

MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH
UNIVERSITY OF AKLI MOHAND OULHADJ-BOUIRA

FACULTY OF NATURAL AND LIFE SCIENCES AND EARTH SCIENCES
DEPARTEMENT OF BIOLOGY



Réf :/UAMOB/FSNVST/2024

END OF STUDIES DISSERTATION

SUBMITTED FOR OBTAINING A MASTER DEGREE

Domaine: Science of Nature and Life

Sector: Biological Sciences

Speciality: Microbial Biotechnology

Presented by:

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Dissertation title

*Analysis of pesticide residues in food commodities
using gas chromatography coupled with tandem
mass spectrometry*

Supported on: 24/06/2024

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Academic year: 2023/2024

Acknowledgements

“We would like to thank God Almighty for giving us the courage, will and patience to complete this work.”

*We begin by expressing our deep recognition and our sincere thanks to our promoter **Dr. YALAOUI-GUELLAL Drifa**, who honoured us by agreeing to direct this work, for all her encouragement and valuable advice that she provided throughout the development of this work.*

*We thank the entire jury, **Dr. LAMRI Naziha** for the honour she does us by presiding this jury and **Dr. IDER Djamila** for having accepted the evaluation of this dissertation and being an examiner*

*We warmly thank **Mrs. TAHRAOUI Alia** for directing us throughout this work and for giving us the benefit of her experience, her kindness and her enlightened guidance. His presence and advice were of great help in establishing this dissertation.*

We also warmly and sincerely thank our teachers in Biology department.

We particularly thank the Central Laboratory of Scientific and Technical Police for their valuable help and their availability and support to carry out this work.

It is impossible to mention all the names, our sincere gratitude goes to all those who, through their advice and skills, made this thesis possible.

Dedications

To my dear parents, I would always like to thank you for everything you have done to date to ensure our education and training, and it is thanks to you that I owe my success. May God grant you good health and a long life, I love you...

With the expression of my gratitude, I dedicate this modest work to those who, whatever the terms embraced, I would never be able to express my sincere love to them.

To the man, my precious offering from God, who owes my life, my success and all my respect: my dear father Saleh.

To the woman who suffered without letting me suffer, who never said no to my demands and who spared no effort to make me happy, my adorable mother Houria.

To my brothers Riad and Iheb, as a testimony of my brotherly affection, my deep tenderness and gratitude, I wish you a life full of happiness and success and may God, the Almighty, protect and keep you.

To my entire family without exception and in memory of my grandparents.

To my partner Ilhem and his family who encouraged us throughout our work.

Nour

Dedications

In the name of Allah, the Most Merciful, the Most Merciful

First of all I would like to thank the Almighty for giving me the courage and patience to reach this stage in order to carry out this work that I dedicate:

To the woman who suffered without ever letting me suffer, who never said no to my demands, who never stopped praying for me, and who sacrificed everything to see me succeed, my adorable mother Dalila.

To my dear father Djelloul, for his encouragement, his support, especially for his love and his sacrifice so that nothing hinders the progress of my studies.

To my dear brother Amine, whom I hope to see succeed and flourish in everything he does, may this work be a source of inspiration and motivation for you.

To my sisters: Wissam, Soumia and Ahlem, their Husbands and their Children. I wish you a future full of joy, happiness, success and serenity.

And to all members of my family without exception. To everyone I have ever known. To all those I love and those who love me.

To my partner Nour and her family who encouraged us throughout our work

Ilhem

Abbreviations list

AOAC: Association of Analytical Communities.

ACN: Acetonitril.

APS: Primary and secondary amines.

EC: European Committee.

EU: European Union.

CI: Chemical ionization.

CL: Liquid chromatography.

PHP: Pre-Harvest Period

ADI: Allowable Daily Intake

EEC: European Economic Community.

EL: Electronic ionization.

LLE: Liquid-liquid extraction.

MLE: Membrane supported liquid extraction.

FAO: Food and agriculture organization.

FFDCA: Federal law on Foods, Drugs and Cosmetic Products.

FIFRA: Federal Law on Insecticides, Fungicides and Rodenticides.

FQPA: Food quality protection law.

GCB: Graphitized Carbon Black.

GC-MS: Gas chromatography coupled with mass spectrometry.

GC-MS/MS: Gas Chromatography tandem-mass spectrometry.

HPLC: High performance liquid chromatography.

JORA: Official Journal of the Algerian Republic.

LC/QTOF-MS: Liquid Chromatography/Quadrupole Time-of-Flight Mass Spectrometry.

MRL: Maximum residue limit.

MADR: Ministry of Agriculture and Rural Development.

m/z: Mass/charge.

MS/SM: Mass spectrometry.

WHO: World Health Organization

ppb: part per billion.

ppm: part-per-million.

NCS: Central nervous system.

PSE: Solid phase extraction.

SPME: Solid phase microextraction.

UHPLC/TOF-MS: Ultra-Performance Liquid Chromatography/Time-of-Flight Mass Spectrometry.

UPLC: Ultra-high-performance liquid.

UPLC/HRMS: Ultra-Performance Liquid Chromatography/High Resolution Mass Spectrometry.

USA: United States of America.

USDA: United States Department of Agriculture.

Figure list

Figure 01: Chemical structures of some herbicides, fungicides and insecticides.....	5
Figure 02: Average pesticide consumption in 2022 in kilograms per hectare of agricultural land.....	11
Figure 03: Turnover of imports from Algeria in pesticides between 2009 and 2017.....	12
Figure 04: Evolution of number of pesticide approval decisions in Algeria (1999-2007).....	13
Figure 05: Main steps to determine pesticides.....	19
Figure 06: Marketing channel for fruits and vegetables	26
Figure 07: Tomatoes: <i>Lycopersicon esculentum</i>	27
Figure 08: Dates: <i>Phoenix dactylifera</i> L.....	28
Figure 09: Potato: <i>Solanum tuberosum</i> L.	29
Figure 10: Strawberry: <i>Fragaria X ananassa</i> Duch.	29
Figure 11: Phases of extraction	32
Figure 12: Purevap-6 evaporator	34
Figure 13: Diagram of chromatography	35
Figure 14: Simplified diagram of the process.....	36
Figure 15: Waterproof direct coupling.....	37
Figure 16: Simplified diagram of a spectrometer	38
Figure 17: Chromatogram of extracts pesticides of tomato.....	41
Figure 18: Mass spectrum of extracts pesticides of tomato.....	42
Figure 19: Spectrum Library.....	43
Figure 20: Chromatogram of extracts pesticides of dates.	43
Figure 21: Mass spectrum of extracts pesticides of dates.	44
Figure 22 : Chromatogram of strawberry extracts.....	45
Figure 23: Chromatogram of pesticides extracts of potato	45

Table list

Table 01: Development of the oldest chemical families.....	6
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Table of contents

Acknowledgements	
Dedications	
Abbreviations list	
Figure list	
Table list	
Introduction	1

Part I: Literature review

I. General information on pesticides	3
I.1. Definition	3
I.2. Classification of pesticides	3
I.2.1. First classification	3
I.2.1.1. Herbicides	4
I.2.1.2. Fungicides	4
I.2.1.3. Insecticides.....	4
I.2.2. Second classification.....	5
I.3. Danger of pesticides	6
I.3.1. Environmental toxicity.....	6
I.3.1.1. Air pollution.....	7
I.3.1.2. Water contamination	7
I.3.1.3. Soil pollution.....	8
I.3.2. Toxicity to humans.....	8
I.3.2.1. Acute toxicity	9
I.3.1.2. Chronic toxicity.....	9
I.4. Use of pesticides	10
I.4.1. Global use of pesticides	10
I.4.2. Use of pesticides in Algeria	12
II. Pesticide residues in foodstuffs	14
II.1. Definition of pesticide residues	14
II.2. Definition of pre-harvest application	14
II.3. Definition of the maximum residue limit	14
II.4. Pesticide Regulations	14
II.4.1. Regulations around the world.....	15
II.4.1.1. In the European Union.....	15
II.4.1.2. In United States.....	15
II.4.1.3. In Japan.....	16
II.4.2. Regulations in Algeria	17
II.5. Methods for detecting pesticide residues in food	18
II.5.1. Storage and preservation of samples.....	19
II.5.2. Extraction and purification	19
II.5.2.1. Liquid-liquid extraction	19

II.5.2.2. Membrane supported liquid extraction	20
II.5.2.3. Solid phase extraction	20
II.5.2.4. Solid phase micro-extraction	21
II.5.2.5. Extracting QuEChERS	21
II.5.3. Pesticide analysis and detection techniques.....	22
II.5.3.1. Gas chromatography	22
II.5.3.2. Liquid chromatography.....	22
<i>Part II : Experimental procedures</i>	
<i>III. Materials and methods.....</i>	24
III.1. Study region	24
III.2. Sampling of fruits and vegetables.....	26
III.3. Botanical classification	27
III.3.1. Tomatoes	27
III.3.2. Dates.....	27
III.3.3. Potato.....	28
III.3.4. Strawberry	29
III.4. Sample preparation	30
III.4.1. Residue analyzes	31
III.4.1.1 Reagents	31
III.4.1.2. Pesticides	31
III.4.2. Analysis protocol.....	32
III.4.2.1. Extraction of pesticide residues.....	33
III.4.2.2. Dispersive solid phase extraction	33
III.4.2.3. Pre-concentration.....	34
III.4.2.4. Chromatographic conditions	34
III.5. Coupling gas chromatography to tandem mass spectrometry	35
III.5.1. Ionization sources.....	36
III.5.2. Interest in GC-MS/MS coupling for pesticide analysis.....	39
<i>IV. Results and discussion.....</i>	40
IV.1. Results.....	41
IV.1.1. Tomato sample	41
IV.1.2. Sample of dates	43
IV.1.3. Strawberry sample.....	44
IV.1.4. Potato sample	45
IV.2. Discussion.....	46
<i>Conclusion.....</i>	49
<i>References.....</i>	51
<i>Appendices</i>	
<i>Abstracts</i>	

Introduction

Agriculture is mainly based on using chemicals to preserve crops against various pests and diseases, thereby increasing yields and improving the quality of agricultural products. However, the intensive use of these chemicals raises significant concerns about food safety and population health. The traces of pesticides in products such as fruits and vegetables can lead to adverse consequences on human health, linked to serious diseases such as cancers, neurological disorders, and endocrine disruption (Tudi et al., 2021).

The use of pesticides in agriculture is frequent in Algeria, with annual quantities estimated between 6,000 and 10,000 tonnes, which constitutes part of the legal requirements. Although the use is significant, the regulation of pesticide residues in food products is still limited. The lack of awareness and adequate training among farmers accentuates this situation, which often pushes them to ignore or not comply with current regulations, leading to the mishandling of pesticides.

In recent decades, there has been an increase in the use of different types of pesticides in agriculture and other human activities. Organisms can accumulate these dangerous chemicals, which are extremely toxic to the environment, animals, and humans, by moving up the food chain. Several studies have demonstrated that long-term exposure to these chemicals, whether direct or indirect, is harmful, including pesticides, through the skin, inhalation, or ingestion, can lead to various birth defects, neurological diseases (such as depression, Alzheimer's, Parkinson's disease), respiratory diseases (asthma, chronic obstructive pulmonary disease) and reproductive disorders (infertility, sterility) (Cui et al., 2022).

In this situation, it is essential to design and implement reliable analysis techniques to identify, and measure traces of pesticides present in fruits and vegetables. The gas chromatography technique associated with mass spectrometry (GC/MS) is particularly effective in this area. Its level of sensitivity and specificity is high, making it possible to detect a wide range of pesticide residues at very low concentrations.

The objective of our work is to identify residues of certain pesticides present in certain fruits and vegetables using advanced analytical methods such as the QuEChERS method for extraction and the GC/MS method for identification. It is subdivided into two main parts.

The first part will be devoted to a bibliographic synthesis which includes two main chapters. In the initial chapter, we provide an overview of pesticides, examining their nature, their use and their consequences on the environment and the health of individuals. It will

examine the different categories of pesticides, their mechanism of action, as well as the risks and potential consequences on ecosystems and individuals. Pesticide residues in vegetables and fruits in Algeria are discussed in the second chapter. It will highlight the difficulties and gaps in the regulation and control of these residues present in food products.

The second part will be dedicated to the experimental part, which is divided into two chapters. The third chapter presents the equipment and techniques used to analyze certain pesticide residues in the samples studied (tomatoes, potatoes, strawberries, and dates). Extraction was carried out using the QuEChERS method and characterization was carried out using gas chromatography coupled with mass spectrometry (GC/ MS). In the fourth chapter, the results obtained are presented and analyzed.

The conclusion of this study is followed by a list of bibliographical references and appendices.

Part I: Literature
review

Chapter I

I. General information on pesticides

I.1. Definition

A pesticide is a product that aims to prevent, eliminate, repel, or control any disease caused by microorganisms or undesirable weeds (Boland et al., 2004). Therefore, a pesticide is a biological substance that has an action on different physiological functions and generally causes the death of the living organism that may have observed it (Calvet et al., 2005).

Pesticides are defined by European Directive 91/414/EEC as active substances and preparations containing one or more active substances that the user receives and which aim to:

- This involves protecting plants or plant products against all harmful organisms or preventing them unless these substances or preparations are defined otherwise below.
- Effect an influence on the vital processes of plants, provided that it is not a nutrient substance (such as a regulator).
- Ensure plant conservation, unless the board or commission specifically regulates preservatives.
- Take into account plant parts and limit or prevent unwanted growth.

In other words, pesticides are all means or products used to prevent, manage, or eliminate organisms classified as undesirable, whether plants, pests, or fungi (Yoanna, 2011).

I.2. Classification of pesticides

It is difficult to classify commercially available pesticides due to their wide variety of chemical structures, functional groups, and activities. The active compounds can be classified according to the nature of the species to be combated, which constitutes the first classification, or according to the chemical nature of the main active substance which constitutes them, which constitutes the second classification (Mrabet, 2009).

I.2.1. First classification

This varies depending on the type of pest to watch for. Pesticides are mainly classified into three categories according to the nature of the intended targets: insecticides, fungicides, and herbicides.

I.2.1.1. Herbicides

The most frequently used pesticides worldwide, regardless of crops. Their objective is to eliminate plants that compete with the plants to be protected by limiting their growth. This is why they are used both for road maintenance and for private gardening. Herbicides have various approaches to act on plants, such as (Mrabet, 2009):

- Different disturbances in the regulation of auxin AIA (a main hormone that promotes cell expansion, like pyridine acids, etc.);
- Photosynthetic interference (triazines, substituted ureas, etc.);
- Divisional interferences (carbamates, dinitroanilines, etc.);
- Lipid interferences (cyclohexanediones, propionates, etc.);
- Cellulosic interferences (benzamides, nitriles, etc.);
- Amino interferences (phosphonic acids, aminophosphonates, etc.);
- Carotenoid interferences (isoxazolidinones, etc.).

I.2.1.2. Fungicides

They are used to manage the spread of plant diseases caused by fungi or bacteria. Their effects can be different: some hinder the respiratory system of plants (dithiocarbamates, copper, sulfur), and others cell division (benzimidazoles). The biosynthesis of amino acids and proteins is also disrupted by certain fungicides, such as anilinopyrimidines, or the metabolism of carbohydrates and phenylpyrroles (Mrabet, 2009).

I.2.1.3. Insecticides

These substances are used to protect plants against insects. What they do is kill them or stop them from reproducing. There are several types such as (Kesraoui, 2008) :

- Insecticides that affect the nervous system (avermectins, organophosphates, etc.)
- Those which affect cellular respiration (phenoxy pyrazoles, rotenone, etc.)
- Those which regulate growth (benzhydrazides, thiadiazoles, etc.).

There are also systemic products that penetrate and move through the plants through the vessels, or contact products which, once applied, form a protective barrier on the surface of the

plant. Preventative effects may be present, when they act before the parasite penetrates the plant tissues or is curative (Louchahi, 2015).

