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GC/EI-MS and UV-Vis analysis of pesticide residues in cultivated *Catha edulis* Forsk (Khat) from selected farms in Meru County, Kenya

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ABSTRACT

In this study, an analysis of pesticide residues was performed using a gas chromatography/electron impact mass spectrometer (GC/EI-MS) to qualitatively assess and characterize pesticide residues in *khat* leaves sampled from selected agricultural farms in Meru County, Kenya. A solid-phase microextraction (SPME) procedure followed by GC/EI-MS analysis led to the detection and identification of six pesticide compounds from the sample-ion chromatograms. They include cypermethrin, acephate, cyhalothrin, cyfluthrin, chlorpyrifos, and chlorfenvinphos. The prevalence rate of pesticide contamination was determined to be 54.5% of the sample size. Of the identified pesticide residues, 50% were compounds based on pyrethroids and the other 50% were based on organophosphate. Four of the six identified pesticides were chlorinated compounds. A quick, easy, cheap, effective, rugged, and safe UV-vis double beam spectrophotometric technique based on copper (II) chelation reactions leading to colored copper pesticide complexes was developed, validated, and applied to quantify and compare the levels of selected pesticide compounds found in the *khat* samples. UV-vis wavelength-scan measurements performed on pesticide compounds chelated with copper (II) ions revealed maximum absorption of Cu-cypermethrin and Cu-acephate at 321 and 207 nm, respectively. The standards calibration curves developed from the UV-Vis quantitation technique showed excellent linearity in the concentration range of 0.5-10.0 μg/L (R^2 = 0.99) for both cypermethrin and acephate standards. The estimated limits of quantification (LOQ) were 0.25-0.26 μg/L, respectively. The UV-Vis quantitation results from the selected samples (in which residues were confirmed to be present) revealed that acephate (an organophosphate residue) occurred at higher concentration levels (range 2.897-7.978 μg/L) than cypermethrin (2.145 μg/L). For the pesticides quantitatively analysed in the selected samples, the levels were below the maximum residue limit (MRL). The hazard quotients (HQ) were in the range of between 0.247-0.797.

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1. Introduction

The *Catha edulis* Forsk plant (Khat) is among the most widely consumed psychoactive stimulant plant substances in the world. The crop is grown in large plantations in eastern Africa, the Horn of Africa, and southwestern parts of the Arabian Peninsula. Young leaves and twigs are consumed daily by more than 20 million people for their psychostimulatory effects. The practice of chewing *miraa* has become deeply rooted in the history, tradition and culture of the indigenous population where it is grown [1]. The highlands of Meru County host the cradleland of Kenya's vast *khat* (locally known as *miraa*) farms. The region has a population of approximately 1.4 million inhabitants and a significant part of it not only consumes *khat* in large quantities but also derives its income from *khat* farming as a very lucrative agribusiness venture [2]. Consequently, the use of various pesticides in *khat* farming for crop protection purposes is widespread within the region.

Pesticide compounds, although beneficial in protecting agricultural food crops from pest infestations to improve yields and quality, can often persist in the environment, bioaccumulate in plant tissues, and then expose their potentially hazardous, acute, or chronic adverse toxic effects to consumers. Some of the adverse health conditions associated with pesticide intake include depression in the respiratory and nervous system, seizures, asthma attacks, mental confusion, and loss of consciousness [3-6]. Several monitoring and evaluation studies have in the past detected traces of pesticide residues persisting in fruit and vegetable cash crops in markets. In some cases, the levels have exceeded the minimum residue limit (MRL) [7,8]. Consumption of large amounts of pesticide-contaminated crops can pose serious health risks if contamination is not detected early enough. This has continued to justify the need for periodic assessments of the nature and quantity of pesticide residues present in cash crops to alert the general public or the defined population to the status of contamination and the potential health risks to which consumers may be exposed.

