, leads to a significant reduction in pesticide residues on these foods. Washing with water only, washing with soap and water, using saline solutions and manufacturing processes such as peeling and pickling have a significant role in removing or reducing pesticide residues in used plant parts as food helps these Processes in reducing pesticide residue in samples taken immediately after treatment from samples taken with a period of treatment for the probability of the pesticide entering the plant parts so that the pesticide or its metabolic product becomes part of the vegetable tissue[14]. The GC/M.S separation method is an effective method for separating mixtures up to several micrometers by passing the sample in a vapor state through a column that contains a liquid or solid medium and moves its components at varying speeds depending on the degree of boiling or solubility. Yassin mentioned that the sample to be separated must be constant under pressure conditions and the temperature used. The sample is usually inserted by injecting it directly at the top of the column where it is carried by the gas moving medium to separate the column and its separated components at the end[15].

2. Materials and Methods

Apparatus:
The (Table 1) Blew shows apparatus that used for detection process of pesticide residues in targeted vegetables and fruits.

<table>
<thead>
<tr>
<th>No</th>
<th>Instrument</th>
<th>Model</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pipes</td>
<td>China</td>
<td>China</td>
</tr>
<tr>
<td>2</td>
<td>Pickut with different size</td>
<td>China</td>
<td>China</td>
</tr>
<tr>
<td>3</td>
<td>Rotery Evaporator RE-300</td>
<td>Stuart</td>
<td>USA</td>
</tr>
<tr>
<td>4</td>
<td>GC/M.S-QP2010 Plus</td>
<td>SHIMAOZU</td>
<td>Japan</td>
</tr>
<tr>
<td>5</td>
<td>Blander</td>
<td>National</td>
<td>Japan</td>
</tr>
<tr>
<td>6</td>
<td>Knife</td>
<td>Tramonna</td>
<td>Brazil</td>
</tr>
<tr>
<td>7</td>
<td>Shaded glass boxes for sample preservation</td>
<td>Samarra</td>
<td>Iraq</td>
</tr>
<tr>
<td>8</td>
<td>Filtration &amp; Microfil Traction</td>
<td>Chmlab group</td>
<td>EEC (SPAN)</td>
</tr>
<tr>
<td>9</td>
<td>Buechner funnel</td>
<td>China</td>
<td>China</td>
</tr>
<tr>
<td>10</td>
<td>Plastic cans</td>
<td>Shiny Face L.L.C</td>
<td>Malaysia</td>
</tr>
<tr>
<td>11</td>
<td>Camshats</td>
<td>Shiny Face L.L.C</td>
<td>Malaysia</td>
</tr>
<tr>
<td>12</td>
<td>Sensitive balance</td>
<td>Sartorius</td>
<td>Germany</td>
</tr>
<tr>
<td>13</td>
<td>Mipore filter</td>
<td>China</td>
<td>China</td>
</tr>
<tr>
<td>14</td>
<td>Magnetic stirrer</td>
<td>Roche</td>
<td>Germany</td>
</tr>
</tbody>
</table>

Chemicals and Solvents:
The Chemicals and Solvents brought company from From multiple companies by OMA International office in Baghdad. Most used materials that are used described in the(Table2)

<table>
<thead>
<tr>
<th>No</th>
<th>Chemicals and Solvents</th>
<th>Model</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetinlineol</td>
<td>Sigma- Aldrich</td>
<td>Germany</td>
</tr>
<tr>
<td>2</td>
<td>Mgso4 Ang.</td>
<td>HIMEDIA</td>
<td>India</td>
</tr>
<tr>
<td>3</td>
<td>NaCl</td>
<td>BAKER J.T.</td>
<td>Denmark</td>
</tr>
</tbody>
</table>

GC/M.S optimal Condition Used for samples Extracted by QUECHERS method.
Were Conducted using Column of type DB-5MS, column length (30m), thickness 0.25 um, diameter of column 0.25mm (Stationary phase). Helium was used as the carrier gas (mobile phase) at flow rate 10°C/ min and temperatures between (280-60) °C 0 and the time needed to separate each sample is (30 min).[16].