In addition to these three main families mentioned previously, others can be mentioned, such as acaricides, intended for mites; nematicides, against nematode worms; rodenticides, against rodents; moleicides, against moles; molluscicides, against slugs and snails; acaricides and corvifuges, respectively against crows and other birds harmful to crops; etc.(Mrabet, 2009).

I.2.2. Second classification

The chemical nature of the active substance, which is the main component of these products, is taken into account in the second classification system of plant protection products. This nature is influenced by the elemental composition, functional composition, and structure of the substance, which are the spatial organization of the atoms that constitute the molecule (Calvet et al., 2005).

Thanks to this chemical classification, it is possible to deepen our understanding of the properties of pesticides and their biological behavior. There are a wide variety of oldest chemical families, The main chemical groups include organochlorines, organophosphorus, carbamates, pyrethroids, triazines, and substituted ureas (Figure 01 and Table 01).

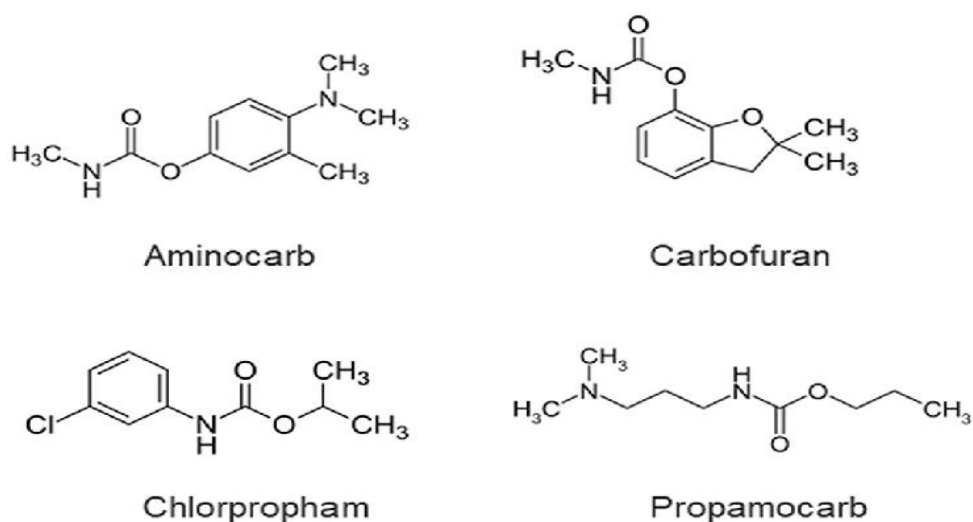


Figure 01: Chemical structures of some herbicides, fungicides and insecticides (Calvet, 2005).

Table 01: Development of the oldest chemical families (herbicides, fungicides, and insecticides) during the 20th century (Parliamentary Office report, 2003).

	Herbicides	Fungicides	Insecticides
Before 1990	Copper sulfate, Iron sulfate	Sulfur Copper salts	Nicotine
1990 -1920	Sulfuric acid		Arsenic salts
1920 -1940	Nitrated dyes		
1940 -1950	Phytohormones		Organochlorine, Organophosphates
1950 -1960	Triazines, Ureas substituted, Carbamates	Dithiocarbamates, Phthalimides	Carbamates
1960 -1970	Dipyridyls, Toluidins	Benzimidazoles	
1970 -1980	Amino-phosphonates Propionates	Triazoles, Dicarboximides, Amides, Phosphites, Morpholines	Pyrethrinoids, Benzoyl-ureas
1980 -1990	Sulfonylureas	Diethofencarb	Imidacloprid
1990 -2000	Isoxaflutole Carfentrazone	SND Strobilurins	Fipronil

I.3. Danger of pesticides

In general, pesticides are considered poisons for living beings, and their degradation is very slow, gradually transforming them into toxic agents that accumulate in organisms over the long term. Various research has been carried out to understand what happens with phytosanitary products after their dispersion in agricultural areas. The results of these studies show that excessive use of pesticides can have harmful repercussions on the health of farmers and consumers, as well as the environment and the economy (Pflieger, 2009).

I.3.1. Environmental toxicity

For almost half a century, pesticides have been detected in all environments: in river water and groundwater, in the air, in rainwater, and the soil. According to Pflieger, 2009, pesticides present in the environment can have repercussions on human health and ecosystems.

Pesticides are found in different compartments of the environment mainly because they are used intentionally on crops and forests (for example by spreading or spraying) to combat pests or for other uses (domestic, public health, fight against vector-borne diseases). but also due to accidents linked to manufacturing, transport, and storage. Pesticides found in the environment cause various pollution which can have harmful consequences on living beings. About humans, except for occupational exposure, exposure to pesticides is indirect, because it comes from the presence of these toxic substances in their environment and is responsible for this situation (Merhi, 2008).

The majority of phytosanitary products penetrate the soil where they undergo a set of processes that determine attitudes and their distribution in other areas of the environment. This dispersion and their accumulation leads to problems of contamination of environments and soils (Barriuso, 2004).

I.3.1.1. Air pollution

The atmosphere plays a crucial role in the dispersion of pesticides. According to De Luca et al. In 2007, pesticides entered the atmosphere through various stages and can then be transported through the different phases of the atmosphere, which can lead to contamination of non-target ecosystems.

Different research groups in France have highlighted the presence of pesticides in all phases of the atmosphere, at concentrations varying over time, sometimes seasonal, linked to the periods of application, and in the space close to the sources. Sometimes, we can also detect low-volatile or prohibited compounds, such as lindane (Aubert et al., 2005).

I.3.1.2. Water contamination

Water contamination varies depending on the flow method: In general, the instantaneous pesticide concentration is highest during runoff, most moderate for artificial soil drainage, and lowest for leaching. During runoff and erosion processes, the majority of pesticide losses occur in solution, with significant particle transport only for the most used pesticides (hydrophobic or poorly soluble in water). The maximum risk of contamination of surface waters occurs during heavy downpours shortly after application or penetration of the product into the soil, when the substance is at its maximum availability in the soil and soil surface conditions are potentially altered (Aubert et al., 2005).

According to [Levine, 2007](#), pesticides can cause groundwater contamination several years after their presence and in areas far from the application area. Consider the agricultural Okanagan Valley and Osoyoos Lake region, where residues (1-5 ppb) of at least 14 organochlorine pesticides have been found in groundwater, which they not been used for about 10 years ([Villeneuve et al., 1987](#)).

I.3.1.3. Soil pollution

Agricultural soils are contaminated by phytosanitary products spread on crops. A large number of plant protection products are used or have been used in the past. As for insecticides, these are almost exclusively chlorinated substances such as DDT. In industrialized countries, some of these compounds are banned but are still used in some developing countries. Although their use has ceased, pesticides (parent molecule and/or metabolites) can remain in the environment even after several decades ([Amiad, 2011](#)).

According to research conducted by [Buck et al., \(1983\)](#) and in [Pimentel and Lehman \(1993\)](#), DDT residues were discovered in Arizona soils 12 years after their application. In addition, microfungi may represent up to 60% of soil biomass, which demonstrates their crucial role in its balance. Fungicides have the ability to suppress some of these beneficial microfungi ([Pimentel, 1995](#)). Consequently, the massive use of fungicides has a considerable impact on the ecosystem balance of agricultural soils. Soil pollution also affects earthworms, responsible for humification processes, leading to a decline in their long-term fertility ([Caplat et al., 2011](#); [Ramade, 2011](#)).

I.3.2. Toxicity to humans

According to [Spea \(1991\)](#), the toxicant is usually tasted in the form of food residue, but it can also be absorbed in drinking water, through inhaled air, or skin contact with the product. It is more likely that the rest of the population will be affected by skin contact or inhalation by farmers and workers who prepare the mixtures and carry out the treatments. In Canada, approximately 99% of people retain DDT (or derivatives of this organochlorine) in their fatty tissues, at a concentration of approximately 4 ppm. Many pesticides have been found in human milk, sometimes more than the amount recommended for the baby ([Hayo et al., 1997](#)).

Recently, it has been proven that pesticides can to modify the immune system or disrupt hormonal regulations in humans, leading to various symptoms. Higher rates of breast cancer, prostate cancer, testicular cancer, endometriosis, birth defects of the male reproductive system,

and reduced sperm count have been linked to the presence of "endocrine disrupting" chemicals among human health problems (Hayo et al., 1997). Two types of risks for human health can arise from plant protection products: chronic effects or acute effects.

I.3.2.1. Acute toxicity

The risk of acute pesticide poisoning is caused by misuse, accidental use, or voluntary poisoning, often serious (Cherin et al., 2012). Regulatory testing on laboratory animals allows the acute sensitivity of chemical compounds to be assessed. The concept chosen is that of the lethal dose 50 which is the quantity of active ingredient that, administered at one time, by ingestion, inhalation, or through the skin, results in the death of 50% of the animals treated. The main data on the acute effects of pesticides on humans come from personal observations and cases of poisoning recorded by poison control centers (Pflieger, 2009).

I.3.1.2. Chronic toxicity

The persistent effects of plant protection products are linked to different conditions and generally appear several years after exposure. These chronic conditions include carcinogenesis, impact on reproduction, and neurological disorders (Capkin et al., 2006; Deleage, 2013).

a. Carcinogenic pesticides

Various international organizations have recognized or probably identified several pesticides as carcinogenic to humans, following epidemiological or experimental studies. Regarding the population exposed to work, it seems that mortality and the incidence of certain cancers are accumulating. Typically, these would be rare or rare cancers, such as lip, ovarian, brain, or skin cancers. Different conditions are suspected in children, such as leukemia and brain tumors. These manifestations seem to be associated with exposure (agricultural work, contamination of the environment or food) of the mother during pregnancy (Pflieger, 2009).

Furthermore, for the general population, the data remain ambiguous in adults, except for non-Hodgkin's lymphoma. To summarize, there is little data available and further research is needed, particularly on the determination of exposure to pesticides and the biological mechanisms of action of the substances. Other risk factors could play an important role in the emergence of certain cancers, particularly in agricultural regions (Kelley and Duggan, 2003).

b. Impact on reproduction

It is now considered that exposure to pesticides with endocrine-disrupting properties is responsible for side effects such as reproductive dysfunction in humans. In the 1960s-1970s, the nematicide DBCP (dibromochloropropane) caused tens of thousands of cases of male sterility during occupational exposures in many countries in tropical and subtropical regions. Furthermore, according to [Clementi and colleagues \(2008\)](#), living in a rural area, where many pesticides are used, seems to increase the risk of infertility. Other products such as chlordecone, carbaryl, and 2,4-D also have harmful effects on male fertility. Many studies investigate the association between pesticides and birth defects. Certain effects on the fetus (death, prematurity, hypotrophy, etc.) are also highlighted. However, these effects remain difficult to highlight through current research ([Pflieger, 2009](#)).

c. Neurological disorders

The action of insecticides (organochlorines, organophosphates, pyrethroids, carbamates, etc.) on pests is based on neurotoxicity. However, because of their insensitivity, these substances have also shown neurotoxic effects on certain animals. As for long-term effects on humans, knowledge is still limited, unlike short-term effects. Additionally, some herbicides may cause neuropsychological disorders such as anxiety, depression, and suicide attempts. Some pesticides are also believed to cause neurodegenerative disorders such as Parkinson's disease. Although several studies have shown that exposure to pesticides increases the risk of developing this disease, the compounds responsible have not yet been discovered ([Pflieger, 2009](#)).

I.4. Use of pesticides

I.4.1. Global use of pesticides

Over the past decades, global consumption of agricultural pesticides has continued to increase and appears to continue (Figure 02). Plant protection products (herbicides, insecticides, fungicides) increased by 82% globally between 1990 and 2019, now reaching more than 4 million tonnes per year. Our map, based on data from the Heinrich-Böll Foundation, shows that certain regions of the world use these products particularly intensively. In South America, in particular, we observed a maximum concentration of pesticides dumped on fields, with an average exceeding 5 kg per hectare of cultivated land in 2019 ([Gaudiaut, 2022](#)).

Colombia and Ecuador even have a consumption of more than 10 kg per hectare, while Costa Rica is the world record with more than 20 kg per hectare, due to its intensive production of exotic fruits which requires significant quantities of pesticides. In Asia, too, farmers use these products massively, with an average consumption of between 3 and 4 kg per hectare in 2019. Countries like China and South Korea even far exceed this level, with more than 10 kg per hectare. In comparison, the European average was around 2 kg per hectare that year. However, the amount of food consumed differs greatly between countries depending on their agricultural culture. The global pesticide industry was estimated to be worth over \$84 billion in 2019, and growth of 11.5% is forecast for 2023, representing over \$130 billion (Gaudiaut, 2022).

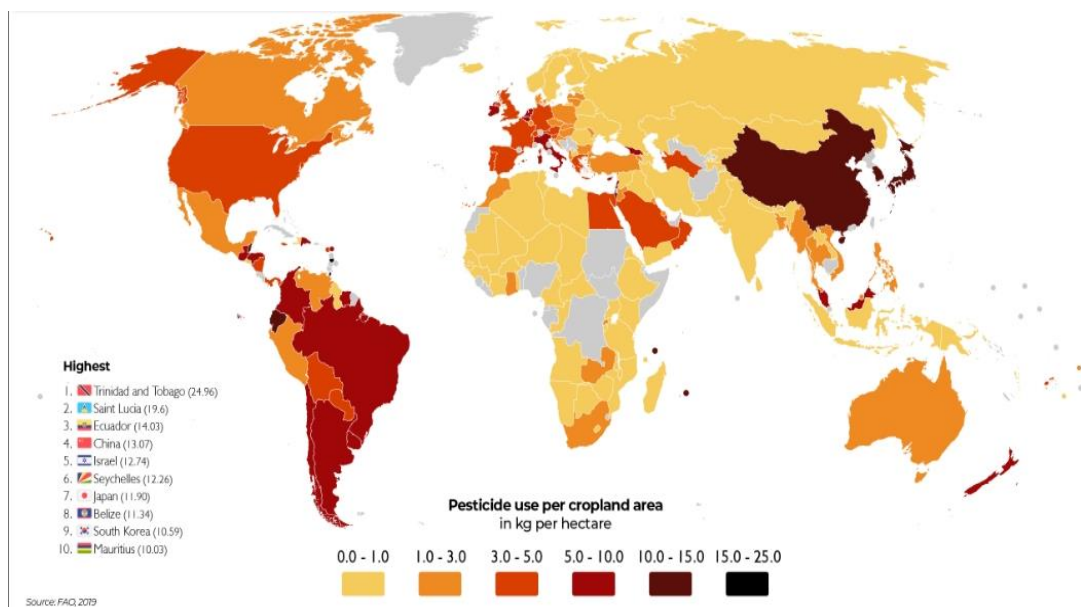


Figure 2: Average pesticide consumption in 2022 in kilograms per hectare of agricultural land (Statista, 2022).

The quantity of pesticides used worldwide in 2020 is shown in appendix 02. Pesticides are mainly used in South America, with a consumption of approximately 770,393 tonnes. Asia ranks second (658 tonnes), while Africa ranks fifth globally (around 106 tonnes), behind North America (487 tonnes) and Europe (468 tonnes). Finally, Ukraine occupies the lowest place (70.42 tonnes).

I.4.2. Use of pesticides in Algeria

The Algerian pesticide market continues to grow (Figure 03). In 2010, Algeria imported 59.6 million US dollars, in 2012, almost 92 million US dollars in 2014, and almost 108 million US dollars in 2015 (FAOSTAT, 2021).

In Algeria, there are around 400 phytosanitary products, of which nearly 40 are used by farmers. The annual consumption of pesticides in Algeria is between 6,000 and 10,000 tonnes, i.e. a usage rate of 15% compared to the total needs increased by 50,000 tonnes. This makes Algeria a major consumer of waste (Moussaoui and Tchoulak, 2005).

According to Moussaoui and Tchoulak (2005), Algeria has a monopoly on the manufacture and importation of pesticides. MOUBYDAL is an autonomous entity that uses a distribution network: the National Agricultural Supply and Service Office (ONAPSA). Between 1990 and 1996, national consumption of pesticides, including fungicides and insecticides, was 30 to 40% imported, and 100% for other products (herbicides, nematicides, and others). After 1996, the national market was opened to pesticide imports exclusively carried out by MOUBYDAL (Autonomous pesticide management and marketing company), Figure 04, imports are experiencing exponential growth (INPV, 2008).