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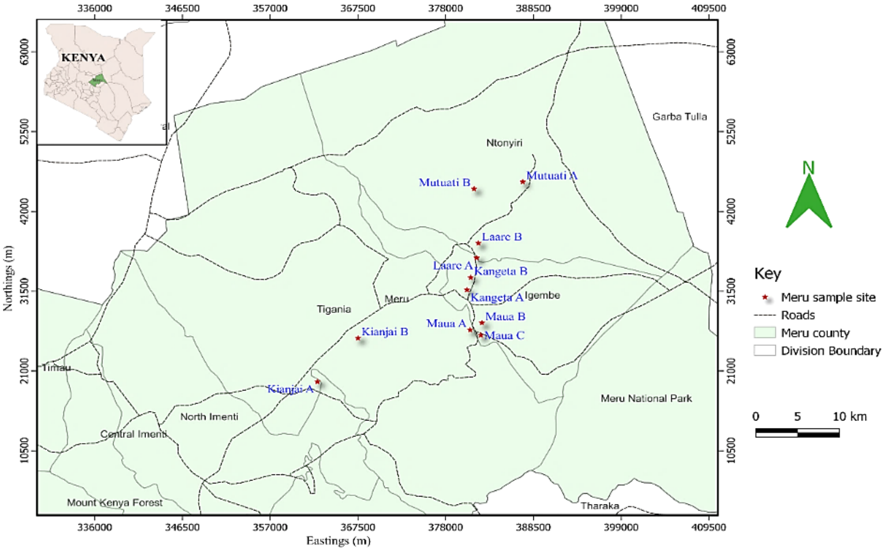

Figure 1. Map of sampling sites within Meru County, Kenya.

Gas chromatography using electron impact ionization mode (GC/EI) coupled with a mass spectrometer (MS) and an ultraviolet-visible (UV-vis) double beam spectrophotometer are instruments that have become increasingly important in the qualitative and quantitative analysis of pesticide residues in many food crops [9-12]. In this study, a GC/EI-MS analytical protocol was applied for the detection, identification, and characterization of organic pesticide residues present in *khat* leaf samples. A developed ultraviolet-visible (UV-vis) spectrophotometric technique based on copper chelation with selected pesticide compounds was used to quantify the levels of a selected organophosphate and pyrethroid pesticide in the *khat* leaves sampled. This study was designed to acquire data and generate scientific reports by documenting the various types of pesticide residue components present in the leaves of *khat* samples obtained from selected farms in the Meru County region of Kenya during the dry season. The prevalence rates of the identified pesticide residues based on the study are also reported in this article.

2. Experimental

2.1. Sample collection

The sampling of *khat* leaves investigated in this study was carried out following the general guidelines and methods adopted from Directive 2002/63/EC of the European Commission (EC) to establish maximum residue limits (MRL) in food crop commodities [13]. They were randomly collected from selected *khat* farms within Meru County, Kenya, as indicated on the sampling map in Figure 1.

2.2. Chemicals and reagents

All organic solvents, i.e., ethyl acetate, acetone, and n-hexane, used in the extraction procedures were of analytical grade (Kobian Scientific, Nairobi, Kenya). The pesticide standards, cypermethrin and acephate, that were used in the quantitative measurements were all high purity (>98.5%) and were purchased from Organix Limited Suppliers, Nairobi, Kenya. The standard stock solutions of the two pesticides were prepared in the solvent system; ethyl acetate: acetone: n-hexane in the ratio of 2:1:1 and stored at -5 °C. Analytical grade C18-bonded silica was purchased from Sigma-Aldrich (Germany). Anhydrous sodium sulfate (Na_2SO_4) and 1.0 g of magnesium metasilicate ($MgSiO_3$) were supplied by Kobian Scientific, Nairobi, Kenya.

2.3. Extraction of pesticides

A 1.0 g ground *khat* leaf sample was placed in a glass mortar and 1.0 g of C_{18} was added. The leaf sample powder was then mixed with the C_{18}-bonded silica material with a glass pestle. The homogenized mixture was introduced into a 100 mm × 20 mm ID polypropylene column, filled with 0.1 g of glass wool at the tap base, followed by, in order, a 1.0 g layer of anhydrous sodium sulfate (Na_2SO_4) and then 1.0 g of magnesium metasilicate ($MgSiO_3$). A 50 mL solution containing 10 mL of acetonitrile (MeCN) and 40 mL of *n*-hexane was added to the packed column to elute in a dropwise manner. The eluent was collected in an Erlenmeyer flask, transferred to a round bottom flask, and concentrated using a rotary vacuum evaporator (water bath temperature 40 °C) to a reduced volume of 1 mL, then a 1 µL part of the concentrate was siphoned for GC/MS analysis.

