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Research Paper

Determination of Residue Levels of DDT and Its Metabolites in *Khat* and Cabbage Samples using QuEChERS Sample Preparation Method Combined with GC-MS Detection

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Abstract

A simple and selective extraction technique based on a quick, easy, cheap, effective, rugged and safe (QuEChERS) sample preparation method coupled with gas chromatography-mass spectrometric detection (GC-MS) was developed and applied for simultaneous determination of 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (p,p'-DDT) and its main metabolites 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (p,p'-DDE) and 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (p,p'-DDD) in cabbage and *Khat* samples. Parameters that primarily affect the extraction efficiency of the analytes were optimized. The significance of the use of cleanup was investigated and its optimum amount was found to be 6 mg PSA and 12 mg C_{18}. The optimum values for acetonitrile volume and pH of the sample was found to be 3 mL and 7, respectively. The linearity of the analytical response was acceptable with correlation coefficients of 0.992 or better. The precision associated with the analytical method, expressed as %RSD were lower than 8.6 and 9.1% for the intraday and interday precision, respectively. The limit of detection (LOD) and limit of quantification (LOQ) of the proposed method for cabbage sample were in the range of $2x10^{-5}$–$4x10^{-5}$ mg/kg and $9x10^{-5}$–$14x10^{-5}$ mg/kg, respectively. The LOD and LOQ of the proposed method for *Khat* sample were in the range of $2x10^{-5}$–$6x10^{-5}$ mg/kg and $7x10^{-5}$–$19x10^{-5}$ mg/kg, respectively. The recoveries of the method were ranging from 97.16 to 107.99 for cabbage and 72.1 to 90.55 for *Khat* sample. The analytical applications of this method indicated the presence of p,p'-DDE, p,p'-DDD and p,p'-DDT in both cabbage and *Khat* samples. The amount of p,p'-DDE, p,p'-DDD and p,p'-DDT in cabbage were found to be 0.004, 0.01 and 0.01 mg/kg, respectively. The amount of p,p'-DDE, p,p'-DDD and p,p'-DDT in *Khat* were found to be 0.01, 0.03 and 0.07 mg/kg, respectively. The results indicate that there should be continuous monitoring of DDT and its metabolites residues in cabbage and *Khat* samples which in turn is helpful to assess the potential risk of the residues to consumers' health.

1. Introduction

Pesticides are widely applied in agriculture during the production, processing, storage, transport or marketing of foods to control destructive pests such as insects, plant disease, weeds and other living organisms that endanger our food supply and health (Beddington, 2010; Damalas and Eleftherohorinos, 2011). Despite their uses, widespread applications of pesticides may affect human health and the environment as a result of residues that remain in environmental and food samples (Ogah and Coker, 2012). As a result, the contaminations of food items by such hazardous substances are a worldwide public health concern (Beena and Kathpal, 2009; Latif et al., 2011).

Dichlorodiphenyltrichloroethane (DDT) is an

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organochlorine pesticide which had been used and still being used in some countries to combat malaria, typhus and biting flies. Organochlorine pesticides such as DDT are known to create certain health problems such as cancer, immune system malfunction, and disruption of hormonal functions for the warm blooded animals including humans (Tomatis et al., 1974; Colborn et al., 1996; Barriada-Pereira et al., 2005). DDT is also known to cause disruptions in the antioxidant system and abnormalities in the central nervous system (Castilla-Pinedo et al., 2010). The most dangerous property of DDT is its high bioaccumulation and biomagnification potentials (Brooks, 1986).

DDT residues are found in the environment because of its slow transformation. DDT persists with a half-life of about 10 years and is metabolized mainly in the liver and partly in the kidneys to its most familiar metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyld-ichloroethane (DDD) in the body (Brooks, 1986; Boul et al., 1994). DDT and its metabolites are strongly lipophylic and show an affinity to the fat tissue of animals and humans; as a result they are stored in the body's fatty tissues. A high DDE/DDT ratio show old pollution, but low DDE/DDT ratio is evidence of recent DDT pollution (Lundholm et al., 1997).

Recently, there has been a growing interest in the detection and quantification of pesticide residues in agricultural produce intended for human consumption (Hercegova et al., 2007; Abdulhamid et al., 2016). Majority of the farmers, in the developing countries like Ethiopia, have little or no knowledge about the health and environmental hazards associated with pesticide handling (Yalemtsehay Mekonnen and Tadesse Agonafir, 2002). Thus, contamination of the environment with pesticides and the pesticides entry into the food chain is unavoidable in these countries (Daniel Daba et al., 2011; Mekonen Seblework et al., 2014). As a result, these factors may be causing contaminations of cabbage and *Khat* samples (Owus-Boateng et al., 2013; Daniel Daba et al., 2011; Shemsu Ligan and Ahmed Hussen, 2014).