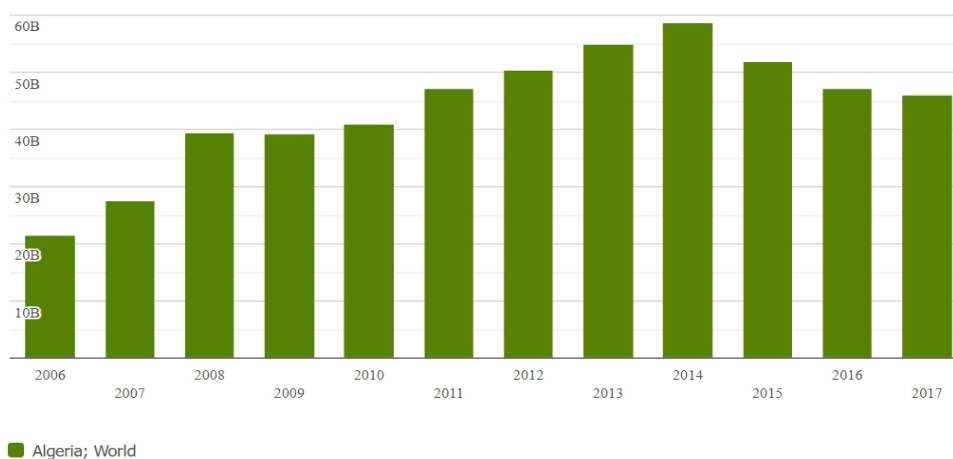


Figure 03: Turnover of imports from Algeria in pesticides between 2006 and 2017 (FAOSTAT, 2021).

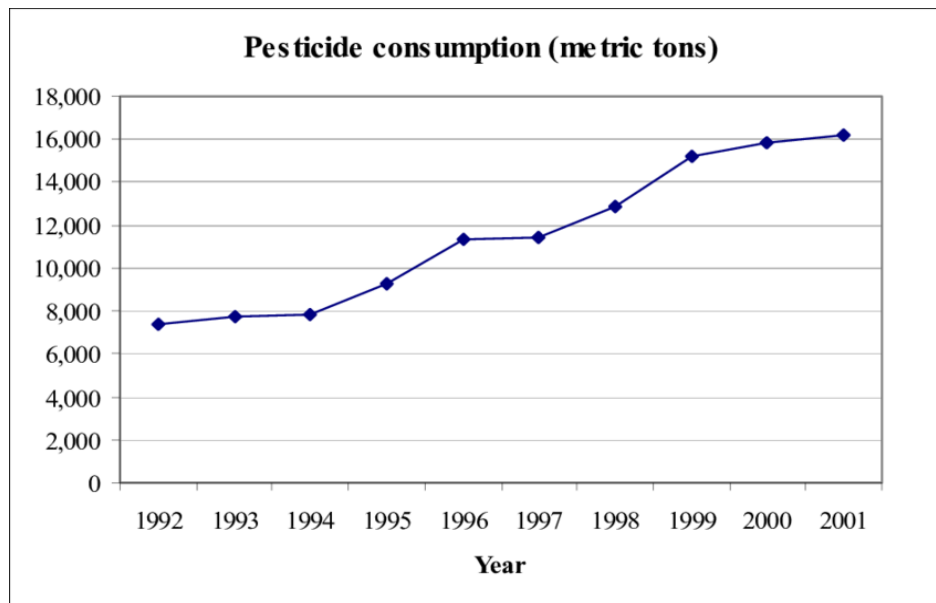


Figure 04: Evolution of number of pesticide approval decisions in Algeria (Moussaoui and Tchoulak, 2005).

According to more recent data from the Algerian Customs Statistical service in 2010, Algeria imported 67 million US dollars of pesticides in 2009, compared to 49.4 million dollars in 2007 (Mokhtari, 2011). However, in the current economic context, several companies specialize in the importation of pesticides and various associated products. Different sources of imported pesticides, but it should be noted that the bulk is European (Germany, France, Great Britain, Holland, Switzerland), Asian (China, Japan), and Arab (Saudi Arabia, Jordan, Arab Emirates, Lebanon).

Chapter II

II. Pesticide residues in foodstuffs

II.1. Definition of pesticide residues

A pesticide residue is a substance resulting from the use of a pesticide in food, agricultural products, or animal feed. This term includes transformation products, metabolites, reaction products or impurities, as well as pesticide derivatives (Food Codex, 2017). Pesticide residues are the remains, including active substances, metabolites, and/or degradation or reaction products of active substances used in pesticides, present in or on foods, following Articles 3 and 2 of the European Commission Regulation No. 396/2005 (EEC, 2005).

II.2. Definition of pre-harvest application

The Pre-Harvest Period (PHP) represents the period required between the last pesticide treatment and the harvest of the crop. It constitutes the minimum duration which must separate the date of treatment from the date of harvest (Lionel, 2006).

The label of the phytosanitary product mentions this period and the Marketing Authorization (MA) decisions determine this period. This waiting period is intended to promote the degradation of pesticide residues, thus ensuring that the harvested food complies with the applicable regulatory Maximum Residue Limits (MRLs). This ensures consumer safety by limiting exposure to pesticide residues in food (Zabeirou, al., 2018).

II.3. Definition of the maximum residue limit

The maximum permitted concentration of a residual substance in a food of animal origin is called the Maximum Residual Limit, such as meat or milk, after the administration of an antibiotic veterinary medicinal product to an animal. These MRLs are established for authorized substances and are regulated by Regulation (EU) No 37/2010. Compliance with waiting periods between the last administration of the medicinal product and the marketing of animal products is essential to avoid non-compliance associated with residues in foodstuffs of animal origin (Fournet, 2015).

II.4. Pesticide Regulations

Today, legislation on pesticides aims to ensure public health and preserve the environment. Thus, products are subject to different regulations that apply at each stage of the pesticide production process: from the authorization of sale of active substances to residue

control, including transport monitoring and labeling of the products used. At the same time, pesticides are regulated at several levels: internationally, European, and national (Pflieger, 2009).

II.4.1. Regulations around the world

II.4.1.1. In the European Union

From 1977 to 1990, three old directives (76/895/EEC, 86/362/EEC, 90/642/EEC) were put in place to regulate pesticides. From January 1st, 1977, Directive 76/895/EEC applied to products intended for human consumption and, in certain cases, animal consumption. According to this directive, pesticide residues included any traces of toxic pesticides, including degradation products, which were found in or on the products concerned. Maximum Residue Limits (MRLs) for vegetables and fruits were also established, as well as the sampling method for their detection. However, did not applicable to products intended for export to developing countries (Chaffey and Dobozy, 2004).

MRLs for cereals are defined by Directive 86/362/EEC, which comes into force on 07/08/1986 and defines the sampling method to detect pesticide residues. This directive did not apply to products intended for export to developing countries, nor to food or feed, or those intended for sowing or planting. The circulation of products containing more than MRL for pesticide residues was prohibited. Directive 90/642/EEC, which entered into force on 14/12/1990, defined residue limits for pesticides in certain plant products, including fruits and vegetables. The circulation of products containing more than MRL for pesticide residues was prohibited (Chaffey and Dobozy, 2004).

II.4.1.2. In United States

Since the first federal legislation on food, food purity, and drug regulation in 1906, interest in pesticide regulation in the United States has evolved significantly. The purpose of this law was to ensure the safety and accuracy of the labeling of food, drugs, and beauty products. The United States Department of Agriculture (USDA) subsequently enacted the first specific federal pesticide law, the Insecticide Act of 1910, which was intended to prevent the production, sale, or transportation of insecticides. or impure or mislabeled fungicides (Chaffey and Dobozy, 2004).

Food law was strengthened in 1938 by the Federal Food, Drug, and Cosmetic Act (FFDCA), which provided authority to set regulatory limits on pesticides and other harmful substances found in foods. More comprehensive regulations regarding pesticides, insecticides, fungicides, and interstate regulations for all pesticides, including herbicides and rodenticides, from the USDA (Chaffey and Dobozy, 2004).

The Miller Reform, which was adopted in 1947, imposed the setting of maximum legal concentrations of rodenticides (FIFRA) in 1954, which requires the registration of sales of pesticide residues in food and feed. Congress passed an amendment to the FFDCA that was controversial and complex. The major regulatory change occurred in 1970 with the transfer of the administration of FIFRA to the United States Environmental Protection Agency (EPA), a new agency (Chaffey and Dobozy, 2004).

In 1972, FIFRA was completely revised, requiring scientific evidence showing that the pesticide has no undue adverse effects on humans and water. The 1988 FIFRA amendments addressed the issue of re-registration of pesticides registered before 1984. The FFDCA was amended on August 3rd, 1996, by the Food Quality Act (FQPA) which created a single food safety standard for pesticides in food. The FQPA also requires that all existing limits be reviewed every 10 years to ensure they meet new health safety standards (Chaffey and Dobozy, 2004).

In establishing these limits, EPA has a responsibility to ensure the safety of children and infants. It is also necessary to assess the risks of all non-occupational sources of pesticide exposure, such as food, drinking water, and household uses, as well as potential effects on the endocrine system following the FQPA. It is essential to combine the risks of chemicals that have a common mechanism of toxicity, to assess the cumulative risks (Chaffey and Dobozy, 2004).

II.4.1.3. In Japan

The Agricultural Chemicals Regulation Act, adopted by the Ministry of Agriculture, Forestry and Fisheries of Japan in 1948, regulates the production, sale, and use of pesticides. This law states that producers and importers can only sell pesticides if they are registered. At the same time, these products are primarily regulated by the Department of Health, Labor and Welfare through the Food Safety Act of 1947. The department creates an ADI (Allowable Daily Intake) for each pesticide based on toxicological assessments. In addition, each crop-pesticide

combination is defined with Maximum Residue Limits based on tests carried out following good agricultural practices. Finally, the responsibility of the Ministry of the Environment is to assess the dangers to food due to chemical substances present in the environment ([Fujimori, 2004](#)).

II.4.2. Regulations in Algeria

Since plant protection products must be used with caution, some laws and decrees govern their use. In addition, with the multiple withdrawals of phytosanitary products and the evolution of interest in the environment, inspections of the application of these laws have been reinforced in recent years in the majority of agricultural operations ([Carrier, 2009](#)).

Law No. 87-17 of 01-08-1987 on phytosanitary protection in Algeria was adopted to regulate the production, storage, distribution, marketing and use of phytosanitary products. Finally, the law prohibits the sale, import or manufacture of an unapproved phytosanitary product. According to information from the official journal of the Algerian Republic n°9 of 18 Safar 1431, February 3, 2010, the approval of phytosanitary products was established in Algeria under the following executive decrees establish the rules concerning the importation and export of phytosanitary products for agricultural use ([Phytosanitary Index, 2017](#)).

Here are some recent regulatory texts related to the use of pesticides ([MADR, 2009](#)):

- ❖ Phytosanitary control at borders is governed by Executive Decree No. 93-286 of 9 Joumada Ethania 1414, published on November 23, 1993. It appeared in JORA No. 78 of 11-28-1993, p.18.
- ❖ Executive Order No. 95-405 of 9 Rajab 1416, dated December 2, 1995, deals with the regulation of phytosanitary products used in agriculture. It appeared in JORA n° 75 of 12/26/1995, p.16.
- ❖ According to Ministerial Order No. 079 of 7 Dhou El Hidja 1420, dated March 13, 2000, the packaging and labeling information and indications of phytosanitary products for agricultural use must be recorded. It appeared in JORA N° 28 of 05/17/2000, p.20.
- ❖ The principles of development, adoption and implementation of sanitary and phytosanitary measures are defined by Executive Decree No. 04-319 of October 7, 2004. It appeared in JORA No. 64 of October 10, 2004, p.18.

- ❖ Executive Decree No. 05-67 of January 30, 2005 establishes the national codex alimentarius committee, which establishes its roles and structure. It appeared in JORA n°11 of 02/09/2005, p.4.
- ❖ The decree of 23 Dhou El Kaada 1428, of December 3, 2007, designates the members of the commission for phytosanitary products for agricultural use. It appeared in JORA n°04 of 01/27/2008, p.21.
- ❖ The Order dated 21 Rabie Ethani 1429, i.e. April 27, 2008, makes changes to the order of 12 Ramadhan 1426, equivalent to October 15, 2005, which establishes the list of candidates for the national committee of the Codex Alimentarius. This publication was made in JORA N°32 of 06/18/2008, p.61.

II.5. Methods for detecting pesticide residues in food

For several decades, pesticides have been widely used in the agricultural sector to prevent, control or eliminate harmful organisms, to obtain high yields. Establishment takes place at various stages of production, both to preserve the crop and facilitate harvesting and post-harvest preservation. Some pesticide residues are present in fruits and vegetables intended for human consumption due to their intensive use. In order to guarantee the health of consumers, limit values have been established and numerous studies have been carried out to evaluate the levels of pesticide residues in fruits and vegetables ([Kardani et al., 2022](#)).

The measurement of pesticides present in the food matrices of fruits and vegetables has been the subject of numerous studies in recent years. Various techniques for analyzing pesticides in fruits and vegetables are presented in this study (Figure 05). It is possible to use these extraction, preparation, purification and analysis methods to assess the levels of pesticides present in fruits and vegetables ([Mrabet, 2009](#)).

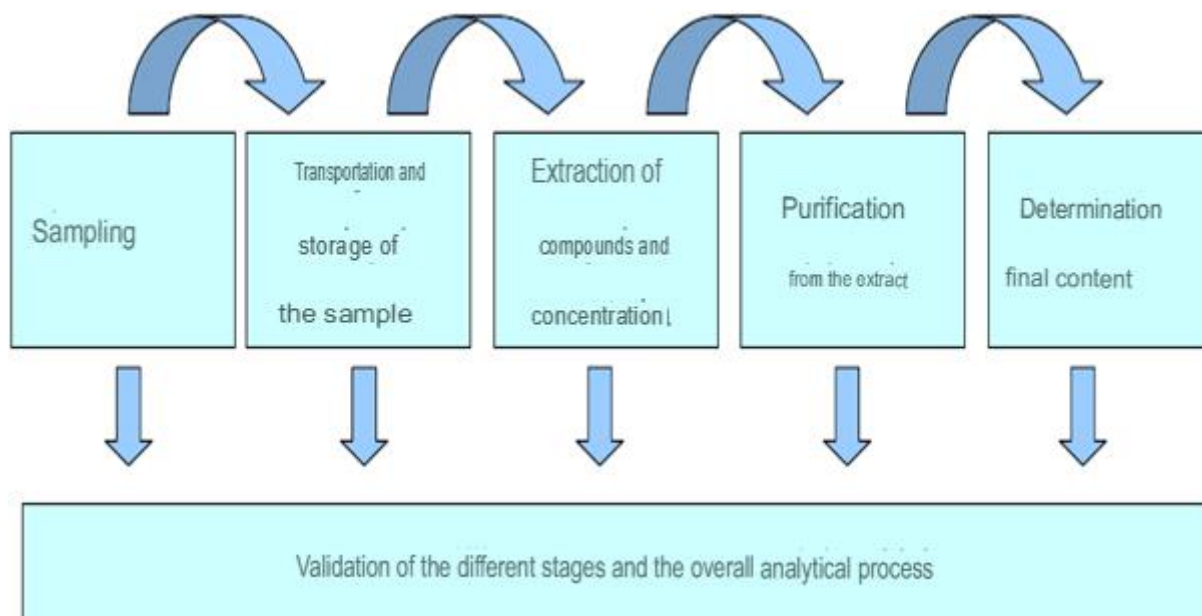


Figure 05: Main steps to determine pesticides (Mrabet, 2009).