2.4. Gas chromatography mass spectrometer (GC-MS) qualitative analysis

Solid phase micro-extraction (SPME) technique was used to adsorb the prepared *khat* leaf extracts. The coating fiber used was polydimethylsiloxane-divinylbenzene (PDMS/DVB). A Shimadzu QP2010 SE series GCMS (Kyoto, Japan) equipped with an electron capture detector was used for the analysis of pesticide residues (Figure 2). A 5 mL sample volume was placed in a 20 mL headspace vial. The PDMS/DVB fiber was inserted into the headspace with heating (40 °C) and agitation (250 rpm) for 30 min. After extraction, it was loaded into the sample injection port of the GC-MS instrument equipped with an SE 30 capillary column (50 m × 0.25 mm ID at 0.25-µm film thickness) in split mode where the chromatographic separation of the volatile components of the leaf sample extracts was carried out. The carrier gas used was helium at a flow rate of 1 mL per min. The oven temperature was programmed as follows: initially held at 40 °C for 4 min, increased at a rate of 10 °C /min, increased to 250 °C, and then hold at 300 °C for 15 min. The MS fragmentation was performed in electron impact mode (EI) (electron energy, 70 eV; ionization temperature, 230 °C). The transfer line temperature was 230 °C. The mass acquisition range was set to 33-450 amu.

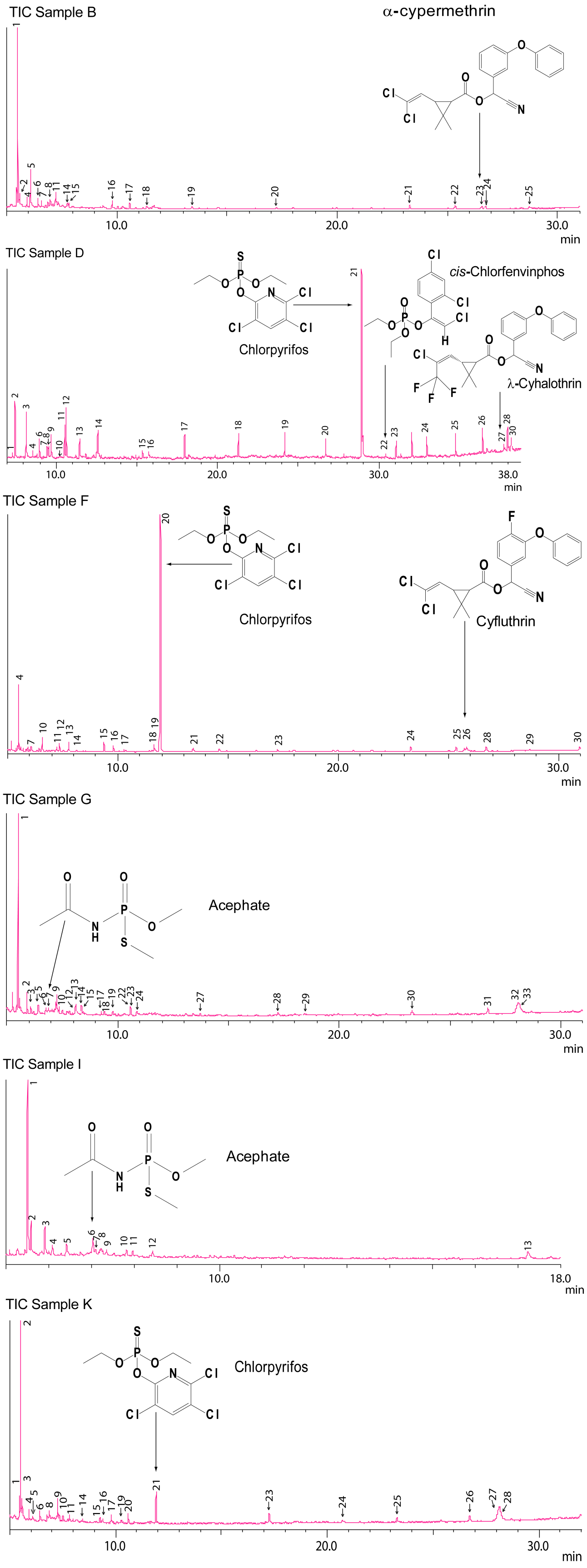

Figure 2. GC-MS total ion chromatograms of the samples with detected pesticide residues.