Determination of pesticide residues
Determination of pesticide residues have been carried out by using gas chromatography(GC/M.S).[16].

Sample Collection
The experiment was conducted for a group of fruits and vegetables imported from different countries as shown in Table (3). Method [16] and [17] was used after some modifications were made according to the possibilities available for the purpose of extracting the samples and then purifying them and finally detecting them using GC / M.S.
Extraction Method
QuEchERS method used for extract pesticide residue from Fruit&Vegetable tissue. The name represent brief for those word,quick,easy,cheap,effective,rugged,and safe.(50 g) of the samples (50g) on vegetables and fruits under study washed and cut into small parts and placed each sample separately in the blender and add 100 ml of acetonitrile (ACN) and mix the mixture for 5 minutes at 3000 cycles / minute, and then extract the minute (D11) for the purpose of disposing of impurities and substances in the extract, take the resulting odor from the filtration process for each sample and add a chloride substance to each sample in a glass flask using Buchner funnel. Sodium NaCl by 1.5 g and MgSO4 Anhy. placed on a magnetic stirrer (Hot Plate& Stirrer) with no heat to be applied when the sample was placed. The voltages and frequency were 230 V 50 H2 and the flask left on the machine for 10 minutes. The filter was then reintroduced in a glass flask Using the Buchner funnel funnel to remove all additives and impurities in the extract, take 100 ml of extract for each sample and put in a round glass flask (evaporator) diameter (32/29) and use the rotary evaporator (300 ° C) and the water bath (40-35 °C). The evaporation was delayed until the acetonitrile droplets stopped falling into the recovery flask. The remaining liquid in the glass beaker of each sample was less than 20 ml. Filter the remaining extract in the round glass beaker for each sample using Milli Pore filters. Chm SHIFT - filtration with pore size 0.45 and diameter 25 mm to ensure a very pure extract and thus obtain accurate results when conducting GC/M.S.[16][17]

3. Results and Discussion

GC/M.S Results
Using GC/M.S analyzed sample instrument after extraction process had been done. (Table 4)Show The results of GC/M.S.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compound</th>
<th>Formula</th>
<th>Retention time</th>
<th>Peak area</th>
</tr>
</thead>
<tbody>
<tr>
<td>American Apple  1</td>
<td>Propen</td>
<td>C6H12O</td>
<td>5.394</td>
<td>25.87</td>
</tr>
<tr>
<td>American Apple  2</td>
<td>Allyl Carbonate</td>
<td>C4H9NO3</td>
<td>6.872</td>
<td>31.59</td>
</tr>
<tr>
<td>Egyptian Strawberry 1</td>
<td>Isopropyl ether</td>
<td>C3H8O</td>
<td>7.986</td>
<td>11.24</td>
</tr>
<tr>
<td>Egyptian Strawberry 2</td>
<td>Hydralcyonitrile</td>
<td>C3H7NO</td>
<td>2.014</td>
<td>1.49</td>
</tr>
<tr>
<td>African grapes   1</td>
<td>Acetonitrile</td>
<td>C3H4N</td>
<td>3.690</td>
<td>8.77</td>
</tr>
<tr>
<td>African grapes   2</td>
<td>2,3 Dihydrofuran</td>
<td>C6H10O</td>
<td>20.546</td>
<td>1.62</td>
</tr>
<tr>
<td>African Pears    1</td>
<td>2Propoxy ethanamine</td>
<td>C6H12NO2</td>
<td>2.141</td>
<td>6.31</td>
</tr>
<tr>
<td>African Pears    2</td>
<td>Eoct</td>
<td>C3H6O2</td>
<td>2.070</td>
<td>9.62</td>
</tr>
<tr>
<td>Iranian Red Pepper 1</td>
<td>Trimethyl hexane</td>
<td>C3H7O2</td>
<td>2.023</td>
<td>31.54</td>
</tr>
<tr>
<td>Iranian Red Pepper 2</td>
<td>Trimethyl pentane</td>
<td>C6H14</td>
<td>2.066</td>
<td>34.24</td>
</tr>
<tr>
<td>Iranian Tomato   1</td>
<td>Allyl carbonate</td>
<td>C6H12O3</td>
<td>2.341</td>
<td>0.35</td>
</tr>
<tr>
<td>Iranian Tomato   2</td>
<td>Butanesulfonyl chloride</td>
<td>C7H14NO2</td>
<td>2.135</td>
<td>43.72</td>
</tr>
<tr>
<td>Turkish cucumber 1</td>
<td>5-Methoxazolidine</td>
<td>C6H12NO</td>
<td>2.632</td>
<td>2.45</td>
</tr>
<tr>
<td>Turkish cucumber 2</td>
<td>Amyl hydroperoxide</td>
<td>C6H12O2</td>
<td>2.111</td>
<td>3.54</td>
</tr>
<tr>
<td>Turkish cucumber 3</td>
<td>Nitrobutane</td>
<td>C6H12NO3</td>
<td>9.341</td>
<td>0.16</td>
</tr>
<tr>
<td>Turkish cucumber 4</td>
<td>2,4-dimethylpentane</td>
<td>C8H16</td>
<td>2.282</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The results of the gas chromatography, where the x-axis represents the time required for the appearance of the sample. The y axis represents the height of the curved tops of the extract.