II.5.1. Storage and preservation of samples

Storage of samples requires special attention. First, after sampling, it is important to protect the sample container from light. Then, we can distinguish two phases of the period which separates sampling from analysis: the first, immediately after sampling, where the temperature of the sample is not adjusted, and the second, when the sample is placed in a refrigerator and the storage conditions are adjusted. Next, it should be pointed out that the instability of the sample increases as the temperature increases. Finally, fourth, the fluctuation of samples during transport can have an impact on the results (Wilson, 1993).

II.5.2. Extraction and purification

To analyze samples, preliminary treatments must be carried out, such as extraction and concentration of the analyte in the sample. This step aims to ensure the purity of the sample by removing any other impurities that could interfere with the analyte assay. Indeed, the pesticides sought are usually found at very low concentrations in complex matrices, which makes their extraction essential. Several different extraction methods are mainly used in the field of pesticides (Barcelo et al., 2003).

II.5.2.1. Liquid-liquid extraction

Liquid-liquid extraction (LLE) is one of the oldest pretreatment methods in analytical chemistry. It offers the possibility of extracting pesticides in a reliable, adaptable and

compatible manner with most instruments. It is based on how the components must be separated between two immiscible liquid phases, usually water and the organic solvent. It is influenced by the relative solubility of the component in the two liquids (Sahyoun, 2022).

II.5.2.2. Membrane supported liquid extraction

Liquid-liquid extraction is a newer and more efficient method, and it requires only a few milliliters of solvent. It integrates two liquid-liquid extraction steps into one, using a porous membrane impregnated (MLE) with an organic solvent which separates two aqueous phases (Bedendo et al., 2012).

II.5.2.3. Solid phase extraction

Solid phase extraction (SPE) is the approach involves concentrating or separating an analyte of interest from a complex matrix onto an adsorbent stationary phase. The interfering matrix which was not retained is effectively effective. Therefore, the analyte can be analyzed within a range of maximum sensitivities using the analytical technique. The compounds are distributed between a liquid phase, the sample, and a stationary phase, the adsorbent, in the solid phase of the extraction. There are four steps in the extraction method (Bakirci et al., 2014):

- The stationary phase may be wetted with an organic solvent to activate the retention sites.
- Quantitative retention of analytes of interest during the stationary phase is the goal of sample deposition, especially interference by simple non-retention.
- Weakly retained interferents are removed by washing, which consists of using a solvent with low eluting strength (methanol/water) to remove them.
- It is recommended to use a solvent with the lowest possible eluting force to avoid strongly retained interferents and entrain all the molecules of interest. Solvent evaporability also plays a role in solvent selection.

II.5.2.4. Solid phase micro-extraction

The solid phase micro-extraction (SPME) method is a recent approach to solid phase chromatography, developed by Pawliszyn in 1989 for processing various environmental samples (Cortada et al., 2009).

It is carried out without using solvents. Analytes with low or medium polarity are extracted from aqueous or gaseous samples by contacting them with a fused silica fiber coated with a selective polymer film, attached to a fine needle on a syringe. After adsorption, the analytes are extracted, separated and measured using an analytical tool. SPME can be performed either using a space head or by directly inserting the fiber into the sample. In general, SPME is compatible with gas chromatography or high-performance liquid chromatography methods or for the analysis of enriched analytes (Cortada et al., 2009).

Fruits and vegetables were analyzed by gas chromatography-mass spectrometry (GC - MS) with methods using SPME, which can also be combined directly with an MS detector without chromatographic separation. Although SPME offers benefits such as the absence of solvent, speed, portability and ease of use, it also has disadvantages such as its high cost, the fragility of its fiber and its limited lifespan, as well as potential sample transfer issues. Additionally, extraction efficiency is frequently restricted due to the interaction between analytes present in the fiber and those present in the sample matrix, restricting the number of pesticides that can be extracted and analyzed at the same time. time (Sahyoun, 2022).

II.5.2.5. Extracting QuEChERS

QuEChERS extraction (which means Quick, Easy, Cheap, Effective, Rugged and Safe) is based on the use of acetonitrile and purification by DSPE (dispersive solid-phase extraction) (Anastassiades et al., 2003). She was the first in the analysis of pesticide residues in fruits and vegetables. Various modifications have been made and adopted by the Association of Analytical Communities and the European Committee (Lehotay et al., 2010).

In addition, this technique easily integrates with chromatographic techniques coupled with mass spectrometry, with a few adjustments (Shaoo et al., 2011). According to Luo et al. (2015), it is possible to combine QuEChERS with other purification methods such as extraction pipette, liquid-liquid dispersive extraction or gel permutation chromatography. Some researchers have recently associated QuEChERS with the use of UPLC/HRMS, LC/QTOF-MS, and UHPLC/TOF-MS.

II.5.3. Pesticide analysis and detection techniques

There are three main reasons why pesticide residue analysis is complex and requires the use of a variety of methods. Plant protection products are part of very varied chemical classes, with a great diversity of matrices on which they are used, using interference positions. However, detection capabilities decrease as security levels increase (Sahyoun, 2022).

Since the 1970s, chromatographic methods have been commonly used to evaluate pesticide residues and their metabolites (Appendix 01). The importance of these sensitive techniques lies in the low concentration of these residues. The general assessment of these substances is as follows: Acquisition, sample preparation, in-depth analysis, identification, validation and measurement (Sahyoun, 2022).

II.5.3.1. Gas chromatography

Due to its high resolution and high sensitivity, pesticide analysis can be combined with mass spectrometry, nuclear magnetic resonance or Fourier transform infrared spectrometry. With a detection capacity of up to $\mu\text{g/l}$. It is used for many pesticides, except those with low use and/or thermal instability, which require derivatization by alkylation or sterilization. The physicochemical properties of the pesticides sought to influence the choice of the stationary phase, the injection system and the detection system. GC associated with a mass spectrometer has been used since the early 2000s to broaden the range of pesticides analyzed, reducing interference and analysis time (Brondi et al., 2011).

★ *Application*

Researchers have been more interested in N-methyl carbamates than other carbamates because of their widespread use in agriculture. Due to the thermo-decomposition of the respective phenols, their analysis is not carried out directly by GC, which requires derivatization and cold injection techniques, as well as the use of short columns. Even if ECD is the most frequently used detector, it is also possible to use GC-MS coupling (Turiel and Martin-Esteban, 2008).

II.5.3.2. Liquid chromatography

Using a methanol-water or acetonitrile-water mixture, liquid chromatography allows separation and detection at room temperature. It is particularly suitable for the analysis of polar compounds and constitutes an alternative to gas chromatography for the analysis of

thermolabile, non-volatile and very highly polar products. It does not require derivatization for the analysis of pesticides and their degradation products. GC - CL coupling is frequently used to evaluate carbamates (Alder et al., 2006).

LC has become the preferred choice for detecting most insecticides and their metabolites, as well as herbicides and plant growth regulators, with the advent of biodegradable pesticides, which are generally more polar than the former. Pesticide analyses by this type of chromatography have been greatly simplified thanks to the possibility of combining LC with the solid phase extraction system and mass spectrometry. Previously, LC analyses were more difficult due to the detectors available for use in combination with LC, which were less efficient and sensitive than GC detectors (Alder et al., 2006).

★ *Application*

Liquid chromatography is often used for the analysis of carbamates due to their ability to degrade under heat. However, not all carbamates can be detected by ultraviolet, only those that contain a UV chromophore such as carbofuran, carbaryl, benomyl and carbendazim. It is necessary to identify other compounds using electrochemical or fluorescence detectors (Schenck and Wong, 2008).

Part II:
Experimental procedures

Chapter III

III. Materials and methods

In this section, we will present the equipment and techniques used during this study. First, we will discuss the study region, the origin of fruits and vegetables. Subsequently, the analytical protocol employed in detail for the process begins with the systematic collection of samples, followed by the extraction of relevant compounds and ends with their identification using advanced analytical methods.

This research aims to analyze the presence of two pesticides, Deltamethrin and Chlorothalonil, in fruits and vegetables collected in the regions of Biskra and Mitidja. The analysis was carried out using gas chromatography coupled with mass spectrometry.

The implementation activities were carried out during February and March 2024, in partnership with the central laboratory of the scientific and technical police in Algiers.

The function of the scientific and technical police is to provide technical assistance and support to investigators during criminal investigations. She takes care of the evaluation and analysis of forensic clues and traces at the request of the Judicial Investigations Department. It also contributes to the training of medico-legal actors and the management of specialized databases ([Sdpst, 2022](#)).

There are a total of 9 departments or services in the laboratory, each with its area of specialization. Forensic ballistics, DNA fingerprinting in forensic biology, drug chemistry, forensic chemistry, forensic microbiology, the criminology department dedicated to fire and explosion incidents thus takes care of the analysis of evidence and the conduct of cybercrime investigations, and the in-depth examination and documentation involved, such as writings and counterfeit currencies, as well as forensic toxicology. All services are led by a specialist team of experts with in-depth knowledge and experience in their respective fields. In addition, the laboratory ensures that it maintains a watch on technological and scientific advances ([Sdpst, 2022](#)).

III.1. Study region

Our research focuses on the Mitidja region, located in north-central Algeria, and framed by four surrounding wilayas: Algiers, Boumerdes, Tipaza and Blida. The climate of this region is Mediterranean, with two very distinct seasons: characterized by a mild and rainy season lasting from November to April and a hot and dry season from May to October. Autumn is often

marked by abundant rainfall and pleasant temperatures, while winter and spring offer moderate weather conditions.

Douccene is a commune located about thirty kilometers southwest of the town of Biskra in Algeria. It is also a city which is renowned for its large expanses of date palm plantations and which constitute the pillar of its agricultural economy. It is marked by high temperatures and low humidity, particularly during very hot summers where temperatures often exceed 40°C, and mild winters characterized by pleasant days and cool nights. During the winter months, precipitation is rare and mainly concentrated (Guehiliz, 2022).

This region occupies a vital position in the agriculture of the wilaya, given its essential contribution in the renowned cultivation of dates. The exceptional quality of the dates is the result of the hard work of its growers and the favorable environment for the growth of date palms, which are appreciated for their sweet taste and tender texture. In addition to the cultivation of dates, the municipality also practices other agricultural products such as the agriculture of cereals, and also vegetables and fruits thanks to modern irrigation techniques to counterbalance the arid climate of the region. (Guehiliz, 2022).

Pesticides have seen a significant increase in recent decades, especially in the agricultural sector, as these products are beneficial in providing several undeniable advantages that result in increased production of superior agricultural products at affordable costs. Their improper use can result in the widespread dispersion of pesticides, thus contaminating food products intended for consumption (Topuz et al., 2005).

The assurance of consumer food safety is based on the monitoring of levels of pesticide residues and the regular assessment of the alarming quantities of these residues accumulated in food matrices. The accumulation of these residues requires immediate measurement (Shamsipur et al., 2016; Sun et al., 2020).

All existing data on the assessment of pesticide residues in fruits as well as vegetables consumed in Algeria have been compiled for in-depth analysis

III.2. Sampling of fruits and vegetables

Observations show that the distribution of fruits and vegetables is mainly organized from the first producer until they arrive at the final customer, it follows three distinct modes (Figure 06):

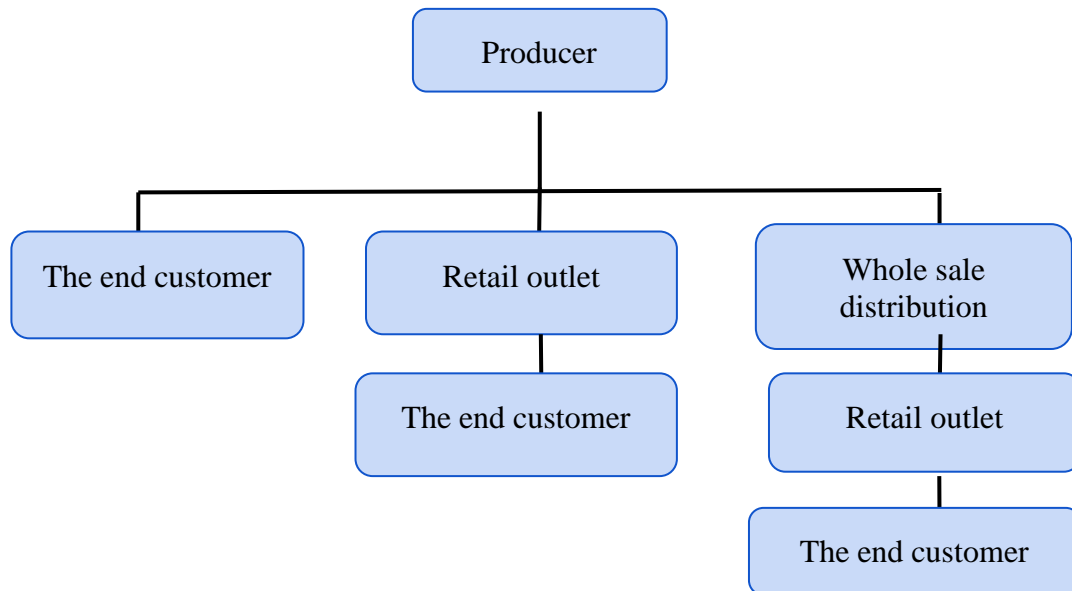


Figure 06: Marketing channel for fruits and vegetables (Mokhtari, 2016).

- In the first configuration, the distribution chain is first routed from the operator to the wholesalers' points of sale, then they are redistributed to retailers before reaching consumers.
- In the second configuration, the distribution mode is sent directly from farms to retailers, who then sell them to consumers.
- In the third configuration, distribution goes directly from the producer to the final consumer, without going through the usual intermediaries.

The collection of samples was carried out both at retail sales points and also at wholesale points in the two areas studied (Appendix 03).

III.3. Botanical classification

III.3.1. Tomatoes

The importance of the *Lycopersicon esculentum* Miller tomato in the human diet lies in its constant consumption throughout the world throughout the year. It was produced approximately 152 million tonnes in 2010 and is the largest cultivated fruit in the world (FAO, 2012).

The tomato occupies first place in terms of consumption and sales globally, making it the leading agricultural product consumed on the national interest market of Rungis. In reality, the tomato is considered a fruit because it is the fertilization of the flower resulting in the formation of a fruit that contains the seeds necessary for the reproduction of the plant. So, biologically, the tomato is a fruit, but culinarily, it is considered a vegetable (Chaux and Foury, 1994). Farmers from southern Spain introduced tomato cultivation in Algeria, because the circumstances offer it advantages. It began to be consumed in the Oran region in 1905 and developed towards the center, particularly on the Algerian coast (Latigui, 1984).

In 1753, the Swedish botanist Linnaeus named the tomato *Solanum lycopersicon* belonging to the Solanaceae family (Figure 07 and Appendix 04), but 15 years later Philip Miller replaced this name with *Lycopersicon esculentum* (Valimunizigha, 2006).



Figure 07: Tomatoes: *Lycopersicon esculentum* (Original photo).

III.3.2. Dates

Phoenix dactylifera generally has an elongated or rounded fruit. His flesh surrounds his hard core. We eat the flesh or pulp of the date (Figure 08). It is composed of a thin cellulosic

envelope known as pericarp or skin. The mesocarp is fleshy, of variable texture depending on the quantity of sugar and dark in color. However, the core is enveloped by an endocarp that is lighter in color and has a fibrous texture, but which can also be similar to a thin, parchment-like membrane (Espiard, 2002).



Figure 08 : Dates: *Phoenix dactylifera* L (Original photo).

The scientific name *Phoenix* given to the date palm finds its origin which is derived from the Phoenician word phoenix (Appendix 05), as well as in the Greek word dactulos which means finger, is found in the specific epithet dactylifera about the shape of the fruit furthermore this species, which is dioecious and monocotyledonous, belongs to the Arecaceae family, a large family of palm trees known for producing dates.

Algeria is one of the main word producing countries of Deglet Nour dates, with 20% of total European imports, Algeria ranks among the largest date producing countries globally. In 2019, date production amounted to 1,094,700 tonnes. With a contribution of 13% of dates worldwide, Algeria is positioned as the main producer, ranking first with the famous Deglet Nour variety, widely recognized worldwide for its quality and quantity (Faostat, 2020).

