

Multi-Residue Analysis of Organophosphorus Pesticides in Vegetable Using GC-MS

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Abstract

This study investigates the levels of pesticide residues in Cucumbers (*Cucumis sativus*), potatoes (*Solanum tuberosum subsp. Tuberosum*) and tomatoes (*Lycopersicon esculentum*). The samples were minced in a food processor initially subjected to extraction followed by cleanup using solid phase extraction (SPE) column. Separation was performed on a GC capillary column (Rtx-5 ms-30 m × 0.25 mm × 0.25 μm). The sample was injected by using splitless mode, helium as the carrier gas followed by quadrupole mass spectrometry detection. The mobile phase flow rates, column temperatures, and MS parameters were all optimized to reach high sensitivity and selectivity. Seven pesticides were detected in tomatoes sample, six in cucumber and four in potatoes samples. The findings indicate risks and concerns for public health.

Keywords

Pesticides, Organophosphorus, Malathion, Environmental Exposure Vegetables, Gas Chromatography-Mass Spectrometry

1. Introduction

Pesticides constitute any substance or mixture of substances, such as insecticides, fungicides, rodenticides, insect repellants, weed killers, antimicrobials intended for preventing, destroying, or mitigating any pest. Pesticides are linked to a variety of diseases such as cancer [1] [2]. Their mode of action is by targeting systems or enzymes in the pests which may be identical or very similar to systems or enzymes in human beings and therefore, they pose risks to human health and the environment through their toxicity persistence, mobility, degradation, bioaccumulation, volatility, and leaching [3] [4]. The greater use of pesticides for high agricultural production has led to increased pollution of soil, water and air [5] [6]. The fate of the pesticides is controlled by the chemical and

physical properties and by the natural processes that might take place such as accumulation, degradation or volatility. Regulations to identify and quantify pesticides are constantly changing to ensure increased food safety, making the screening and routine quantitation of pesticide residues an important and demanding application in food safety. WHO and the Expert Committee on Pesticide Residues in Food (PRiF) had issued a number of guidelines that regulate the use of pesticides [7] [8] [9].

The toxicity of pesticides had been accelerated by their improper use and lack of awareness of their potential risks. Many people die or severely affected from pesticides poisoning [10] [11]. More selective and safer pesticides and new chemical groups emerged had been introduced in the last four decades to ensure selectivity and minimal side effects [12] [13].

A plethora of analytical and spectroscopic methods had been introduced and utilized for the determination of pesticides residues [14]-[18]. Advances in GCMS instrumentation had been introduced to increase the sensitivity, mass accuracy determination, resolution and the detectability of this technique. LC/MS/MS can be used to simultaneously monitor hundreds of potential contaminants—including those difficult to detect by GC [19] [20]. While the MS/MS detector allows for specific, sensitive detection of the pesticide species, the LC column specifications such as particle size is vital to ensure the highest quality data. Ultra-high pressure LC (UHPLC) can also be used with MS/MS detection for monitoring pesticide residues. UHPLC allows for higher sample throughput when used in conjunction with a highly efficient < 2 μm particle size column [21].

1.1. Experimental

Sample Preparation and Processing

Cucumbers (*Cucumis sativus*), potatoes (*Solanum tuberosum subsp. Tuberosum*) tomatoes (*Lycopersicon esculentum*) samples were bought from a local vendor, Khartoum, Sudan. Organophosphorus pesticides and malathion standard reference material were supplied by Shimadzu, Japan.

Standards

The pesticide standards used in this study are: Dichlorvos, Fenobucarb, Simazine, Propyzamide, Diazinon, Fennitrothion, Thiobencarb, Isoprothiolane Isoxathion, Tetrachloroisophthalonitrile (TPN), Chlornitrofen (CNP) (Phosphonothioic acid, phenyl-, O-ethyl O-(4-nitrophenyl) ester EPN and iprobenfos. A mixture of the pesticide standards was prepared with ethyl acetate in the concentration to give a concentration of 0.001 ppm. Malathion standard (10 ppm) also was prepared with ethyl acetate.

1.2. Samples Preparation

1.2.1. Extraction of Vegetables Samples for Pesticides Determination

Sample preparation and extraction were conducted within 24 hours after sampling. 20 g grams of each of the vegetables were weighed into a conical flask and

20 g of anhydrous sodium sulfate and 5 g of sodium hydrogen carbonate were added. 100 ml of 1:1 (v/v) ethyl acetate/dichloromethane mixture were added and the mixture was shaken. The content of the conical flask were mixed thoroughly by shaking the conical flask. Another 20 g of anhydrous sodium sulfate were further added to the content of the flask and 20 g of sodium hydrogen carbonate were added. Each conical flask was corked tightly and the mixture was shaken thoroughly for 10 min and was allowed to stand for 3 h. The organic layer was decanted into a 200 ml round bottom flask and evaporated using the rotary evaporator at 40°C. Finally each sample was dissolved and collected with 2 ml of ethyl acetate and transferred into a 2 ml vial and ready for the clean-up.