Cabbage (*Brassica oleraceavarcapitata*) is a vegetable with high nutritive value and one of the most consumed vegetables in Ethiopia. It is used in stews, eaten boiled and raw in salads. Pesticides are widely used in fruits and vegetables to control pests and diseases during farming, transportation, and storage because of their susceptibility to insects and disease attacks (Kamrin, 1997; Zawiya et al., 2007).

Khat (*Catha edulis*) is an evergreen perennial shrub plant that belongs to the *Celastracene* family. The leaves are chewed by millions of people, mainly in Africa and the Middle East, for its psychostimulatory effects due to the presence of the phenylalkylamines in the plant (Minaleshewa Atlabachew et al., 2015). The plant is one of the cash crops and Ethiopia is most likely the major grower and exporter and it is the second most important source of foreign exchange earner for the country after coffee (Dechasa Lemessa, 2001; Toennes et al., 2003; Ermias Dagne et al., 2010). *Khat* leaves used for human consumption often contain contaminants such as pesticide residues. The contamination of *Khat* plants by pesticides may result from the use of pesticides during cultivation or due to environmental contamination (Shemsu Ligan and Ahmed Hussen, 2014; Tilahun Beniam and Ahmed Hussen, 2014). The levels of p,p'-DDT and p,p'-DDE in *Khat* samples, collected from various districts of Sidama Zone, Southern Ethiopia, were reported to be in the range of 10.8-19.7 and 3.5-18.6 µg/kg, respectively (Shemsu Ligan and Ahmed Hussen, 2014). All the *Khat* samples investigated by these workers contained residues higher than the EU maximum residue limit (MRL) for total DDT (Alimentarius, 2011).

The finding of the study performed on pesticides residues analysis from the run-off of the fields growing *Khat* around Haramaya, one of the known *Khat* producing areas in Ethiopia, has indicated contamination of the nearby lake which resulted in severe pollution of the ecosystem. This shows that although DDT is officially banned for agricultural application, contamination of food still occurs which most likely results from illegal use of pesticide obsolete stocks (Amera Tadesse and Asferachew Abate, 2008). This necessitates the study of the possible occurrence of DDT and its metabolities in *Khat* and cabbage grown in these areas since several crops are known to accumulate DDT in their edible parts up to critical levels, which may contribute to intake of the contaminants. Thus, the monitoring of DDT and its metabolities residues in *Khat*

and cabbage samples aids the assessment of the potential risks of these products to consumers' health.

The determination of pesticide residues in food samples is a difficult task, because of the complexity of the matrices and the low concentrations at which these compounds are usually present. Thus, despite advances in the development of highly efficient analytical instrumentation for their final determination efficient sample preparation remains an important part of obtaining accurate quantitative results for trace level detection and identification which in turn is helpful to protect the environment and consumer health (Barr et al., 2002; Beyer et al., 2008). The increasing public concern over the potential health hazard associated with exposure to pesticides has led to the strict regulation of maximum residue limits (MRLs) of pesticide residues in food commodities. Generally, the complex matrix of agricultural products adversely affects analysis precision, and it is necessary to remove the matrix interference by sample pretreatment, such as extraction and clean up steps (Zambonin et al., 2004). The method of extracting pesticide residues from food samples and preparing them for analysis is a time consuming, expensive, and labour intensive process.

One of the sample preparation techniques employed for selective enrichment and determination of pesticides in fruits, vegetables, grains and herbs samples is the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method which was introduced in 2003 (Anastassiades et al., 2003). The method is characterized by using a polar solvent, acetonitrile, for extraction of water containing matrices and addition of salts in order to get phase separation (partitioning of the acetonitrile extract from the water in the sample). The sample cleanup is carried out by using dispersive solid-phase extraction (d-SPE) or adsorbent materials. It is one of the recent approaches utilized for the isolation of pesticide residues from various food matrices (Wilkowska et al., 2011). Therefore, the aim of this study is to develop a sensitive, versatile and selective multiresidue method for the quantitative determination of DDT and its metabolites in cabbage and *Khat* samples collected from Haramaya District of the Oromia Regional State, Ethiopia by extraction with QuEChERS followed by GC-MS detection.