In Algeria, the cultivation of date palms is mainly concentrated in the South-East such as the regions of (Biskra, El-Oued and Ouargla), but also in the South-West such as (Béchar, Adrar), as well as the regions of South-Central such as (Ghardaïa, Tamanrasset, Tindouf, Illizi) and also in some other isolated regions (Merrouchi and Bouammar, 2015).

III.3.3. Potato

Solanum tuberosum L., commonly known as potato, mainly from South America it is a perennial and dicotyledonous plant. Belonging to the Solanaceae family, it is classified in the genus *Solanum* (Appendix 06) (Aksoy et al., 2021).



Figure 09: Potato: *Solanum tuberosum* L (Original photo).

III.3.4. Strawberry

Fragaria small perennial plant, from the Rosaceae family, cultivated for its fruit or strawberry (Figure 10 and Appendix 07), but also growing wild in certain undergrowth and on embankments (Hancock et al., 1991).

The fruit, which botanically is a false fruit, is formed by the entire fleshy receptacle of the flower. It has a red or whitish yellow color depending on the variety, and a more or less rounded oblong ovoid shape (Lucas and Vincenot, 2006). In 2019-2020, the quantity of strawberries produced in Algeria amounted to approximately 700,000 tonnes (Caw, 2018).



Figure 10: Strawberry: *Fragaria X ananassa* Duch (Original photo).

III.4. Sample preparation

The introduction of the QuEChERS method has radically significantly changed practices in the analysis of pesticides. Thanks to this technique which simplifies the different procedures such as extraction and also purification for numerous molecules from different chemical families, it is possible to obtain satisfactory results. This technique has been implemented for different food matrices ([Musarurwa et al., 2019](#)).

Although several methods have been approved and have given satisfactory results, the extraction of certain molecules such as pyrethroids from complex matrices such as oilseeds remains difficult due to the polarity of the compounds or the lipophilic nature of certain molecules, which negatively affects recovery rates in these matrices.

In addition, some matrices contain compounds that could disrupt the molecules of interest. In the following part, we will mainly describe the QuEChERS method used to extract pesticides from food matrices. Subsequently, we will present the different adaptations of the QuEChERS method to improve its analytical performance will be described, followed by an exploration of its use in the extraction of pesticides from complex matrices such as cereals, also teas, and oilseeds. and as well as the spices ([Santana-Mayor et al., 2019](#)).

This extraction process has been used for samples containing a water content of 80% or greater, and it is crucial to determine the percentage of water present in the sample to ensure we are within the proper scope of the method. Food samples with low water content need to be hydrated carefully. But if the food sample contains a lot of water, it is not essential to add water to moisten it again ([Santana-Mayor et al., 2019](#)).

Various samples were studied, with and without washing, with and without skin. This approach aims to determine whether pesticides remain on the surface or deep within agricultural products. This research examines whether simply washing and peeling fruits and vegetables can reduce the concentration of pesticides, which is important for health-conscious consumers. ([Santana-Mayor et al., 2019](#)).

III.4.1. Residue analyzes

III.4.1.1 Reagents

- ❖ **Solvents:** the solvent used is Acetonitrile from the SIGMA Aldrich brand.
- ❖ **Powder reagents:** they are: anhydrous sodium sulfate (Na_2SO_4), sodium chloride (NaCl) and activated carbon, which were previously contaminated by drying them in an oven at 200°C for 4 hours.

III.4.1.2. Pesticides

The following information relates to the pesticides chosen for analysis taken from the Pan Pesticides Database, which is a widely used resource in this field.

a. Deltamethrin: A synthetic pyrethroid type insecticide (Graeve et al. 1986).

→ **Physico-chemical properties:** FM: $\text{C}_{22}\text{H}_{19}\text{Br}_2\text{NO}_3$; MM: 505.2 g/mol; Solubility in water: 0.002 mg/l at 20°C ; Solubility in acetone: 300 mg/l at 20°C ; Melting point = 98°C .

→ **Toxicological information:** Classified as very toxic if ingested, inhaled or in contact with skin, it is also suspected of having disruptive effects on the endocrine system, of being carcinogenic and of having neurotoxic effects.

→ **Ecotoxicological effects:** Deltamethrin is very toxic to aquatic and terrestrial species, and can remain in the environment for several weeks to months, depending on conditions. It also tends to accumulate in the tissues of living organisms.

b. Chlorothalonil: A fungicide belonging to the organochlorine category (Graeve et al. 1986).

→ **Physico-chemical properties:** FM: $\text{C}_8\text{Cl}_{14}\text{N}_2$; MM: 265.91g/mol; Solubility in water: 0.6mg/l at 20°C ; Solubility in acetone: 20 g/l at 20°C ; Melting point = 250°C .

→ **Toxicological information:** Classified as very toxic if ingested, inhaled or in contact with skin, it is also suspected of being an endocrine disruptor and a carcinogen.

→ **Ecotoxicological effects:** Considered very toxic to aquatic as well as terrestrial species.

III.4.2. Analysis protocol

The main approach of this method consists of extracting pesticides with acetonitrile, then purifying the extract obtained using dispersant solid phase extraction. This step has the necessary goal of removing all interferences from the matrix, thereby reducing the effects of the matrix on a wide range of solutes of different polarities. Recently, the introduction of a predefined internal element made it possible to minimize the errors linked to the various steps of the QuEChERS method (Anastassiades, 2003).

The chemical structures of the molecules and their labeled counterparts are very similar, resulting in similar physicochemical properties. Therefore, it is likely that signal suppression or enhancement is observed in an almost identical manner for both compounds (Figure 11) (Rejczak, 2015).

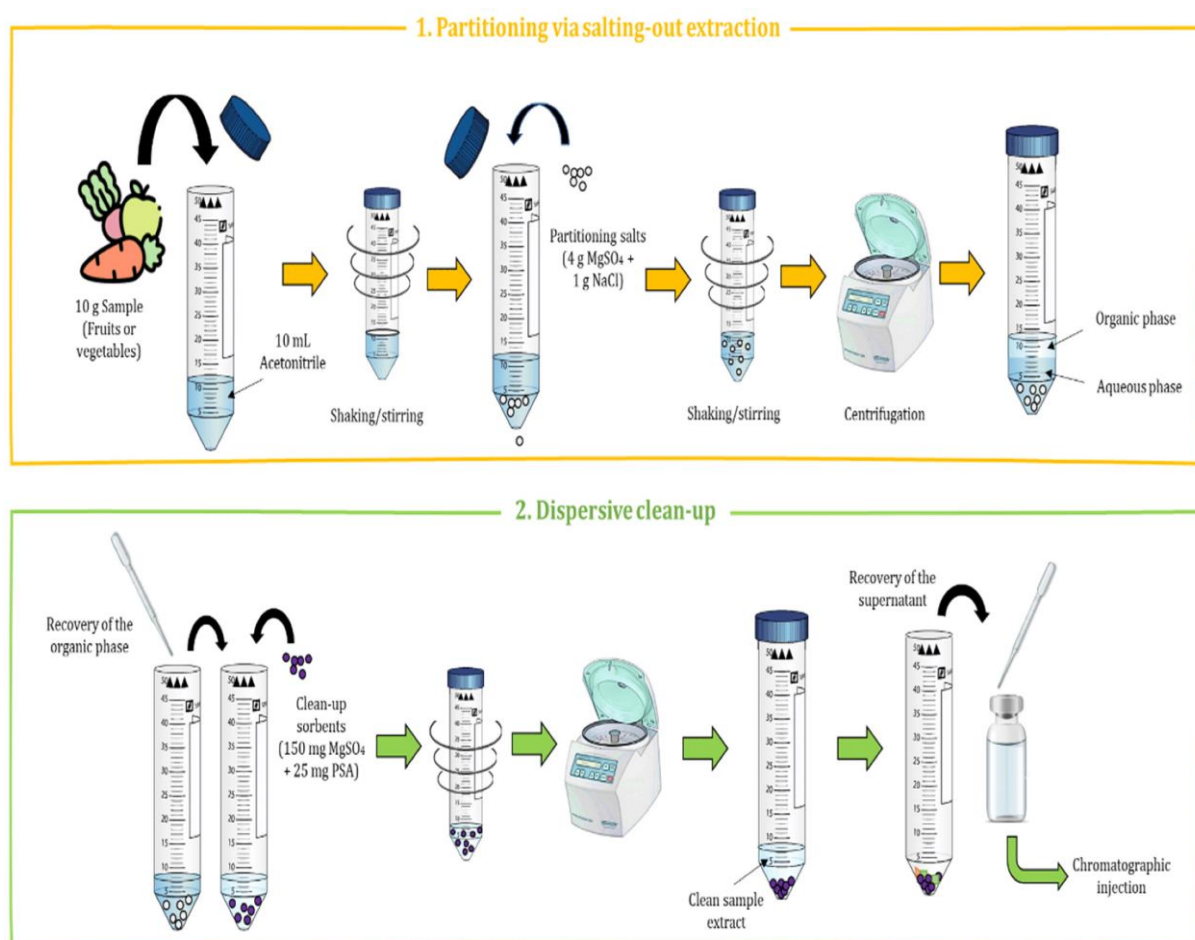


Figure 11: Phases of extraction (Casado et al., 2022).

III.4.2.1. Extraction of pesticide residues

The pesticide residues were extracted a versatile technique was employed which is the QuEChERS method, which is a multi-residue technique suitable for various matrices such as fruits and vegetables. Here is a summary of the steps involved in residue extraction:

- The homogenization of the samples is carried out using a Clatronic UM 3284 type homogenizer to guarantee perfect homogeneity.
- For weighing, 10 g of each ground sample are placed in a 50 ml conical centrifugation container equipped with a precision balance ($D=0.1$ mg).
- To initiate the extraction, 10 ml of acetonitrile is poured, then the sample is shaken for 1 minute using a vortex mixer.
- 4g of $MgSO_4$ and 1g of $NaCl$ are added, then stirred for 1 minute using a vortex mixer.
- The samples are then centrifuged at 4500 rpm for 5 min using a SIGMA brand centrifuge.
- After centrifugation, the organic phase which is the supernatant is recovered and 1.8 g of $MgSO_4$ is added.
- After centrifuging the mixture once again, the organic phase is recovered.
- After concentration using nitrogen flow, the organic phase is formed by 1 ml of acetonitrile to form a dry residue.

III.4.2.2. Dispersive solid phase extraction

The entire organic phase is carefully sampled for subsequent steps. Then the organic phase is transferred into a tube containing 150 mg of magnesium sulfate are carried out simultaneously for the total elimination of residual water and 25 mg of APS and thus allowing the extract to be purified. (Pagliano, 2015).

APS absorbs polar impurities very well, including organic acids, and also sugars and in particular certain pigments. Subsequently after centrifugation the solid and liquid phases are separated and contain the residual water and the adsorbed impurities are retained in the solid phase, while the purified extract is in the liquid phase. Separation and purification of the extract by centrifugation is essential to significantly improve the quality of analytical results in subsequent steps including chromatography and mass spectrometry (Pagliano, 2015).

III.4.2.3. Pre-concentration

The final extract was pre-concentrated using an evaporator under nitrogen flow, as shown in (Figure 12). To stabilize the extract by adding 4 mL of supernatant was added to a vial containing 40 μ L of a 5% formic acid solution dissolved in acetonitrile for each extract. This mixture was kept under a light flow of nitrogen until its final volume was reduced and reached 200 μ L. The next step consisted of analyzing the final extract was carried out by a gas chromatography method coupled with tandem mass spectrometry (Casado et al., 2022).



Figure 12: Purevap-6 evaporator (Casado et al., 2022).

The chromatography apparatus in this study is carried out in the gas phase, specifically a GC - MS which integrates with a mass spectrometer for this analysis "CLARUS 500" from the Perkin-Elmer brand. It is composed of an electron impact ionization source, The instrument includes a simple quadrupole analyzer in association with a data injector, which has a mass spectral library containing data from several libraries (Graeve et al. 1986).

III.4.2.4. Chromatographic conditions

The chromatography conditions of this study (Figure 13), as described below, were applied to the analysis according to the pesticide standards studied:

- The sample is injected in Splitless mode at a temperature of 240°C with a volume of 1 μ l.
- The chromatography column used is an Elite series 5, 30 meters long, with an external diameter of 0.25 mm and an internal diameter of 0.25 μ m, passed through by helium at a flow rate of 0.8 ml /min.

- The heating program starts at 70°C for 4 minutes, then gradually increases by 4°C/min until it reaches 220°C, where it remains for 15 minutes.
- For detection, a mass detector is used with source and transfer temperatures of 230°C, as well as an ionization potential of 70 eV, for a total analysis time of 56.5 minutes.

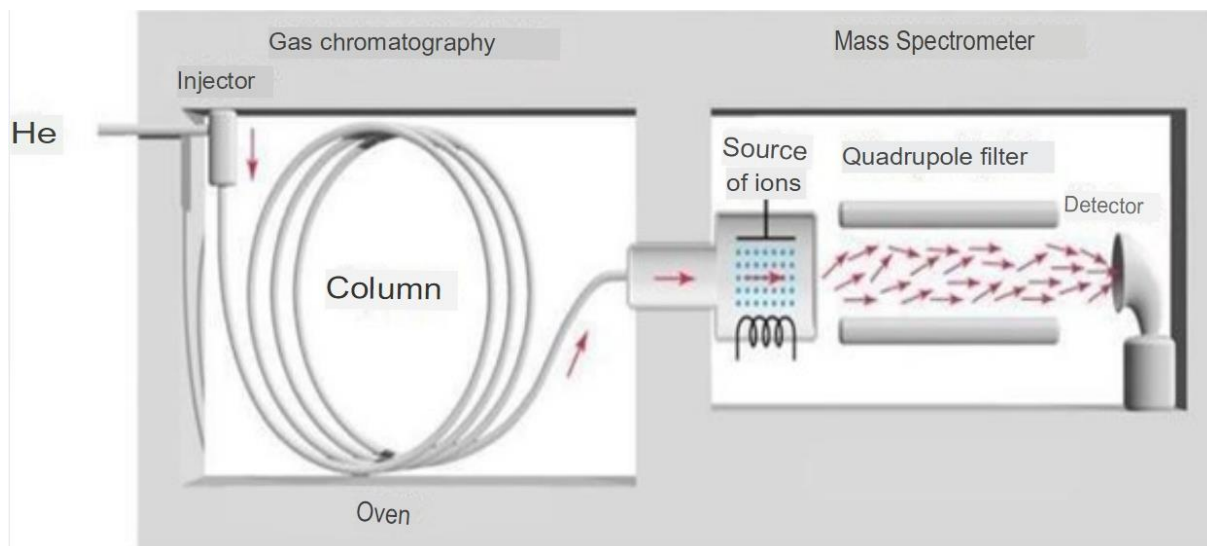


Figure 13: Diagram of chromatography (Gaskell, 1997).

III.5. Coupling gas chromatography to tandem mass spectrometry

A large part of the analysis devices used operate with low resolution in GC-MS//MS coupling are mass spectrometers equipped with quadrupole analyzers, for three main reasons.(Bouchonnet, 1999):

- 1- They are often purchased, their price is affordable and their maintenance is easy. An essential element for the analysis is the quality of the vacuum.
- 2- Its use allows and facilitates the release of neutral molecules including the carrier gas, nitrogen, oxygen and water vapor, which are not involved in and are usually ionized due to low ionization efficiencies.
- 3- In addition, this ensures the smooth running of the filament and the electron multiplier, which are very sensitive to excessive pressure.



Figure 14: Simplified diagram of the process (Original photo).

III.5.1. Ionization sources

When molecules enter the mass spectrometer source, they undergo ionization to produce gaseous ions. The selection and choice of source depends on the physical state of the analyte. This consideration is particularly important in the context of using a gas chromatograph. In use of a gas chromatograph, where the student compounds are introduced into the spectrometer in gaseous form, the main sources are electronic ionization and chemical ionization (Figure15). One of the critical aspects of mass spectrometry analysis is to maintain the source at an elevated temperature that reaches between 200 and 300°C to avoid condensation of the analytes. (Hajšlová, 2007).