1.2.2. Clean-Up of vegetable Extracts Using Silica Gel

Solid phase extraction cartridges (SPE) were used to extract the samples. 10 ml of 1:1 (v/v) ethyl acetate/dichloromethane mixture were used to wet and rinse the cartridges. The 2 ml extract residue in the vial were transferred into the cartridge and the extract vial rinsed (three times) with 2 ml ethyl acetate. The cartridges were eluted with 80 ml portion of ethyl acetate/dichloromethane at a rate of 5 ml/min into a conical flask as fraction one. Further elution was conducted with 50 ml portion of ethyl acetate/dichloromethane for the second elution. The first and second extract were mixed together. All the fractions of each sample were concentrated to dryness using a rotary evaporator at 40°C. The extract were dissolved in 2 ml ethyl acetate and collected in a vial for gas chromatograph analysis.

1.2.3. De-Fattening of the Extract

The 2 ml extract for pesticides analysis was transferred into a 100 ml separator funnel and 50 ml of 1:1 (v/v) hexane/acetonitrile solution were added. The separator funnels were gradually shaken gently for 3 min and were allowed to stand for 20 min so as to allow separation of the organic solvents. The fraction that contained the acetonitrile fractions of the pesticides were collected into a 50 ml beaker, while the other fractions that contained the fat in the hexane solvent phase was discarded. The acetonitrile fraction that contained the pesticides extract was further cleaned-up by using 25 ml of the pure hexane. The acetonitrile fraction was concentrated to dryness using a rotary evaporator at 40°C. The extract from the de-fattening process were further dissolved using 2 ml of ethyl acetate and collected into a 2 ml vial. The vial containing the pesticides extracts were stored in the refrigerator at 4°C for GCMS analysis.

1.3. GC/MS Conditions for Organophosphorus Pesticides

The sample was injected by using splitless mode, helium as the carrier gas passed with flow rate 1.69 ml/min, the temperature program was started from 50°C with rate 20°C/min to 140°C then the rate was changed to 10°C/min reaching 280°C as final temperature with 3 minutes as hold time, the injection port temperature was 250°C, the ion source temperature was 170°C and the interface

temperature was 250°C.

1.4. GC/MS Conditions for Malathion

The sample was injected by using splitless mode, helium was passed with flow rate 1.08 ml/min, the temperature program was started from 150°C with rate 10°C /min to 280°C as final temperature, the injection port temperature was 290°C, the ion source temperature was 200°C and the interface temperature was 280°C.

1.5. Instrument

The qualitative and quantitative analysis of the sample was carried out by using GM/MS technique model (GC/MS-QP2010-Ultra), Shimadzu Company, Japan with serial number 020525101565SA and capillary column (Rtx-5 ms-30 m × 0.25 mm × 0.25 μm).

2. Results

The identification of pesticides in foodstuffs is a difficult task, which requires selective techniques for unambiguous confirmation, since interfering species from the matrix often mask the signal of the target compounds. For these reasons, the use of chromatographic techniques coupled with MS detection is highly desirable in order to attain satisfactory results. These techniques enable unequivocal identification and confirmation of target species, unlike less selective detectors (e.g., NPD and ECD), avoiding matrix interferences and both false positives and false negatives.

An amount of 10 ppm of pesticides mixture was injected into the GCMS and the spectra were collected. The sample was analyzed by using scan mode in the range of 60 - 350 m/z. The total run time was 20 minutes. Subsequently the vegetables samples were injected separately. The obtained results were recorded and shown in **Figure 1** and **Table 1**. GCMS analysis can be performed in two modes: Single-ion monitoring (SIM): 1 - 4 ions are observed selectively as they provide improved signal-to-noise ratio for ions of interest and Total ion current (TIC): sum of all ions—can be noisy but also captures potential unknown m/z ratios. Single-ion monitoring (SIM) was chosen based on spectra of the pesticides taken from a full mass range analysis of a high level standard. The second mode is the total ion current (TIC) and in this mode a scan acquisition allows the ion selection to be monitored post-acquisition.

In the analysis of organophosphorus pesticides, the ions which give the highest abundance in the EI mass spectra, were selected for monitoring in GC-MS analysis. Increasing the number of ions monitored will only reduce the overall sensitivity of analysis, thus increasing the detection limit.

The most conventional GC-MS detector for pesticide analysis in vegetables is the single quadrupole as it provides high selectivity, high sensitivity and speed of analysis.