2. Material and Methods

2.1. Chemicals and reagents

The analytical standard p,p'-DDD (99% purity), p,p'-DDE (99%) and p,p'-DDT (99%) were obtained from the Dr. Ehrenstorfer (Augsburg, Germany). HPLC grade acetonitrile (ACN) was purchased from Sigma Aldrich (Steinheim, Germany) and used as extraction solvent. All other chemicals used in this study were of analytical grade reagents. The salts used as salting-out agents including NaCl and $(NH_4)_2SO_4$ were from BDH Chemicals Ltd (Poole, England). Hydrochloric acid (HCl) was the product of Sigma-Aldrich (St. Louis, MO, USA) and NaOH was from BDH Chemicals Ltd (Poole, England). A 0.1 M aqueous solution of each of the HCl and NaOH were prepared and used to adjust the pH to the required values. Ultrapure water was obtained by purifying with double distiller, A 8000 Aquatron water Still (Bibby Scientific, Staffordshire, UK) and deionizer (EASYPure LF, Dubuque). Then, it was filtered under vacuum through cellulose acetate filter paper (0.45 µm, Micro Science) before use. The stock standard solution of 100 mg/L, containing each target analyte, was prepared in n-hexane. Intermediate standard solution of 10 mg/L was obtained from the stock solution by dilution. Both intermediate solutions and other solutions of lower concentrations were prepared by diluting with reagent water. All solutions were stored in a refrigerator at 4 °C when not in use. Parameter optimization including the use of cleanup, acetonitrile volume and pH of the sample were performed by spiking cabbage and *Khat* samples with 0.15 mg/kg of a p,p'-DDE, p,p'-DDD and 0.3 mg/kg of p,p'-DDT. The following experimental conditions: sample size, 1 g of each sample; extraction solvent, 3 mL of acetonitrile; volume of water added, 5 mL and salt type and amount, 2.2 g $(NH_4)_2SO_4$ and 1 g NaCl were used to evaluate the use of cleanup. The cabbage and *Khat* samples were also spiked with a mixture of the analytes at six concentration levels: 0.05, 0.1, 0.2, 0.4, 0.8 and 1.6 mg/kg for p,p'-DDE and p,p'-DDD, and 0.1, 0.2, 0.4, 0.8, 1.6 and 3.2 mg/kg for p,p'-DDT to construct calibration curves.

2.2. Sampling sites and sample pretreatment

The cabbage and *Khat* samples were collected from farmers' cultivation plots in Haramaya District of the Oromia Regional State, Ethiopia. Haramaya is located at 9º24'44.89"N latitude and 42º02'01.06"E longitude

with elevation of 2021.13 m above sea level. Both cabbage and *Khat* samples were randomly collected from four plots. The four samples were wrapped in aluminum foil separately and placed into polythene bags and transported to the Analytical Research Laboratory, Department of Chemistry, Addis Ababa University for pesticide residue analysis. Each sample was chopped into small pieces, air dried under shade, mixed thoroughly to have a representative sample and ground using mortar and pestle. Blank samples were obtained from farmer villages; 5 km away from the sampling sites, where pesticides were not used. They were treated exactly in the same way as were done for the contaminated samples. The presence of pesticide residues were also checked by standard addition. It was found that no traces were detected in all the blanks.

2.3. QuEChERS extraction procedure

A 1 gm of each finely ground cabbage and *Khat* samples were weighed accurately into 50 mL Teflon centrifuge tubes. Three milliliters (3 mL) of acetonitrile and 5 mL water at pH 7 were added to dissolve polar compounds in the matrix, and then samples were shaken vigorously for 5 min by shaker to ensure that the solvent interacts well with the entire samples. After that, 2.2 g $(NH_4)_2SO_4$ and 1 g NaCl were added to the sample mixture and vortexed immediately for 1 min and then centrifuged at 3000 rpm for 5 min. The acetonitrile extract was collected from the upper layer and transferred to the d-SPE tube containing 6 mg PSA and 12 mg C_{18} sorbent for clean-up. The d-SPE tube was sealed and vortexed for 1 min, and then centrifuged at 3000 rpm for 5 min. The extract obtained was filtered using a 0.22 µm nylon syringe filter, transferred to an auto-sampler GC vial and 1 µL of the extract was injected to GC-MS for chromatographic analysis.