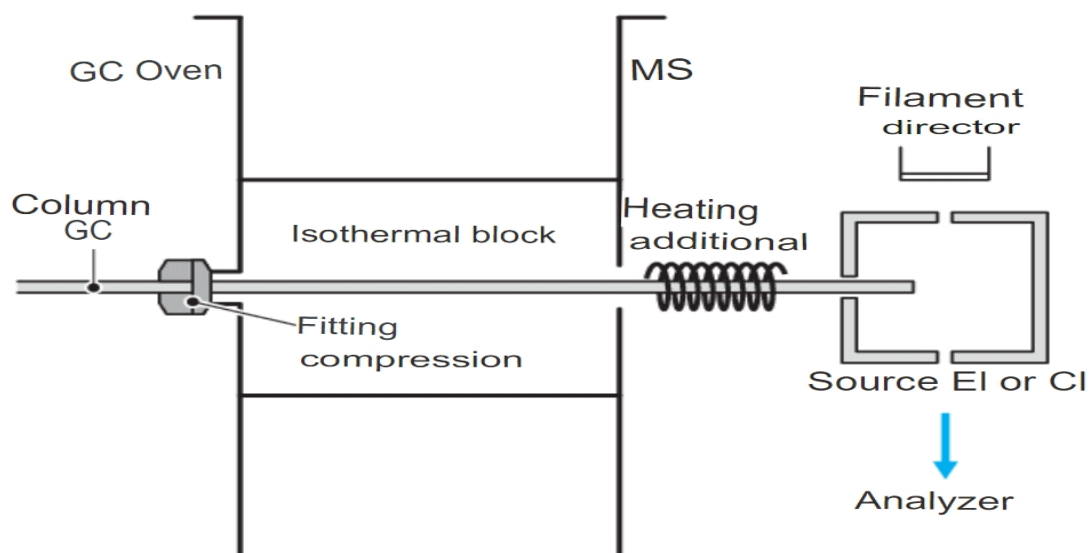


Figure 15: Waterproof direct coupling (Simon, 2008).

In mass spectrometry, electron ionization is a fundamental method where molecules are ionized by being bombarded by high-energy electrons. A “collision” of an electron with an M molecule (although physicists have shown that this is not a true impact) knocks an electron out of the molecule, which gives rise to a radical ion M^+ . The amount of internal energy of the M^+ ion is such that the M^+ ion spontaneously fragments into ions of lower m/z ratio, known as daughter ions or fragment ions (Hajšlová, 2007).

Heating a metal filament usually made of tungsten when using an ionization energy of 70 eV, the mass spectra produced are reproducible on different mass spectrometry instruments. This reproducibility is crucial for generating exhaustive databases, each instrument being able to contain tens of thousands of different spectra. Mass spectrometry databases are analyzed by algorithms that compare the obtained spectra with reference spectra for compound identification. The obtained spectra may have variations during data analysis. The obtained mass spectra may vary in terms of relative intensity of the ions observed depending on the analyzer used, which can make the identification of compounds more complex. The performance of electron ionization lies in its generality, because electron ionization allows almost all molecules to be ionized (Hajšlová, 2007).

Chemical ionization is also commonly used in addition to electronic ionization. IC exhibits greater selectivity and does not ionize all eluted molecules, which can be beneficial for particularly complex samples. CI is a gentle ionization method compared to EI: The internal

energy of MH^+ ions obtained in CI is much lower than that of M^+ ions produced by EI, resulting in much lower fragmentation (Hajšlová, 2007).

The molecular ion of the compound is always informed by the CI spectrum. While the chemical ionization technique offers more direct identification of the molecular ion in a spectrum, electronic ionization, despite its informational advantages structural, does not make it possible to confirm with certainty the presence of the molecular ion. This makes the interpretation of EI spectra more difficult (Hajšlová, 2007).

The mass spectrometry section is connected to the chromatograph, which allows neutral molecules to be divided into charged ions in an ionization chamber. Using the three quadrupoles, it is possible that ions can be identified based on their m/z ratio, then detected, and converted into a digital signal. A triple quadrupole consists of: The initial ion will be chosen by the first quadrupole according to its mass to charge ratio, then this ion will be fragmented again in the second quadrupole which plays the role of a collision chamber, and finally the third quadrupole will choose a last ion according to its m/z ratio (Longevialle, 1981).

The simplified diagram of a triple quadrupole mass spectrometer is illustrated in Figure 16. As a collision cell, the quadrupole thus allows the possibility of fragmenting ions, which is useful for performing analyzes in single or also good in tandem (Longevialle, 1981).

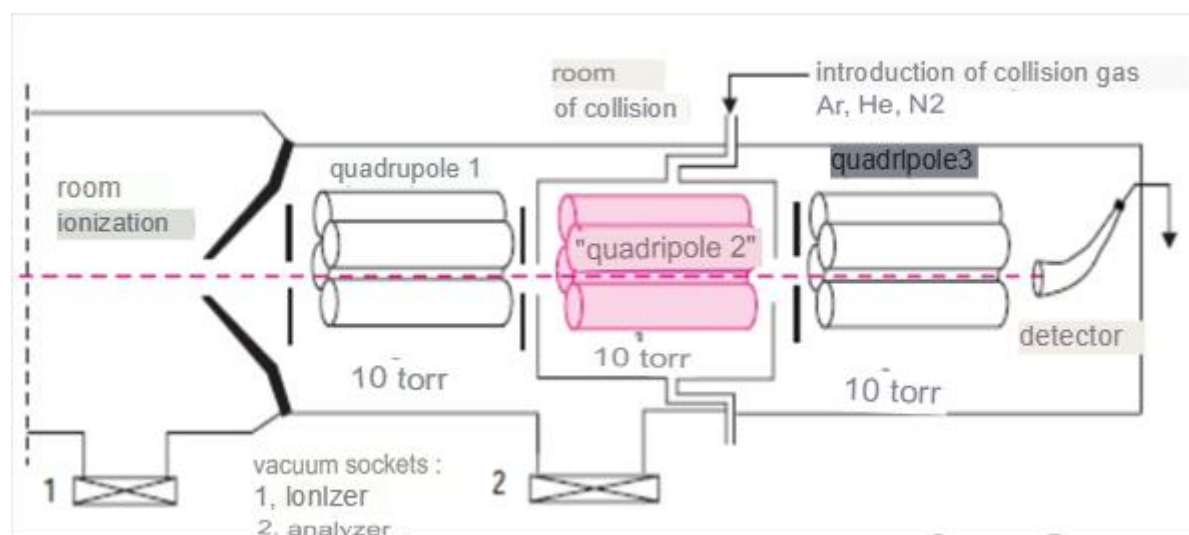


Figure 16: Simplified diagram of a spectrometer (Buszewski, 2012).

III.5.2. Interest in GC-MS/MS coupling for pesticide analysis

After being separated by gas chromatography, the compounds to be analyzed are in gas form, which facilitates their introduction into the mass spectrometer. This coupling with tandem mass spectrometry makes it possible to achieve the levels of sensitivity and selectivity required for trace analysis (Fernández, 2001).

The use of the method, which combines to analyze pesticides in different chemical families, with an increasing number of molecules analyzed at the same time more than 300. It was used for the first time on fruit and vegetable matrices. More recently, GC MS has been employed for its effectiveness in analyzing pesticides due to its high sensitivity and selectivity especially in difficult matrices, such as dry matrices. In addition, the precision of ms/ms spectrometry made it possible to simplify the sample preparation steps, which were both long and specific to each chemical family (Fernández, 2001).

This specificity paved the way for the application of the method to efficiently extract pesticides on a large scale from various food matrices. However, the use of ms/ms sometimes presents time and development challenges, as each transition must be carefully optimized, and the number of analyzable compounds is restricted by the scanning speed. Therefore, although the use of low-resolution mass spectrometry can help reduce interference, scientists are increasingly turning to combinations of hplcc or gc with high-resolution mass spectrometers to overcome these challenges in pesticide analysis (Fernández, 2001).

Chapter IV

IV. Results and discussion

We aim to carry out an in-depth qualitative analysis to detect chemicals present in various food samples, including tomatoes, dates, potatoes and strawberries, collected systematically from two separate sites Mitidja and Biskra.

Pesticides detected in fruits and vegetables can be present at extremely low levels, ranging from trace amounts to higher concentrations. It is not possible to analyze all pesticides simultaneously, because each pesticide has distinct physicochemical properties. Additionally, once present in foods, some molecules can be strongly bound to the matrix, making analysis more difficult. Due to the diversity of physicochemical properties of pesticides and the low residual concentrations in fruits and vegetables, analyzes become particularly more complex (Yoanna, 2011).

Typically, the QuEChERS method is adopted to detect pesticides in food matrices such as agricultural products due to its ability to simplify the process by (Anastassiades et al., 2003), is based on a series of key steps: extraction with acetonitrile, then purification. The purified extracts are then analyzed by GC/MS/MS, requiring a change of solvent (hexane/acetone 70/30) due to the low compatibility of acetonitrile with the very high injection volumes (Gwenola Burgot and Burgot, 2024).

The compounds are separated based on their affinity which allows precise and relative analysis for two distinct phases: a mobile phase and another stationary phase, is possible thanks to chromatographic techniques, while tandem mass spectrometry allows to improve quantitative and qualitative detection. The gas chromatography technique is used to study volatile and semi-volatile and thermally stable compounds, with a chromatograph consisting of an injector, a column in an oven and a detector.

The inert gas, usually helium, hydrogen or nitrogen, is chosen for its high purity. MS/MS allows specific analysis and increases detection limits by avoiding interference, although some compounds cannot be analyzed directly by GC due to their low volatility, high polarity or thermal instability (Hernandez, 2005).

IV.1. Results

IV.1.1. Tomato sample

Figure 17 shows the chromatogram of extracts pesticides tomato analyzed by GC and Figure 18 illustrates their mass spectrum.

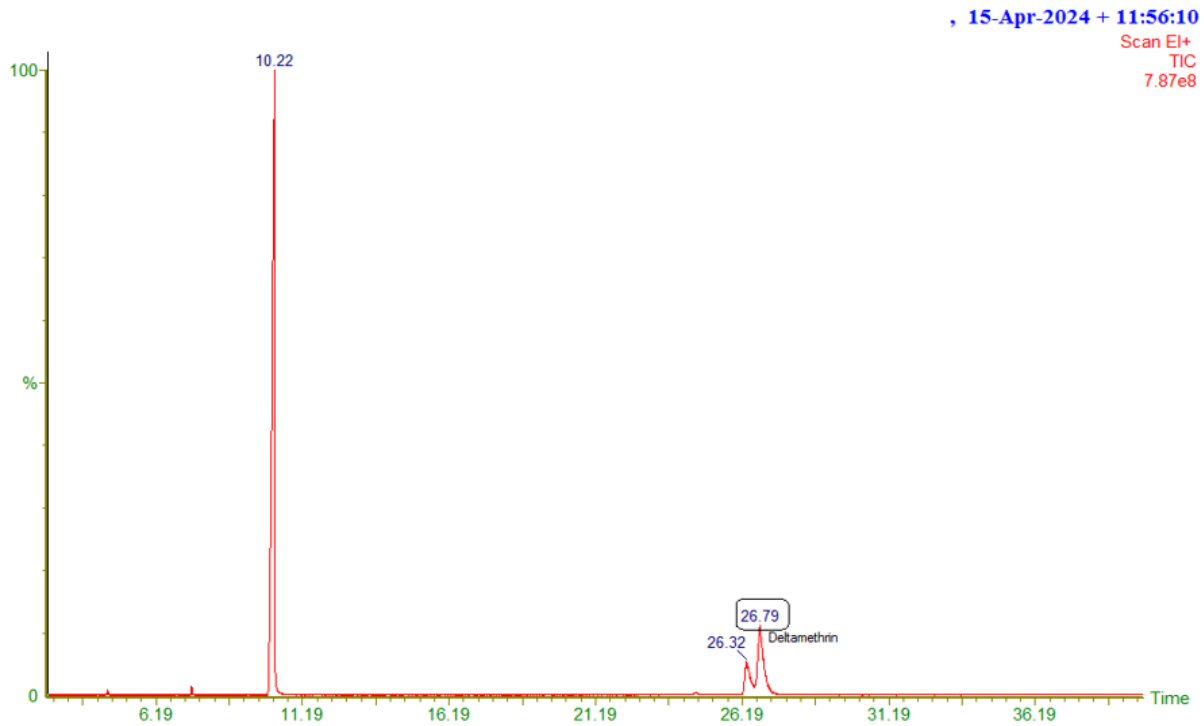


Figure 17: Chromatogram of extracts pesticides of tomato.

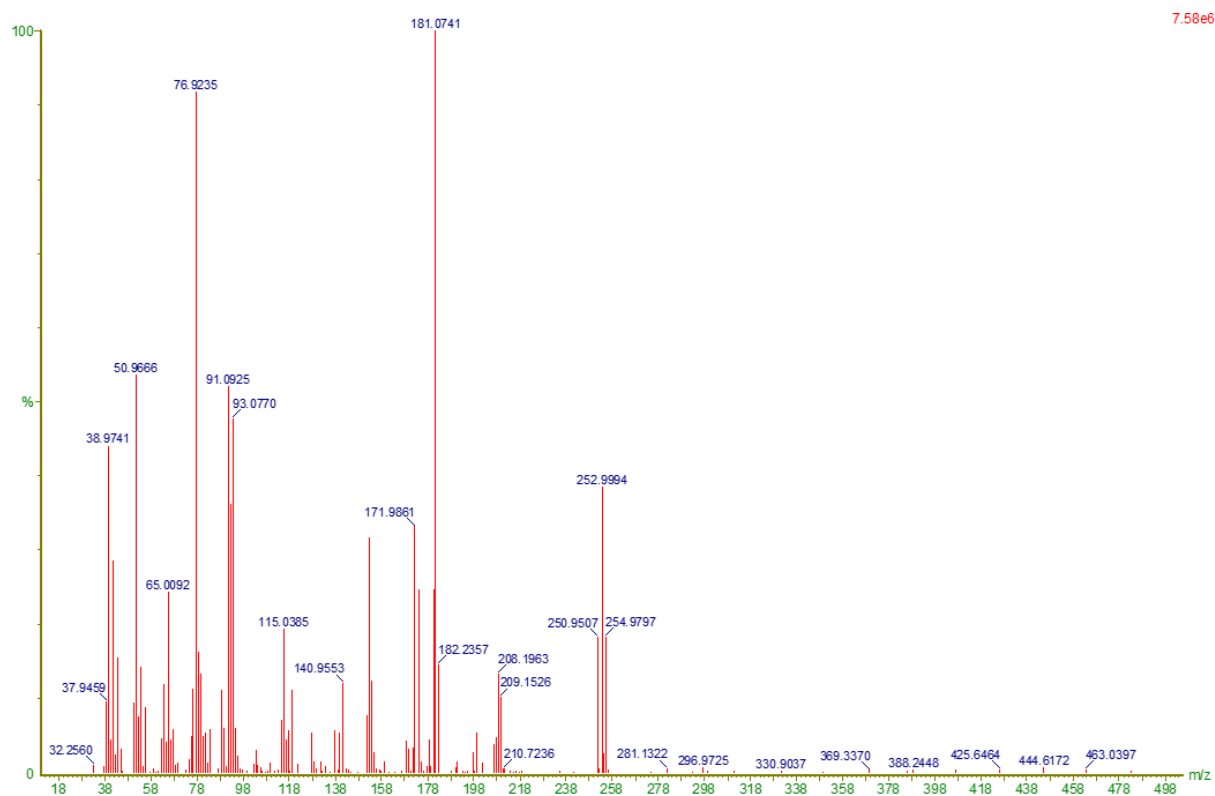


Figure 18: Mass spectrum of extracts pesticides of tomato.