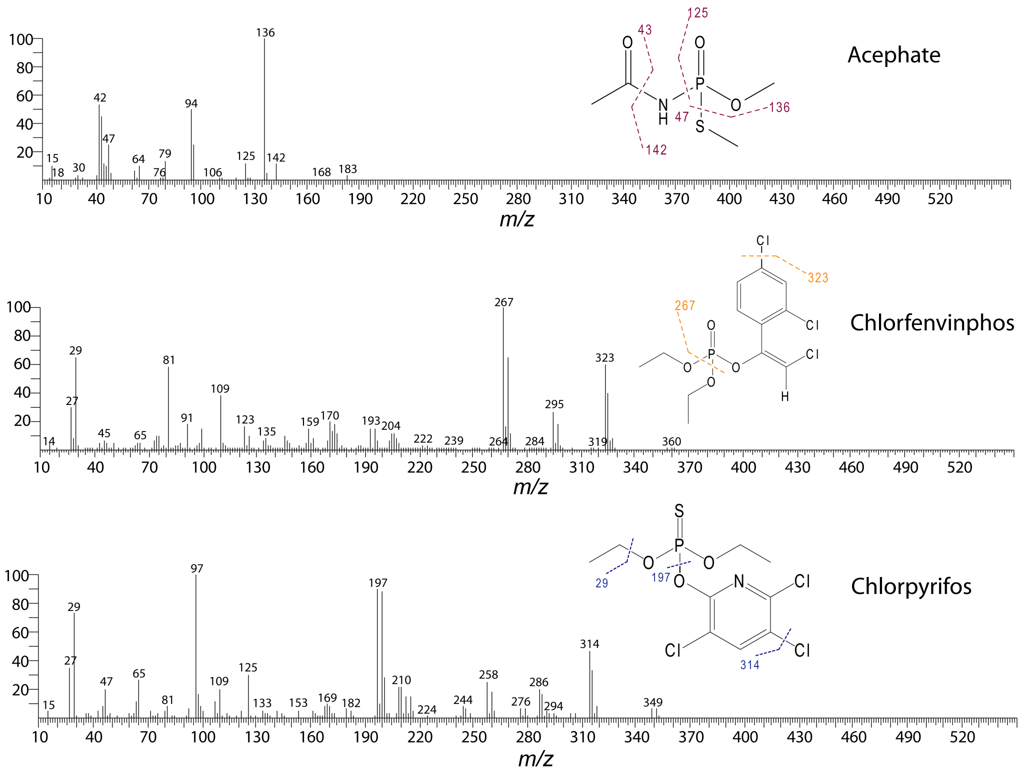

Figure 3. Molecular fragmentation of the detected organophosphate pesticide residues.

The National Institute of Standards (NIST 11) database was used to confirm the identity of the hits in the mass spectra. The identifications were then confirmed by injection of the authentic compounds into the GC-MS on the basis of the comparison of mass spectra and GC retention time.

2.5. Ultraviolet-visible spectrophotometric quantitative analysis

A double beam K9000® UV-visible spectrophotometer equipped with 10 mm path-length quartz cuvette cells, fitted with a silicon diode detector, and deuterium and tungsten/ halogen lamps were used to acquire the spectral data. Analytical grade ethanol, *n*-hexane, and acetone were used in the development of the solvent system for the extraction of pesticide components from the *khat* leaf extracts. Stock solutions of acephate (100 µg/L) and cypermethrin (100 µg/L) pesticides were prepared from which aliquots were siphoned to prepare a set of working standards in the range between 0.5 to 10 µg/L in a solvent system of ethanol: *n*-hexane: acetone in a ratio 2:2:1.

Analytical grade chemicals were used to prepare solutions of 0.1 M copper (II) nitrate ($Cu(NO_3)_2$), 0.1 M potassium chloride (KCl), and 20 % of 0.1 M sodium hydroxide (NaOH) and pH = 7 phosphate buffer, including double-distilled water, were prepared for quantitative UV-visible analysis. 2 mL of the solution containing 10 mL of $Cu(NO_3)_2$, 4 mL of KCl, and 4 mL of NaOH were added to the standard solution, stirred in a warm bath (50 °C for 15 min) to form coloured Cu(II)-pesticide complexes to allow quantitative spectrophotometric analysis.

3. Results and discussion

3.1. GC-MS analysis

Figure 2 shows the six GC-MS total ion chromatograms obtained from each of the six *khat* leaf samples from which pesticide compounds were detected. It can be noted that in four out of the six samples, aromatic-based pesticides were identified and therefore the most prevalent compared to the nonaromatic ones identified only in samples G and I. All aromatic pesticides were chlorinated based on their structural identity. Pesticides containing phosphate esters were identified in samples labelled G and I.