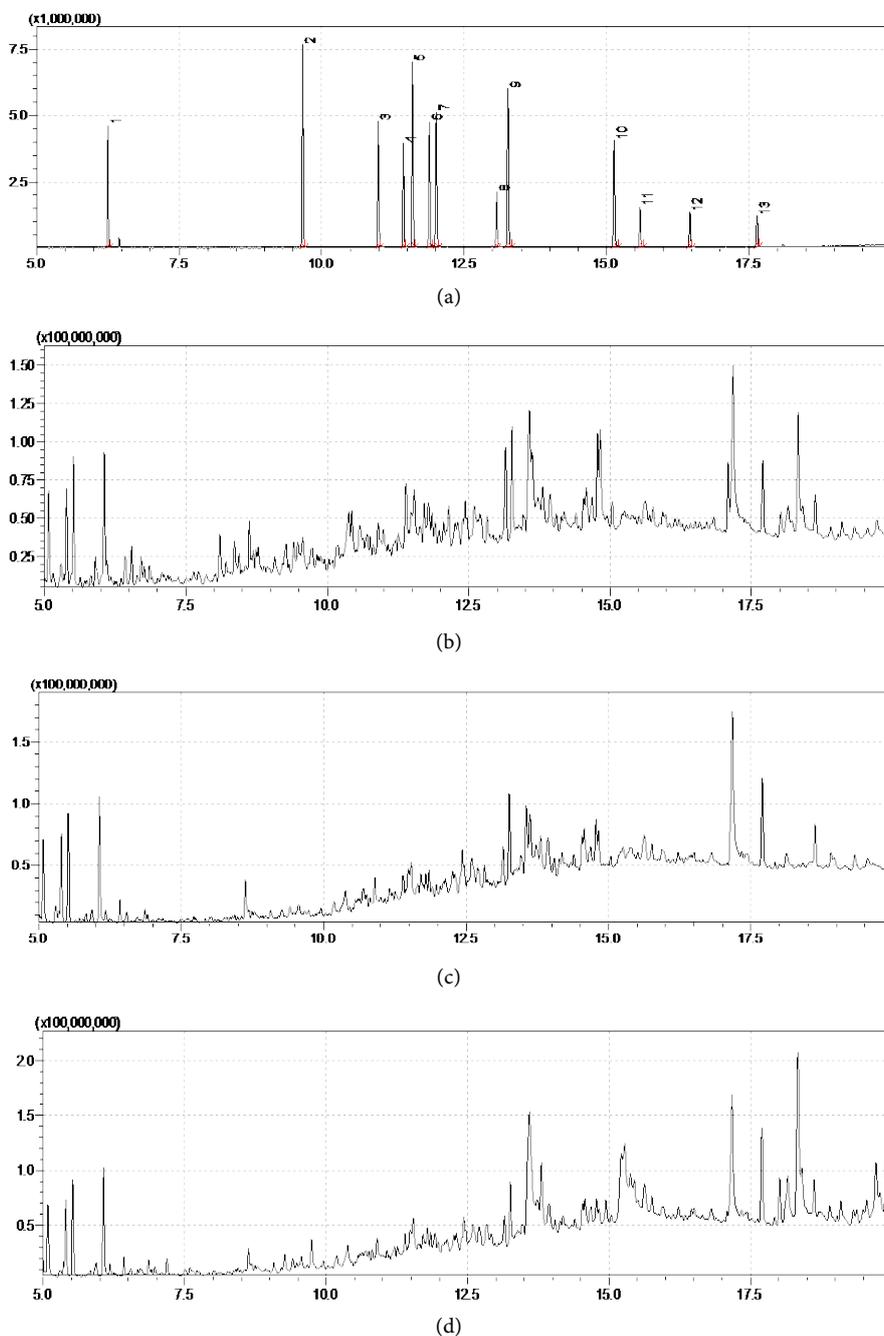


Figure 1. GC chromatograms of (a) Organophosphorus Pesticides Mixture; (b) Tomatoes sample; (c) Potatoes sample; and (d) Cucumber sample.

The GC chromatogram of the organophosphorus pesticides show sharp, well resolved-noise free peaks whereas the chromatograms of the samples show several background peaks were apparent and associated with noise and this is due to the complex matrix of the samples despite extract cleanup of the sample. Nevertheless, pesticides were detected.

Quantitation of the different levels of the pesticides was achieved by the use of single standard method and the results obtained are depicted in **Table 1**.

Table 1. The ions selected for analysis.

| No | Pesticide | Monitoring ion(m/z) |
|----|-------------|---------------------|
| 1 | Simazine | 201, 186 |
| 2 | Propyzamide | 255, 173 |
| 3 | TPN | 266, 264 |
| 4 | Iprobenfos | 204, 91 |
| 5 | CNP | 291,217 |
| 6 | EPN | 169, 157 |
| 7 | Thiometon | 127, 125, 93 |
| 2 | Malathion | 127, 125, 93 |

3. Malathion

The ions selected (127, 125, 173) and the total run time was 16 minutes. The (m/z) 173 provides a good selectivity and also be monitored with confidence at low levels. Lower mass ions intensities such m/z 125 and 127), m/z 173 are also informative.