Figure 1: Examination of the gas chromatography of the American apple extract

Figure 2
Shows the presence of another substance called Allyl Carbonate Fermium is added to the pesticide for the purpose of strengthening it and increasing its susceptibility to killing by attracting insects to the active ingredient of the pesticide.

The rest of the results were not mentioned because they are only natural compounds within the composition of the crop[19].
Figure 2: Examination of the gas chromatography of the American apple extract

Figure 3: Examination of the gas chromatography of the Egyptian strawberry extract

Figure 4: Examination of the gas chromatography of the Egyptian strawberry extract

Figure 3
Shows the compounds in the strawberry extract from the presence of Iso propyl ether, a substance added to the acetonitrile solvent used to dissolve the active ingredient of the pesticide as the pesticide appeared in the form of fumigant residues where these evaporators As new ways to control agricultural pests if they are better in terms of effectiveness as well as lower production cost compared to the usual pesticides used. The acetonitrile solvent or other solvent can be introduced as a developer of the pesticide and may also be incorporated into the pesticide formulation [20].

Figure 4
Shows the compound Hydracrylonitrile, a compound in the synthesis of unsaturated organic acid (Cyanoalkyl propiolates) and the latter has the potential to inhibit the growth of micro-organisms (especially microorganisms), so it is used as a fungicide [21].
Figure (5):
Shows the compounds obtained from the gas chromatography examination of African grapes if the acetonitrile solvent is present. It is used here to dissolve the pesticides and to prove that the acetonitrile solvent is used in the pesticide industry by efficiently removing the pesticide from the plant tissue because it is dissolved. The plant cells are confined to the plant and are used on a concentration basis where it works more than the dilution and selects its appropriate [22].

Figure 5: Examination of the gas chromatography of the African grape extract

Figure (6):
shows the presence of Article 2,3-Dihydrofuran and this article has the ability to stop feeding the insect where it is added to the pesticide as an antifungal agent to feed the insect and therefore when the feeding of the insect gets regression in the insect society, meaning that the number of insects decreases and therefore when reducing the number of insects that strike Plant less control processes and this has a good economic return [23].

Figure 6: Examination of the gas chromatography of the African grape extract

Figure 7:
Shows the compounds obtained from the gas chromatography of the African pea extract, the presence of the substance (2-Propoxy ethanamine). This material is produced by Triflumizole and the latter is a fungicide [24].

Figure 7: Examination of the gas chromatography of the African Pea Extract
Figure (8):
Shows the presence of a compound (Eoct), a pesticide registered by the National Commission for Pesticides accredited in India [25]. The rest of the results were not mentioned because they are only natural compounds within the composition of the crop.