From the GC-MS analysis, a single pesticide compound was detected in four samples (B, G, I, and K), while the other samples were found to contain multiple pesticide residues. Three different pesticide compounds were detected in sample D. In sample F, two different types of pesticide compounds were detected. Only two of the six samples containing pesticide residues had non-aromatic pesticide compounds, while the other four contained aromatic pesticide compounds. The pesticide compounds containing cyano-groups (*i.e.*, cypermethrin, cyhalothrin, and cyfluthrin) were dominant as they were identified from at least half of the total samples that had pesticide contamination.

Figure 3 shows the mass spectra of each of the organophosphate pesticide compounds identified using GC-MS analysis. The mass fragmentations are indicated by hatched lines on the molecular structures in the respective spectra. The molecular ion base peaks for each pesticide are identified and illustrated by the fragmentation patterns. It can be noted that in all identified organophosphate pesticide compounds, the molecular fragments arising from the breaking of the phosphorus-oxygen bonds (P-O; in the case of chlorfenvinphos and chlorpyriphos) and the phosphorus-sulfur and phosphorus-nitrogen bonds (P-S and P-N; in the case of acephate) can be deciphered in the respective mass spectra. For example, the fragmentation of acephate along the P-N bond yields an ion peak at 125 *m/z,* whereas the breakage of the P-S bond gives the molecular ion base peak at 136 *m/z*.

Table 1. Summary of the pesticide compounds detected based on GC/EI-MS analysis.

Pesticide name	Classification / Chemical group	Molecular formula	*m/z* ion base peak (Observed)	*m/z* ion peak (Confirmatory)	Prevalence rate (%) *
Acephate	Organophosphate	$C_4H_{10}NO_3PS$	136	142, 94	18.18
Cypermethrin	Pyrethroid	$C_{22}H_{19}Cl_2NO_3$	163	209, 77	9.09
Cyfluthrin	Pyrethroid	$C_{22}H_{18}Cl_2FNO_3$	163	206, 77	9.09
Chlorfenvinphos	Organophosphate	$C_{12}H_{14}Cl_3O_4P$	267	205, 145	9.09
Chlorpyrifos	Organophosphate	$C_9H_{11}Cl_3NO_3PS$	97	244, 153	27.27
Cyhalothrin	Pyrethroid	$C_{23}H_{19}ClF_3NO_3$	181	197, 77	9.09

* Number of particular detected pesticide occurrences/total number of all pesticide-contaminated samples.