The observed peaks are very well defined, which contrasts with minimal background noise, allowing clear identification of the compounds. The retention times measured are 26.79 minutes for tomatoes. Furthermore, the mass fragments detected in the samples exactly match those of the pesticide deltamethrin standard, thus confirming its presence in the tomato samples.

The compounds are identified by gas chromatography coupled to mass spectrometry (GC/MS) by comparing the mass spectra obtained with those of reference spectral databases.

NIST/EPA/NIH contains thousands of specific mass spectra of different chemical compounds, allowing rapid and accurate identification of analytes present in samples (Figure 19).

When a compound is detected by the device, its mass spectrum is compared to those stored in the library. If the sample spectrum matches a reference spectrum, the compound is delineated with a high degree of confidence. Detection and identification of trace compounds is particularly beneficial in areas such as toxicology, environmental and food analysis.

By combining these reference spectral databases with the separation and detection capabilities of gc/ms, this technique has become a powerful and widely used analysis method,

ensuring reliable and accurate detection (Cardot, 2020). We confirmed the presence of the pesticide deltamethrin using the spectrum library of our GC/MS device (Figure 19).

Hit	REV	for	Compound Name	M.W.	Formula	CAS	Library
1	929	832	Decamethrin P1944 Univ Homburg/Saar	503	C22H19O3NF32	52918-63-5	Pfleger
2	912	817	DELTA METHRIN	503	C22H19O3NBr2	52918-63-5	NST
3	885	813	DELTA METHRIN	503	C22H19O3NBr2	52918-63-5	NST
4	868	345	Butoflin \$\$ Butox \$\$ Decamethrin \$\$ Decamethrine	503	C22H19O3NBr2	62229-77-0	Wiley9
5	802	637	DELTA METHRIN	503	C22H19O3NBr2	52918-63-5	NST
6	801	637	Deltamethrin isomer1 \$\$ Deltamethrin isomer2 \$\$ Deltamethrin \$\$ Butoflin	503	C22H19O3NBr2	52918-63-5	Wiley9
7	801	637	Butoflin \$\$ Butox \$\$ Decamethrin \$\$ Decamethrine	503	C22H19O3NBr2	62229-77-0	Wiley9
8	792	639	DELTA METHRIN	503	C22H19O3NBr2	52918-63-5	NST
9	775	621	DELTA METHRIN	503	C22H19O3NBr2	52918-63-5	NST
10	775	305	9-Methylbenzofindole	181	C13H11N	999104-25-3	Wiley9
11	734	320	(syn)-2-Phenyl-3-(3-pyridyl)-isoxazolidine-5-carbonitrile	251	C15H13ON3	0-0-0	Wiley9
12	697	358	Benzenamine, N-(phenylmethylene)- (CAS) \$\$ N-BENZYLIDENE PHENYLAMINE	181	C13H11N	538-51-2	Wiley9
13	672	395	Benzenamine, N-(phenylmethylene)- (CAS) \$\$ N-BENZYLIDENE PHENYLAMINE	181	C13H11N	538-51-2	Wiley9
14	644	317	PROPANAL, 2,3-DIOXO-3-(3-PYRIDYL)-, 1,2-BIS(PHENYLHYDRAZONE)	343	C20H17ON5	349497-81-0	NST
15	643	317	Propanal, 2,3-dioxo-3-(3-pyridyl)-, 1,2-bis(phenylhydrazone)	343	C20H17ON5	349497-81-0	Wiley9
16	638	426	N-BENZYLISATOIC ANHYDRIDE	253	C15H11O3N	35710-05-5	NST
17	635	380	Decamethrin-Martifact (HOOC-) ME P1542 Univ Homburg/Saar	310	C9H12O2F32	0-0-0	Pfleger
18	617	346	1H-Benzotriazole, 1-(phenylmethyl)- (CAS) \$\$ 1-Benzyl-1,2,3-benzotriazole \$\$ 1-	209	C13H11N3	4706-43-8	Wiley9
19	615	307	3-METHYLCARBAZOLE	181	C13H11N	4630-20-0	NST
20	613	382	4-Cyclohexene-1,2-dicarboxylic acid, 4-methyl-, dimethyl ester, trans- (CAS)	212	C11H16O4	20586-29-2	Wiley9

Figure 19: Spectrum Library.

IV.1.2. Sample of dates

Figure 20 illustrates the chromatogram of the extracted pesticides of dates analyzed by GC and their mass spectrum is shown in Figure 21.

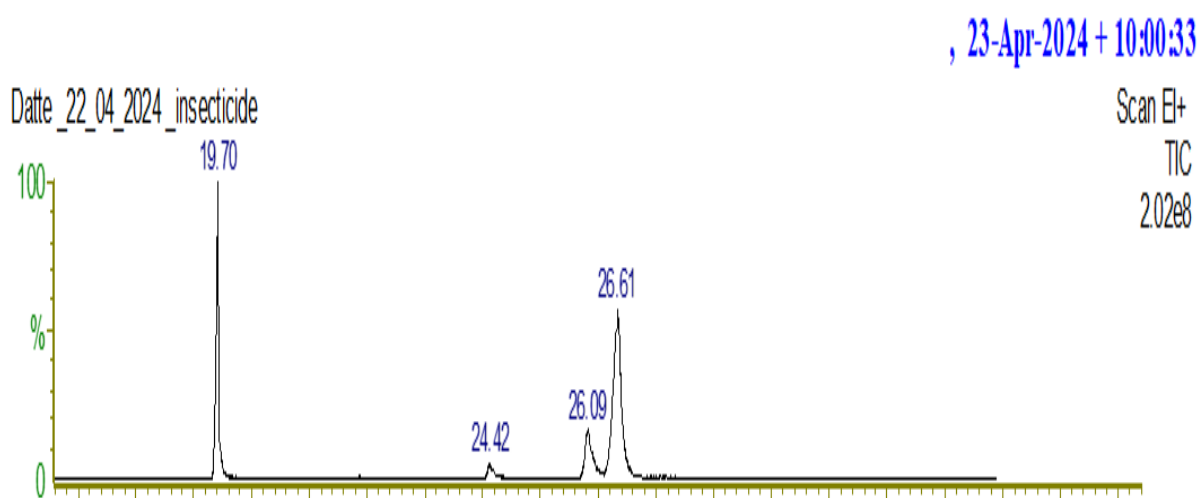


Figure 20: Chromatogram of extracts pesticides of dates.

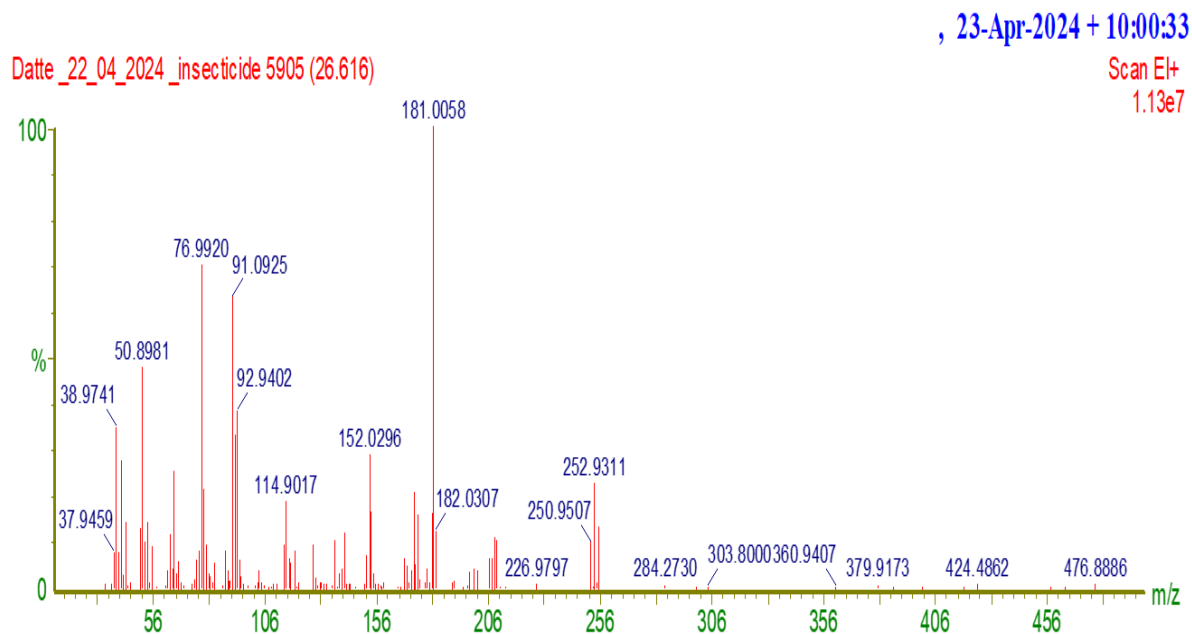


Figure 21: Mass spectrum of extracts pesticides of dates.

Deltamethrin, a commonly used pesticide, appears clearly in the chromatogram of the date sample extracts in Figure 21. The observed peaks are clearly identifiable, allowing precise identification of the compounds. The compounds were accurately identified, with pesticide extracts from dates showing retention times of 26.61 minutes. However, the results of its particle mass observed (Figure 22) in the samples are identical to those of the pesticide deltamethrin standard, which corroborates its presence in these samples. The detection of the pesticide deltamethrin was validated comparing to the spectrum data library (Figure 19).

IV.1.3. Strawberry sample

As presented in Figure 22, the chromatogram was obtained from the strawberry extracts, suggesting that the targeted chemicals are not present.

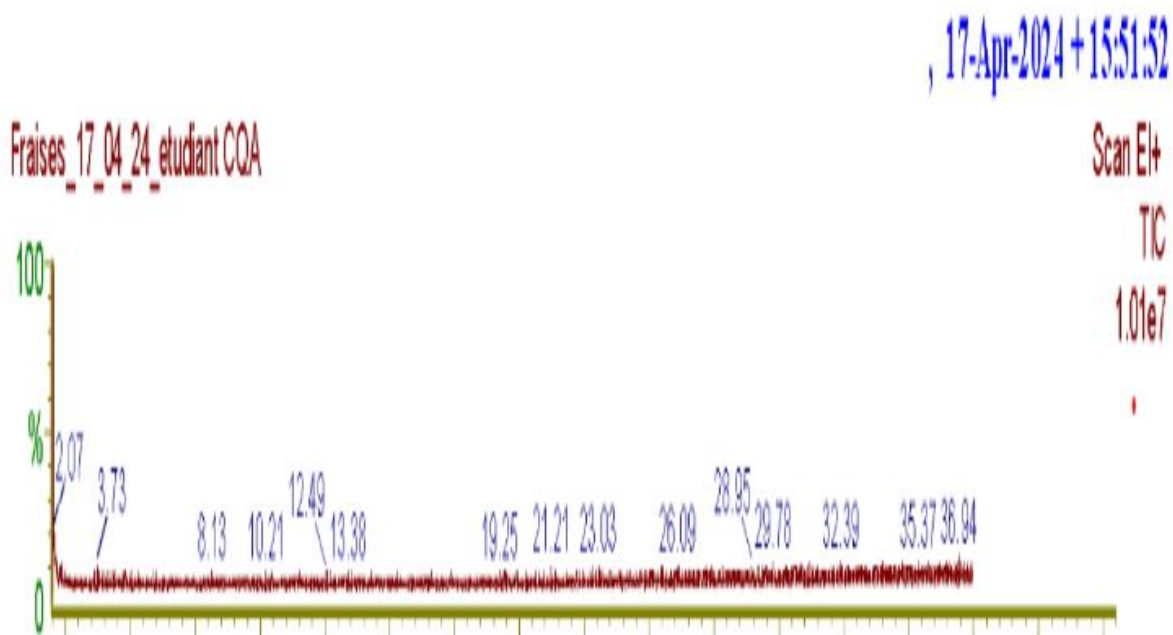


Figure 22: Chromatogram of strawberry extracts.

The peaks observed on this chromatogram are poorly defined, which suggests that the targeted pesticides are not present in detectable quantities. The lack of peak identification, combined with the absence of distinctive mass fragments characteristic of the pesticides of interest, confirms that these substances are not present in the strawberry samples.

IV.1.4. Potato sample

Figure 23 shows the chromatogram of extracts pesticides of potato.

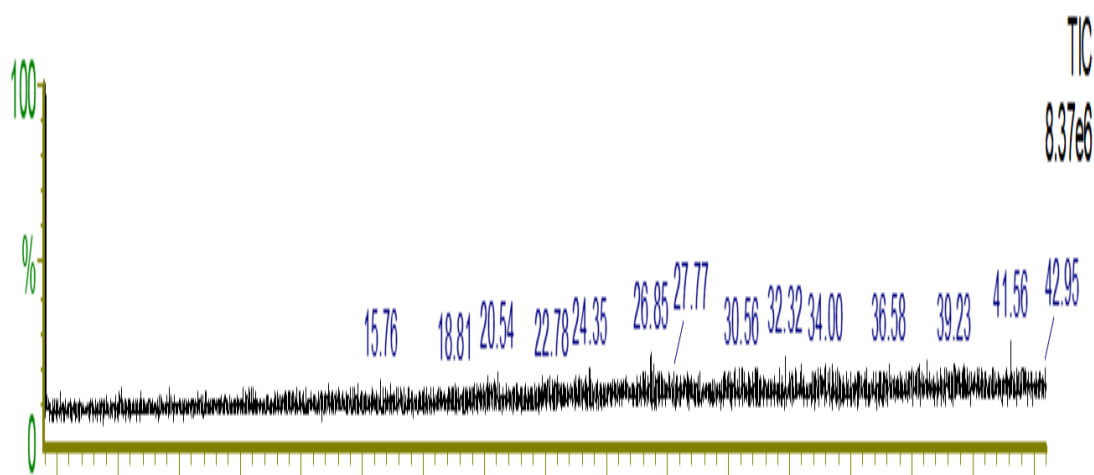


Figure 23: Chromatogram of pesticides extracts of potato.

In particular, the indistinct peaks present on this chromatogram suggest that the targeted pesticides are not present, which suggests that the targeted pesticides are not detectable in these samples. The lack of identifiable peaks and mass fragments specific to the desired pesticides suggests that these substances are not present in the potato samples.

IV.2. Discussion

Pesticides have seen a significant increase globally in recent decades, positioning them as the primary means of combating crop pests. Indeed, their application aims to ensure large-scale food production of superior quality while supporting increased yields and regularity of production cycles. However, the adverse impacts on non-target organisms have eloquently highlighted the challenges and risks inherent in these compounds to the environment, ecosystems and population health ([Inserm, 2013](#)).

In this study, we sought to identify the pesticides used and to highlight several results concerning the different samples examined, namely tomato, date, strawberry and potato harvested from these two regions Biskra and Mitidja, in order to identify the various categories of pesticides used by farmers. The farmers in these samples have a preference for market gardening because it has a short cultivation period, around two and a half months, and it requires little maintenance compared to citrus and fruit trees.

Tests carried out on fruits and vegetables harvested in the Biskra and Mitidja regions, analyzed using the gc - ms technique, revealed that deltamethrin was the only pesticide present in the date and tomato samples, thus highlighting the need for continuous monitoring of these crops.

The detection of this pesticide in the analyzed samples is explained by its predominant use in the region, representing 90% of the pesticides used, as indicated by local agricultural data. Deltamethrin is mainly used to combat harmful insects: phytophagous caterpillars, whiteflies, aphids ([DPVCT, 2015](#)).

According to current market trends, the plant protection products sector is growing, offering a wide range of products from various chemical families and different generations. Farmers have a wide choice of products. Field data suggests that fungicides and insecticides are most commonly used, while other types of pesticides, such as herbicides, are less prevalent in comparison. Farmers report that their crops face many threats, highlighting the complex challenges they face in their farming business, leading to reduced agricultural yields. This is

why these farmers use a wide variety of phytosanitary products for preventive and/or curative purposes. (Khay et al., 2008).

Algerian farmers rely on chlorpyrifos, deltamethrin, cypermethrin and lambda-cyhalothrin, insecticides approved for widespread use on various crops, following local regulations. On the other hand, this means that traces of these products can be found in all plant products (DPVCT, 2015).