2.4. GC-MS analysis

An Agilent 7820A gas chromatograph (GC) equipped with 5977E mass spectrometer, MS, (Agilent Technologies, USA) with an inert ion source was used to analyze the pesticide residues level. A DB-5MS (USA) ultra inert capillary column (30 m x 250 µm and 0.25 µm i.d.) was used for GC separations. Helium gas of purity 99.999% was used as carrier gas at a flow rate of 1 mL/min. The instrumental responses obtained were interpreted using mass hunter ChemStation software. The GC injection port temperature was kept at 250ºC. Splitless injection mode was used during the whole analyses. The oven temperature program was set as follows: 130ºC for 0 min; increased to 185ºC at 25ºC/min ramp rate and held at this temperature for 1 min; then increased to 200ºC at 9ºC/min ramp rate and maintained at this temperature for 1 min; and finally increased to 290ºC at 10ºC/min ramp rate and held for 1 min.

Peaks were identified by their retention time and mass spectra after acquisition of the total ion chromatogram. In order to confirm the retention times of all analytes, scan mode was carried over the range m/z 50-550. Selective ion monitoring (SIM) mode was used for determination of all the analytes. Confirmation of the identity of pesticides was made by selecting the most abundant characteristic target ions of each pesticide and two characteristic fragment qualifier ions. The *m/z* selected for SIM mode detection was as follows: p,p'-DDE (176.1, 246 and 317.9), p,p'-DDD (165.1, 235 and 237), p,p'-DDT (199, 235 and 246). The instrumental response was reported as peak area and the average peak areas of the triplicate analyses were used for comparison.

2.5. Method validation

In order to validate the proposed analytical method, linearity, precisions and limits of detection (LOD) were evaluated. The linearity of the method was evaluated at six concentration levels 0.05, 0.1, 0.2, 0.4, 0.8 and 1.6 mg/kg for p,p'-DDE and p,p'-DDD, and at 0.1, 0.2, 0.4, 0.8, 1.6 and 3.2 mg/kg for p,p'-DDT. Each level was extracted under optimum conditions and injected in triplicate starting with the lowest concentration level. Then, calibration curves were obtained by considering the peak areas as the instrumental response versus the analyte concentrations. Repeatability or intraday precision (at intervals 4 hours within a day) and reproducibility or interday precision (for three consecutive days) of the method was evaluated by spiking blank cabbage and *Khat* samples with 0.15 mg/kg of p,p'-DDE and p,p'-DDD; and 0.3 mg/kg of p,p'-DDT. Determination of the recoveries of the analytes in both samples were done by comparing the concentration obtained by extracting spiked sample at 0.15 mg/kg of p,p'-DDE and p,p'-DDD; and 0.3 mg/kg of p,p'-DDT to the concentration of spiked extract at the

same level. The limits of detection (LOD) and limits of quantification (LOQ) were calculated based on the minimum analyte concentrations yielding 3 and 10 times the signal to noise (S/N) ratio of the blank, respectively (Abera Gure et al., 2014).

3. Results and Discussion

3.1. QuEChERS parameters optimization

In order to obtain the optimal QuEChERS conditions, various parameters including the use of cleanup, volume of the extraction solvent (acetonitrile) and sample pH were studied. The significance of the d-SPE cleanup step was investigated by analyzing the acetonitrile extracts of cabbage and *Khat* samples with application of the d-SPE cleanup procedure, utilizing a combination of 6 mg PSA and 12 mg C_{18}. C_{18} is suitable to extract non-polar and medium-polar compounds from the polar samples. PSA has a weak anion exchange function and applies to extract polar compounds from the non-polar samples (Tesfa Bedassa et al., 2015). The experimental results revealed that the use of 6 mg PSA for cabbage and 12 mg of C_{18} for *Khat* removes several co-extracts to the extent that they could not be measured in the extracts. A combination of PSA and C_{18} as clean up was evaluated at 1 mg interval and below the optimum amount the extract is colored (physical observation). It is impossible to inject this colored extract to GC-MS. Therefore, a mixture of 6 mg PSA and 12 mg of C_{18} sorbent were used for clean up in the presence of 45 mg anhydrous $MgSO_4$ to absorb water for both *Khat* and cabbage samples for further experiments.

The effect of the volumes of extracting solvent (acetonitrile) was investigated using different volumes of the extractant, 3-6 mL, with a constant mass of *Khat* samples (Figure 1). Below 3 mL of acetonitrile, the organic layer formed is not sufficient to collect. As can be seen from Figure 1, peak areas of the target analytes decreased as the volume of acetonitrile increased from 3-6 mL. The increase in peak areas with decreasing acetonitrile volume may be attributed to the preconcentration of the target analytes (Melo et al., 2013). But, further reduction of the volume of the acetonitrile below 3 mL was found to be inconvenient since the volume of the extract collected was too small for the subsequent d-SPE clean up procedure. Therefore, 3 mL acetonitrile was chosen as the optimum volume for further studies.