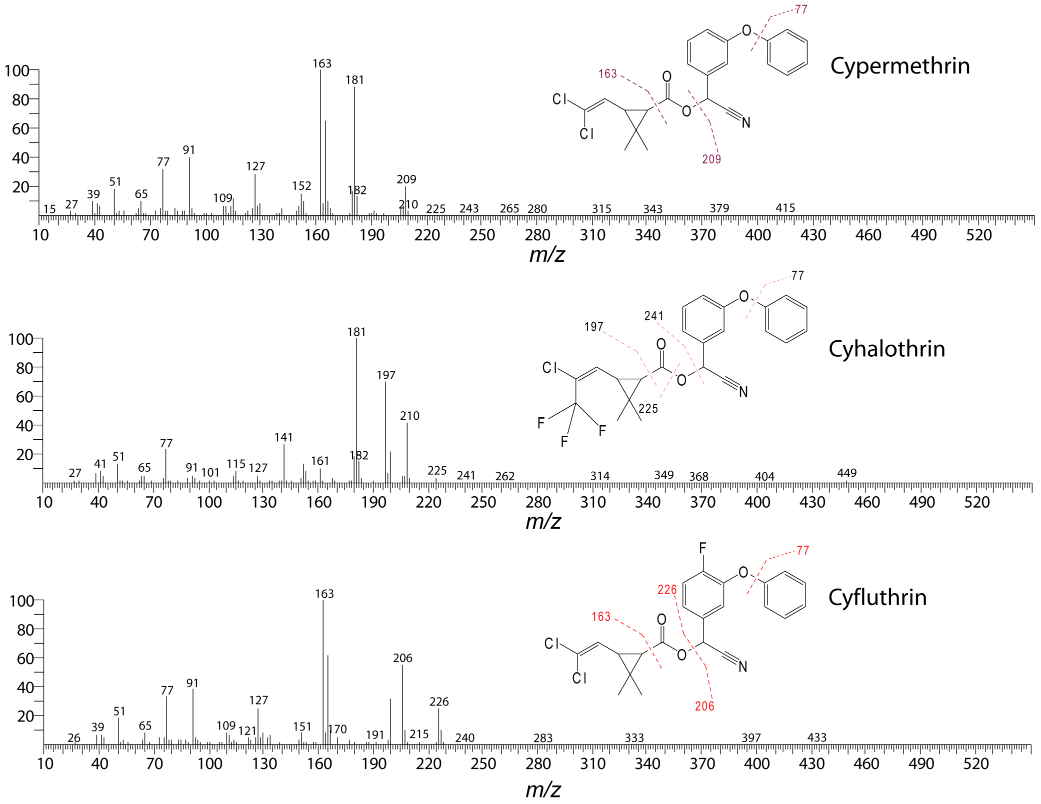

Figure 4. GC-MS mass spectra of the detected pyrethroid-based pesticides.

The base peak of chlorfenvinphos observed at 267 *m/z* arises due to the cleavage of the P-O bonds highlighted in the molecular fragmentation figure. In the case of chlorpyrifos, cleavage of the P-O leads to the detected 197 *m/z* peaks.

Figure 4 shows the mass spectra of each of the three pyrethroid-based pesticidal compounds detected and identified from the *khat* leaves using the GC-MS analysis. They include cypermethrin, cyhalothrin, and cyfluthrin. Common among their structures are the biphenyl ether aromatic rings, a cyano substituent group, and a cyclopropyl group. The molecular ion base peaks detected at 163 *m/z* in the spectra of both cypermethrin and cyfluthrin arise from fragments that contain cyclopropyl groups attached to the halogen-substituted ethylene groups in the respective compounds, as indicated in the respective spectra.

A similar cyclopropyl side chain fragmentation in cyhalothrin gives rise to the prominent ion peak detected at 197 *m/z*. The molecular ion peak detected at 77 *m/z* in all mass spectra of the pyrethroids is due to the fragmentation of a phenyl group from the bulkier diphenyl ether group found in all three molecules.

Table 1 gives a summary list of all pesticide compounds that were detected in *khat* leaf samples using GC-MS separation and qualitative analysis. The identities are characterized by the observed base-peak MS data, which are represented in the table. Three pesticide compounds belonging to the organophosphate class and three other pesticides belonging to the pyrethroid class were identified. The molecular ion base peaks observed in the spectra were used in conjunction with the molecular fragmentations to confirm their structural identity using the NIST database.

Out of the six identified pesticide compounds, five were found to be chlorinated aromatic compounds. Out of the eleven samples analysed in this survey, two had confirmed traces of acephate representing, a prevalence rate of 18.18%. The pesticides, cypermethrin, cyfluthrin, chlorfenvinphos, and cyhalothrin, had similar prevalence rates of 9.09%. Organophosphate chlorpyrifos recorded the highest prevalence rate of 27.27%.

3.2. UV-vis spectroscopic analysis for quantitation

3.2.1. Maximum UV absorption for cypermethrin and acephate pesticides

Figures 5 and 6 illustrate the UV-vis wavelength scan absorption spectra obtained from selected standards of the copper (II) complexes of cypermethrin and acephate, respectively. The two pesticides are reportedly the most widely applied pesticides used in the cultivation of *khat* within the Meru region.

Table 2. Linearity of the calibration curves for cypermethrin and acephate.

Pesticides	**Working / curve range (µg/L)**	**Slope**	R^2	**LDR (µg/L)**	**LOQ (µg/L)**
Cypermethrin	0.50-10.0	0.01044	0.9987	1.5-6.5	0.252
Acephate	0.50-10.0	0.01073	0.9997	1.8-7.0	0.261

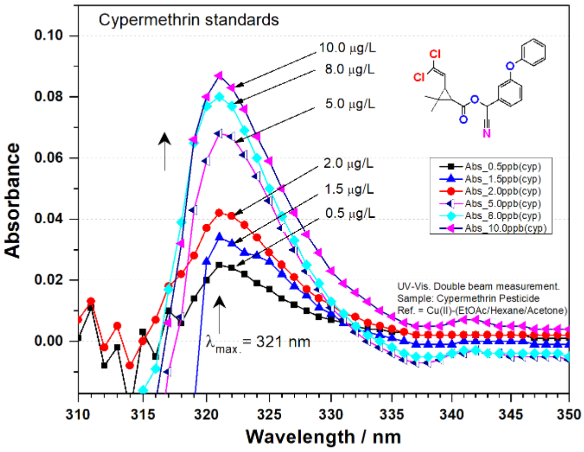

Figure 5. UV-vis absorption spectra of Cu(II) complexes formed with the cypermethrin standard.