Figure 8: Examination of the gas chromatography of African pears

Figure (8):
The presence of the compound (Eoct) in the extract isolated from the potato crop, which is a pesticide registered by the National Committee for pesticides approved in India [26]. while the rest of the results did not mention Because they are only natural compounds within the composition of the crop

Figure 9: Examination of the gas chromatography of Turkish potato

Figure 10:
Shows the presence of the Trimethylhexane compound in the Iranian Red Pepper crop, which is a compound that increases the affinity between the pesticide and the water. In increasing intimacy, the solubility will increase and thus increase the plant's absorption of the active ingredient of the pesticide [27].

Figure 10: Examination of the gas chromatography of the extract of the Iranian red pepper

Figure (11):
Shows the presence of the compound (Trimethyl pentane), which is also a compound that increases the familiarity between the pesticide and water and when increasing the affinity will increase the solubility and thus increase the absorption of the plant to the active substance of the pesticide [28]. The rest of the results were not mentioned because it is only a Natural compounds within the composition of the crop.
Figure 11: Examination of gas chromatography of the extract of Iranian red pepper

Figure 12: Shows the compounds obtained from the gas chromatography examination of the Iranian tomato extract. The presence of Allyl carbonate, a substance used in the manufacture of the early stages of the cyclization precursor. This initiator is used in the manufacture of fermons and pheromones added to the pesticides to increase the efficiency of the pesticide because it works to attract the insect for the active ingredient of the pesticide [29].

Figure 13: Shows the presence of Butanesulfonyl chloride, a herbicide used to prevent bush growth in the irrigation channels of Paddy rice and bush growing on the edges of irrigation channels. Butanesulfonyl chloride is used in the manufacture of Pyrozole and the latter is used in paddy rice[30]. The rest of the results were not mentioned because they are only natural compounds within the composition of the crop.
Figure 14:
Shows the compounds obtained from the gas chromatography examination of the cucumber extract of the Turkish cucumber (5-methloxazolidine) if they are used as fungicides, which are used as insecticides. Tetrahydrooxazine is added to it and works together as an insulating layer and the layer has an insect repellent activity[31].

Figure 15:
Shows the presence of the substance (Amyl hydroperoxide) in the Turkish cucumber crop and this article works to inhibit phosphorus pesticides[32].

Figure 16:
shows the presence of nitrobutane in the Turkish cucumber crop. This substance is mixed with bordex and works together to break down the insect wings and thus lead to its death and reduce its damage to the crop[33].
Figure (17) Shows the presence of a substance (2,4-dimethyl pentane) in the Turkish cucumber crop. This article contains the cyclic boric acid (boric acid) and this acid value as starting materials or intermediates in the production of chemical derivatives can be used as additives in production of pesticides [34].

4. Conclusions

We conclude from this study that imported fruits and vegetables carry many toxic and harmful substances to the health of the consumer as a result of the transactions carried out to ensure their access to the consumer of good quality. Therefore, it is preferable to encourage local agriculture on a regular and good basis and to protect the crops from the pests that they destroy through the optimum use of the pesticide within the permissible limits or the use of less toxic pesticides instead of importing crops subject to different treatments to ensure that they reach the consumer of high quality. Protection of consumer health is second to encourage domestic product to compete importer.

References


Volume 6 Issue 10, October 2017

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Paper ID: ART20177569

DOI: 10.21275/ART20177569 1965
Berkeley California 94

| DOI: 10.21275/ART20177569 | 450 University Research center, Dreijenplein 8, 6703 B


Paper ID: ART20177569 | DOI: 10.21275/ART20177569 | 1966


[18] A. Lajiness, Thomas; Racine , Wis. 1972. Oxazo idine andtetrahydrooxazine compounds having insect repellent activity, assignor to no drawing. Filed mar. ser. No.20,097 Int.cl.co7 d 87/06, 85/26,3,707,541.