The GC chromatogram of malathion is shown in **Figure 2** and the amount calculated for the three different samples are shown in **Table 2**. The quantities of the detected pesticides are shown in **Table 2**. The insecticide thiometon in the tomatoes sample was above the MRL limit whereas malathion level was below the MRL. In cucumber and potatoes samples neither of the pesticides were detected.

The maximum residue levels for the reported pesticides in the EC [22] database and detected in this study are tabulated in **Table 3**.

The other detected pesticides. *i.e.* Tetrachloroisophthalonitrile (TPN), Chlor-nitrofen (CNP) and (Phosphonothioic acid, phenyl-, O-ethyl O-(4-nitrophenyl) ester) (EPN) are not reported in the EC database but their toxicity had been investigated by different authors [2] [23]-[27].

Multi-residue surveillance of pesticides in vegetables and fruits is an ongoing project for regulatory agencies worldwide. Regulations to identify and quantify pesticides are constantly changing to ensure increased food safety, making the screening and routine quantitation of pesticide residues an important and demanding application in food safety.

The use of GCMS produces very reliable methods for the determination of pesticides at trace level in vegetables. However, matrix interferences can complicate the analysis and compromise the selectivity and specificity of the method. The EU commission has issued guidelines for pesticides analysis that involves the use of MS techniques in order to meet the confirmation requirements. This fact highlights the need for improved sample treatment method. New extraction techniques were introduced for sample treatment that include supercritical fluid extraction, microwave-assisted extraction, solid-phase microextraction, matrix solid-phase dispersion and pressurized fluid extraction—accelerated solvent

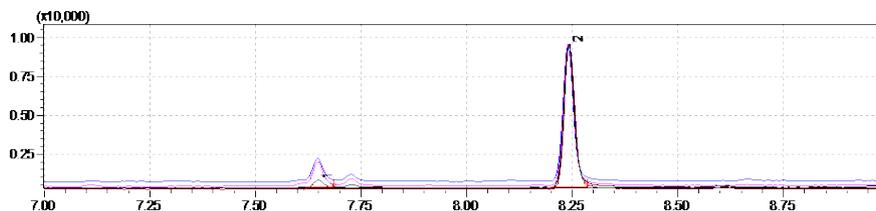


Figure 2. GC Chromatograms of Malathion and thiometon mixture. The relevant MS were collected in the SIM mode. For thiometon, retention time 7.7 min, the ions are $m/z = 127$ (Blue), $m/z = 125$ M (Pink) and $m/z = 88$ (Black). For Malathion retention time 8.25 min, the ions are $m/z = 127$ (Blue), $m/z = 125$ M (Pink) and $m/z = 88$ (Black).

Table 2. The quantities of the detected pesticides.

| ID | Name | Ret. time | Tomatoes | Cucumber | Potatoes |
|----|-----------|-----------|----------|--------------|--------------|
| 1 | Thiometon | 7.647 | 16.03470 | Not detected | Not detected |
| 2 | Malathion | 8.239 | 8.04479 | Not detected | Not detected |

Table 3. The maximum residue levels of pesticides in the vegetable samples (ug/kg).

| Vegetables | Malathion | Propyzamide | Simazine | Isoprothiolane |
|------------|-----------|-------------|----------|----------------|
| Potatoes | 0.02 | 0.01 | 0.01 | 0.01 |
| Tomatoes | 0.02 | 0.01 | 0.01 | 0.01 |
| Cucumbers | 0.02 | 0.01 | 0.01 | 0.01 |

extraction. For instance the introduction of QuEChERS had brought about the ease, effectiveness, rapidity, ruggedness and safety to the sample treatment method. Many authors had reported the advantages of the use of QuEChERS in pesticides and multi-residue analysis. Pesticide residue surveillance food and environmental samples is an ongoing project for regulatory bodies worldwide [28] [29] [30].

In pesticides analysis, multi-residue analysis is the common practice. Pesticides comprise a large group of chemicals that differ in their physicochemical properties e.g. polarity molecular size and charge. A single run for such determination may affect the sensitivity of the analysis due to such differences which may jeopardizes the analysis and requires careful optimization of the technique.

An important aspect in pesticides analysis is sample history *i.e.* the information regarding the time of application *i.e.* before harvesting and the duration as well as other climatic conditions. All these factors are important in understanding the take-up, metabolism and biotransformation of pesticides.

4. Conclusion

GC with quadrupole mass analyzer is a powerful technique in determination of pesticides at low levels. The results presented in this study showed that the samples analyzed were contaminated by pesticide residues, indicating that periodic monitoring programs are important to reduce exposure, accumulation and toxicity of pesticides.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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