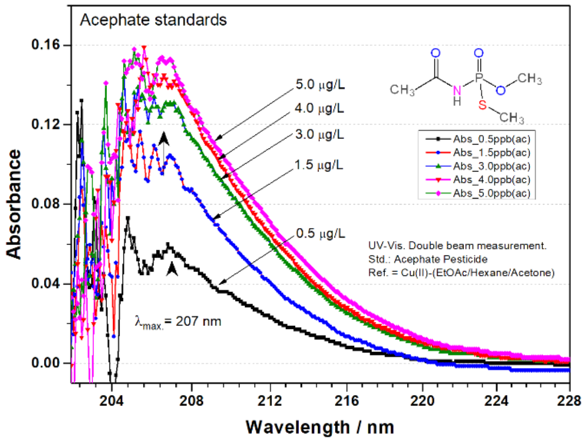

Figure 6. UV-vis absorption spectra of Cu(II) complexes formed with acephate standard.

The solvent system used was EtOAc/hexane/acetone in a 2:2:1 ratio. The reference used in the double beam measurements was $CuCl_2$ diluted in the solvent EtOAc/hexane/acetone. In both Figures 5 and 6, the normalized absorption spectra obtained from each of the respective standards are plotted as a function of the scanned wavelengths in the UV-visible region.

It can be noted that both the organometallic Cu(II)-cypermethrin and Cu(II)-acephate complexes exhibit absorption in the UV-visible region. Under the measurement conditions, Cu-Cypermethrin exhibits maximum absorption at about 321 nm, while the Cu-Acephate complex has its maximum absorption at about 207 nm. Quantification methods that exploit the formation of heavy metal chelates have been performed using ultraviolet-visible (UV-vis) spectrophotometry. The binding of Cu(II) ions in the current case plausibly occurs through oxygen, nitrogen, and sulfur-ligating donor atoms that are present in pesticide molecules according to the chelate effect [8].

3.2.2. Calibration curves: Quantitation of cypermethrin and acephate

Figures 7 and 8 show the calibration plots derived by recording the absorptions of standard solutions of Cu-cypermethrin and Cu-acephate at 321 and 207 nm, respectively. The linearity of the standard curves was determined by plotting the mean absorbance values (including the standard errors) against the concentration of the respective standards (in µg/L). The plots were fitted applying linear regression, both of which showed a good fit with a very strong coefficient of determination $R^2 > 0.99$ and very low standard errors in the gradients and intercepts. The linear regression equations used to determine the concentrations (in µg/L) of the pesticides are indicated in the respective calibration plots.

The linearity data are shown in Table 2. There was a strong linear relationship between mean absorbance values and analyte concentration in the working/calibration range between 0.50-10.0 µg/L for both the cypermethrin and acephate standards based on R^2 values. The estimated linear dynamic range (LDR) was 1.5-6.5 and 1.8-7.0 µg/L for cypermethrin and acephate, respectively. The limits of quantification (LOQ) were estimated to be 0.252 µg/L for cypermethrin and 0.261 µg/L for acephate. The estimated values of LDR and LOQ were determined by applying validation procedures that consider the standard deviation (SD) of the signal response (in this case, the measured absorbance values) and the slope of the calibration curves (S) [14,15].

The results indicate that the developed spectrophotometric techniques can act as a useful alternative analytical quality control laboratory method for the trace level determination and comparison of pesticide residue levels (PRLs) within the range of between 1.0 to 10.0 µg/L.

Table 3. Estimated levels of cypermethrin and acephate in the *khat* samples investigated.

Sample	Cypermethrin (µg/L)	Acephate (µg/L)	Hazard quotient (HQ) **
Sample B	2.145 +/- 0.047	ND *	0.247
Sample D	ND *	2.897 +/- 0.034	0.289
Sample F	ND *	7.978 +/- 0.056	0.797

* ND: Not detected by the GC-MS analysis.
** Exposure concentration / reference MRL value.