Date farming is one of the main agricultural activities in this region in Algeria. According to data, Algeria ranks first in Africa and seventh in the world (FAO,2020).

Deltamethrin is widely used in date production to effectively control insect pests, which helps improve the quality and quantity of the crop (DPVCT, 2015).

Under common agricultural practices, tomatoes may contain residues of deltamethrin, a pesticide used to protect crops against insect pests, which could help increase production and improve the quality of tomatoes. Tomatoes play a vital role in agriculture in Algeria, playing a vital role in the local economy and being widely employed.

In contrast, the results of analyzes carried out on strawberries and potatoes from the Mitidja region indicated the total absence of residues, thus highlighting the purity of these products in the study. This can be explained by several hypotheses: farmers in Mitidja could use other types of pesticides not included in this study, or agriculture in Mitidja could an approach focused on the diversification of agricultural techniques, particularly in terms of cultivation and of crop protection, could lead to a reduction in the use of pesticides. This strategy would pave the way for the integration of more sustainable biological control methods. Then, the climatic and environmental conditions of Mitidja may vary, which has an impact on the nature and quantities of pesticides used, as well as on their interaction with crops.

Examination of pesticide residues revealed diverse trends, with results showing both significant similarities and divergences between samples studied by GC/MS. Endeosulfan, Procymidone and Deltamethrin were the active substances most observed in 66 tomato samples (Zein, 2004).

Similar analyzes were carried out in the Mitidja region, where he discovered the presence of the same family of pesticides, pyrethroids, in tomatoes and strawberries, notably bifenthrin (Mokhtari, 2011).

In 2012, A research has found the presence of deltamethrin in 197 tomato fruit samples examined (Errami et al. 2012).

This comparison reveals that each region uses specific pesticides adapted to its local conditions, such as soil type and climatic factors. Furthermore, the results of our studies indicate the total absence of residues in the matrices which come from the Mitidja area. This observation suggests that the pesticide used in this region was not included in our data and was therefore not detected during the analysis. However, it is too early to conclude that the presence of only one type of pesticide in the Biskra region means the absence of other pesticides used. It is entirely possible that other pesticides were used, but were simply not taken into account in our study.

The rate of use of the two chemical families (Organophosphates, Pyrethroids) remains significant (8%). Pesticides in this family have been associated with harmful effects on human health, having been demonstrated by numerous studies and their ability to alter the endocrine system (76%). It has also been noted that pyrethroids are extremely toxic also to living aquatic invertebrates and in particular the majority of fish (Laurin, 2007).

Synthetic pyrethroids, such as deltamethrin, lambda-cyhalothrin, and cypermethrin, are widely preferred by farmers for their proven effectiveness against a variety of insect pests, affordability compared to newer formulations, and market availability. These conclusions are corroborated by several recent studies (Donkor et al., 2016).

The progressive use of pesticides by spraying increases the risk of contact, because generally most farmers do not take sufficient necessary protective precautions. increases the risk of contact with these products. Indeed, pesticides released in the form of droplets can be inhaled or exposed to the eyes or skin of the user, which explains why among these farmers, allergic reactions like stinging eyes and other effects observed. Plant protection product waste mainly consists of plastic, cardboard and/or paper packaging. These hazardous wastes must be collected and disposed of by farmers.

The packaging of the products used is often burned, stored, abandoned or thrown into nature by farmers. Greenhouse gases are released by burning packaging in the open air, such as CO₂, methane (CH₄) and nitrous oxide (N₂O) (Lozowicka et al., 2015).

Conclusion

Pesticides are used extensively throughout the world to protect crops grown for human consumption from various threats, such as pests, fungal infections and weed growth. The use of these tools makes it possible to improve and obtain agricultural yields and guarantee sufficient food production to meet the growing demand of the world's population. However, the use of these chemical substances inevitably generates residues on fruits and vegetables. To protect the health of consumers, it is essential to comply with strict safety standards which are closely monitored by the competent authorities. These standards establish residue limits that set the tolerable quantity of pesticides that can be found in food. This ensures that their consumption remains without health risks (Cui et al. 2022).

There has been an increase in the use of various types of pesticides in agriculture and other areas of human activities over the decades. As they follow the food chain, these dangerous chemicals can be accumulated by organisms, which proves to be extremely toxic to the environment as well as to animals and humans. Various health problems can occur following prolonged direct or indirect exposure to these chemicals, including pesticides, via the skin, inhalation or ingestion. A multitude of studies have demonstrated this (Cui et al. 2022).

It is primordial to assess of the quality of food, to prevent any risks to human health. Additionally, it is essential to assess the level of chemical contamination present in the environment and its sustainability by analyzing pesticide residues.

The contribution of our work is to look for pesticide residues in market garden crops. Its role is to examine the traces of pesticides present in the foods studied (tomato, dates, strawberries and potatoes), which were collected from two sample collection areas (Biskra and Mitidja). These fruits and vegetables have been purified using QuEChERS advanced extraction method followed by purification. The concentrated extracts were then analyzed using gas chromatography coupled with GC/MS mass spectrometer. The aim is to assess the presence and levels of contamination, identify the most common pesticides and provide valuable information to improve food safety standards.

Through this approach, we were able to obtain satisfactory results where the pesticide deltamethrin was identified on tomatoes collecting dates in the Biskra region. While fruits and vegetables from the Mitidja region were free of pollutants.

Recommendations to reduce consumer exposure to pesticides will make it possible to strengthen regulation and control of the use of pesticides in Algerian agriculture can be

formulated based on the results found. Thus, this research will contribute to a better understanding of pesticide contamination in local agricultural products, helping to protect public health and ensure safer food for the population.

This study shed light on the use of its products by farmers, Therefore, further research needs to be carried out in other regions to assess all possible effects of these pesticides on the environment and health.

It is also essential that consumers become aware of contamination by pesticide residues. Actions and gestures can have significant repercussions on the preservation of health in the face of these chemical substances. Pesticide contamination can be reduced by several common practices such as washing well and peeling before eating primarily fresh and or cooking (Keikotlhaile et al., 2010; Shabeer et al., 2015).

We should encourage the development of strategies aimed at reducing the use of pesticides on fruits and vegetables. As :

- Confirm in particular the information on the packaging of the pesticide used and take into consideration the weather conditions before and after crop treatment;
- The importance of respecting the pre-harvest delay period, which must be respected between spraying pesticides and consuming vegetables.

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Appendices

Appendix 01 : Examples of pesticide detection techniques.

<i>Analytical method</i>	<i>Molecules studied</i>	<i>LDDs</i>	<i>LDQs</i>	<i>References</i>
GC-MS	129 pesticides	–	0.005–0.07 mg/kg	Walorczyk (2008)
	24 pesticides	0.0013–0.0065 mg/kg	0.0044–0.02 mg/kg	De Oliveira and al. (2012)
	80 pesticides	0.0025–0.02 mg/kg	0.01–0.1 mg/kg	Lima and al. (2017)
	14 pesticides	0.0003–0.008 mg/kg	0.001–0.027 mg/kg	Abdul Ra'ouf and Tan (2015)
	OCPs	0.12–26.28 ng/L	–	Montory and al. (2017)
	Multi-class pesticides	0.5–1 ng/kg	–	Shamsipur and al. (2016)
	PPOs	0.59–1.57 µg/kg	–	Wu and al. (2016)
	250 pesticides	0.2–7 µg/kg	7.1–24 µg/kg	Kardani and al. (2022)
GCMS/MS	39 pesticides	–	10 mcg/kg	Tripathy and al. (2022)
	140 pesticides	0.006–0.008 mg/kg	0.01 mg/kg	Fernández Moreno and al. (2008)
	Multi-class pesticides	0.005–0.025 mg/kg	–	Machado and al. (2017)
	243 pesticides	–	0.01 mg/kg	
	4 pesticides	–	0.01 mg/kg	Ucles and al. (2018)
	205 pesticides	–	50 ng/g	Hakme and al. (2018)
	Fipronil, fipronil desulfinyl and fipronil sulfone	–	0.005 µg/kg	Biswas and al. (2019)

	33 pesticides	–	1–54.9 µg/kg	Ma and al. (2018)
	47 pesticides	–	0.1–52.5 µg/kg	Li and al. (2017)
	Metribuzin, desaminometribuzin and desamino-diketo-metribuzin	–	60–280 µg/kg	Xie et al. (2017)
	35 pesticides	–	0.3–14.2 µg/kg	Zoccali and al. (2017)
	10 pyrethroid pesticides	0.3-4.9 µg/kg	1-15 µg/kg	Lin and al. (2018)
	88 pesticides	0.1-6.3 µg/kg	3.0-21.0 µg/kg	Ferracane and al. (2021)
	35 pesticides	0.01-20 µg/kg	0.03-61 µg/kg	Khetagoudar and al. (2022)
GC-FID	PPOs	0.02–0.61 mg/kg	–	Blankson and al. (2016)
	11 pesticides	0.34–5 µg/L	–	Farajzadeh and al. (2015)
LC/MS/MS	57 pesticides	0.001–0.02 mg/kg	0.002–0.06 mg/kg	Andrade and al. (2015)
	5 PPOs	0.0001–0.001 mg/kg	0.0005–0.005 mg/kg	Narendaran and al. (2019)
	150 pesticides	–	0.01 mg/kg	Afify and al. (2012)
	Carbendazim, Thiabendazole, 6-benzyl aminopurine	0.002–0.003 mg/kg	0.005–0.01 mg/kg	Cho and al. (2013)
	15 carbamates	–	0.5–5 µg/kg	Zhou and al. (2018)

Appendix 02: Global pesticide consumption in 2020, by region in tonnes (Statista, 2022).

quantity of pesticides used worldwide in 2020

Region	North America	Centrale America	South America	Asia	Europe	Africa	Oceania
Quantity (Tons)	486 732	90 163	770 393	658 529	486 732	105 757	70 421

Appendix 03: Types and origins of samples analyzed.

Fruits and vegetables	Organic	Non-organic	Wash	Unwashed	Without skin	With Skin	Water content (%)	Origin
Date		X		X		X	80%	Biskra
Strawberry		X		X		X	90%	Mitidja
Tomato		X		X		X	95%	Biskra
Potato		X		X		X	80%	Mitidja

Appendix 04: Botanical classification of tomatoes.

Reign	Plantae
Under Reign	Tracheobionta
Division	Magnoliophyta
Class	Magnoliopsida
Sub Class	Asteridae
Order	Solanales
Family	<i>Solanaceae</i>
Gender	<i>Solanum Or Lycopersicon</i>
Species	<i>Lycopersicon Esculentum</i>

Appendix 05: Botanical classification of the date palm.

Reign	Plantae
Division	Angiosperm
Class	Liliopsida
Order	Arecales
Family	Arecaceae
Gender	<i>Phoenix</i>
Species	<i>Phoenix dactylifera</i>
Binomial nomenclature	<i>Phoenix dactylifera L</i>

Appendix 06: Botanical classification of potatoes.

Reign	Plantae
Order	Polemonial
Family	<i>Solanaceae</i>
Gender	<i>Solanum</i>
Species	<i>Solanum tuberosum L</i>

Appendix 07: Botanical classification of Strawberry.

Reign	Plantae
Under Reign	Tracheobionta
Division	Magnoliopsida
Class	Magnoliopsida
Under Class	Rosidae
Order	Rosales
Family	<i>Rosaceae</i>
Gender	<i>Fragaria X</i>

Résumé : Ce travail porte sur la recherche de résidus de certains pesticides dans divers fruits et légumes (tomates, dattes, fraises et pommes de terre) extraits par la méthode d'extraction avancée QuEChERS, suivi par la purification d-SPE, puis les résidus extraits concentré ont été analysée par chromatographie en phase gazeuse couplée à la spectrométrie de masse (GC/MS), dans les régions de la Mitidja et de Biskra, ainsi que sur l'estimation de leur risque potentiel pour le consommateur algérien. Les résultats obtenus ont révélé une contamination par des résidus de pesticide le Deltaméthrine ou leurs métabolites dans les échantillons de tomates et des dattes de la région de Biskra Cependant, ces résultats peuvent être confirmés par une vérification des pourcentages de similarité et une comparaison avec les temps de rétention et les spectres de masse obtenus lors de l'analyse quantitative à l'aide des étalons analytiques purs des pesticides. Ces résultats devraient servir de référence pour un suivi futur et pour la mise en place de mesures préventives visant à minimiser les risques pour la santé humaine. En agriculture, les pesticides sont employés pour protéger les cultures des ravageurs, mais ils peuvent également contaminer l'écosystème, exposant ainsi les humains par le biais de l'eau, de l'air et de l'alimentation. Les légumes sont particulièrement susceptibles d'être contaminés par ces substances. Pour encourager une agriculture durable, il est essentiel d'adopter une gestion intégrée de l'utilisation des pesticides, tout en tenant compte des risques pour les consommateurs.

Mots clés : extraction par QuEChERS ; méthode de d-SPE ; technique de GC-MS ; Résidus de pesticides.

Abstract: This work emphasis on the search for residues of certain pesticides in various fruits and vegetables (tomatoes, dates, strawberries and potatoes) extracted by the advanced QuEChERS extraction method, followed by d-SPE purification, then the concentrated extracted residues were analyzed by gas chromatography coupled with mass spectrometry (GC/MS), in the regions of Mitidja and Biskra, as well as on the estimation of their potential risk for the Algerian consumer. The results obtained revealed contamination by pesticide residues of Deltamethrin or their metabolites in samples of tomatoes and dates from the region of Biskra However, these results can be confirmed by checking the similarity percentages and comparing with the retention times and mass spectra obtained during quantitative analysis using the pure analytical standards of the pesticides. These results should serve as a reference for future monitoring and for the implementation of preventive measures aimed at minimizing risks to human health. In agriculture, pesticides are used to protect crops from pests, but they can also contaminate the ecosystem, exposing humans through water, air and food. Vegetables are particularly susceptible to contamination by these substances. To encourage sustainable agriculture, it is essential to adopt integrated management of pesticide use, while taking into account the risks for consumers.

Key words: Extraction by QuEChERS ; d-SPE method; GC-MS technique ; Pesticide residues.

ملخص: يركز هذا العمل على البحث عن بقايا بعض المبيدات في الفواكه والخضروات المختلفة (الطماطم والتمر والفراولة والبطاطس) المستخرجة بطريقة الاستخلاص المتقدمة QuEChERS ، تليها تنقية d-SPE ، ثم تم تحليل بقايا المستخلصات المركزة بواسطة كروماتوغرافيا الغاز مقرونة بمطياف الكتلة (GC/MS) في منطقتي متيجة وبسكرة، فضلا عن تقدير مخاطرها المحتملة على المستهلك الجزائري. أظهرت النتائج المتحصل عليها وجود تلوث ببقايا المبيدات دلتامثرين أو مستقبلاتها في عينات من الطماطم والتمور من منطقة بسكرة ومع ذلك، يمكن التأكد من هذه النتائج من خلال التحقق من نسب التشابه ومقارنتها مع فترات الاحتفاظ وأطياف الكتلة التي تم الحصول عليها خلال التحليل الكمي باستخدام المعايير التحليلية البحتة للمبيدات. ينبغي أن تكون هذه النتائج بمثابة مرجع للرصد المستقبلي وتنفيذ التدابير الوقائية التي تهدف إلى تقليل المخاطر على صحة الإنسان. في الزراعة، تُستخدم المبيدات الحشرية لحماية المحاصيل من الآفات، ولكنها يمكن أن تلوث النظام البيئي أيضًا، مما يعرض البشر للخطر من خلال الماء والهواء والغذاء. الخضار معرضة بشكل خاص للتلوث بهذه المواد. ولتشجيع الزراعة المستدامة، من الضروري اعتماد الإدارة المتكاملة لاستخدام مبيدات الآفات، مع مراعاة المخاطر التي يتعرض لها المستهلكون.

الكلمات المفتاحية: الاستخراج بواسطة QuEChERS ؛ طريقة د-SPE ؛ تقنية GC-MS ؛ متبقيات المبيدات.