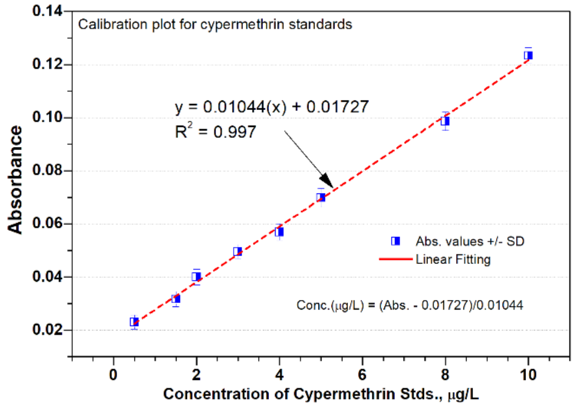

Figure 7. The calibration curve developed from the Cu(II) complexes formed with cypermethrin pesticide standards.

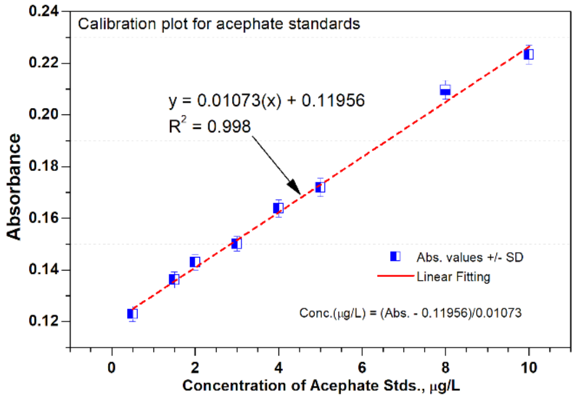

Figure 8. The calibration curve developed from the Cu(II) complexes formed with acephate pesticide standards.

Table 3 shows the results from the UV-Vis spectrophotometric quantification measurements of the concentration levels of cypermethrin (a chlorinated pyrethroid pesticide) and acephate (an organophosphate pesticide) as determined from the samples from which they were detected using GC-MS analysis. For the samples analysed six weeks after the pesticide spray reported, it was found that acephate exists at a higher concentration than cypermethrin. The was a significant variation in the acephate pesticide residue content between samples D and F. The concentration levels were all below the maximum residue limit (MRL) values set by Codex [16]. According to the quantitative analysis, the hazard quotients (HQ) are calculated based on the MRL values [17]. They were 0.247 for cypermethrin and between 0.287 and 0.797 for acephate.

4. Conclusions

In this study, a modified qualitative GC/EI-MS technique was successfully used to perform chromatographic separation, detection, and profiling of pesticide residues present in *Khat* leaf samples. The pesticides identified and characterized included three organophosphates: acephate, chlorpyrifos and chlorfenvinphos, and three pyrethroids: cypermethrin, cyhalothrin, and cyfluthrin. An ultraviolet-visible spectrophotometric analytical method was developed, optimized and applied for the quantitative analysis of pesticide residues, proving a fast and inexpensive technique for the estimation and comparison of pesticide levels in leaf samples of *khat*. The light-brown Cu-pesticide chelate complexes exhibited maximum absorption in the ultraviolet region based on double-beam wavelength scan spectrophotometric measurements. The intensities of the maximum absorptions for the prepared Cu-cypermethrin and Cu-acephate standards were found to relate linearly to the respective concentrations. The relationship obeyed the *Beer-Lambert* equation with excellent linearity in the ppb range of 0.5-10.0 µg/L ($R^2 > 0.99$). From the samples investigated by UV-Vis quantitative analysis, it was found that acephate (an organophosphate pesticide residue) occurs within the range of 2.897-7.978 µg/L whereas the determined concentration of cypermethrin was 2.145 µg/L. Their levels were below the maximum residue limit (MRL) with moderately low hazard quotients as well. The developed UV-VIS analytical method can potentially find application in food safety control laboratories as a technique for the quantification of pesticide residues in vegetable samples.

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Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered to.
Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Albert Morang'a Oyugi; Methodology: Albert Morang'a Oyugi; Methodology; Software: John Onyango Adongo; Cynthia Muhavi Mudalungu Validation: Albert Morang'a Oyugi; Formal Analysis: Albert Morang'a Oyugi; Investigation: Albert Morang'a Oyugi; Resources: Albert Morang'a Oyugi; Data Curation: Albert Morang'a Oyugi; Cynthia Muhavi Mudalungu; Writing - Original Draft: Albert Morang'a Oyugi; Writing - Review and Editing: Joshua Kiprotich Kibet; Visualization: Albert Morang'a Oyugi; Supervision: John Onyango Adongo; Joshua Kiprotich Kibet; Project Administration: Albert Morang'a Oyugi; John Onyango Adongo; Joshua Kiprotich Kibet.

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