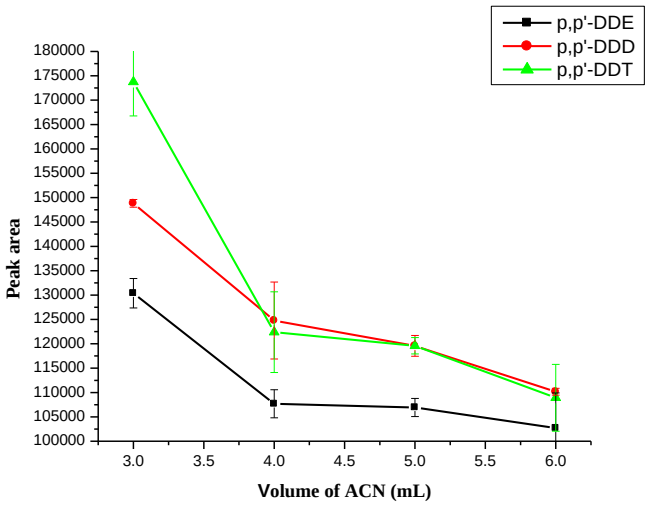

Figure 1: Effect of volume of acetonitrile. Experimental conditions: sample size, 1 g; extraction solvent, acetonitrile; volume of water added, 5 mL; amount of salts added, 2.2 g $(NH_4)_2SO_4$ and 1 g NaCl; spiking level, 0.15 mg/kg for p,p'-DDE, p,p'- DDD and 0.3 mg/kg for p,p'-DDT.

The pH of the solution is also one of the important parameters in this study. The extraction efficiency of a weak organic base or acid depends on the pH value of the sample solution (Razmara et al., 2011). The pH was varied in the range of 5-9 using either 0.1 M HCl or 0.10 M NaOH solution. The experimental results demonstrated that the signals the analytes increased by increasing the pH up to 7 and slightly decreased with further increase in pH. The results are presented in Figure 2. Based on the above results, the pH value of 7 was selected for subsequent studies.

3.2. Analytical method validation

The performance of the proposed QuEChERS extraction technique combined with GC-MS was evaluated utilizing matrix-matched calibration curves in order to compensate for the matrix effects. The coefficients of determinations (R^2) of the calibration curves obtained from the peak areas as the instrumental response versus the analyte concentrations were 0.992 or better indicating a good linearity of the analytical method over the concentration range studied. The limits of detection (LOD) and limits of quantification (LOQ) ranged from $2x10^{-5}$–$6x10^{-5}$ mg/kg and $7x10^{-5}$–$19x10^{-5}$ mg/kg, respectively. The amount of p,p'-DDE, p,p'-DDD and p,p'-DDT in cabbage was found at

concentration level of 0.004, 0.01 and 0.01 mg/kg, respectively. Furthermore, the amount of p,p'-DDE, p,p'-DDD and p,p'-DDT in *Khat* was found to be 0.01, 0.03 and 0.07 mg/kg, respectively. The amount of all compounds was below the maximum residue level set by European Commission for these pesticides (0.2 mg/kg) in both samples (Regulation (EC) No. 398/2005; Regulation (EC) No. 149/2008). The performance characteristics of the proposed method in both samples are given in Table 1.

The precision of the method was also determined by the repeatability (intraday precision) and reproducibility (interday precision) studies of the method and expressed as the relative standard deviation (RSD). Repeatability (at intervals of 4 hours within the same day) and reproducibility (for three consecutive days) of the method was evaluated by spiking blank cabbage and Khat samples with 0.15 mg/kg of p,p'-DDE and p,p'-DDD; and 0.3 mg/kg of p,p'-DDT. Determination of the recoveries of the analytes in both samples were carried out by comparing the concentration obtained by extracting spiked sample at 0.15 mg/kg of p,p'-DDE and p,p'-DDD; and 0.3 mg/kg of p,p'-DDT to the concentration of spiked extract at the same level. The results were given in Table 2. The results of the recovery studies demonstrated that the method has satisfactory recovery, precision and sensitivity for pesticide analysis in the samples under study. The chromatogram of unspiked and spiked cabbage and *Khat* samples are given in Figure 3.

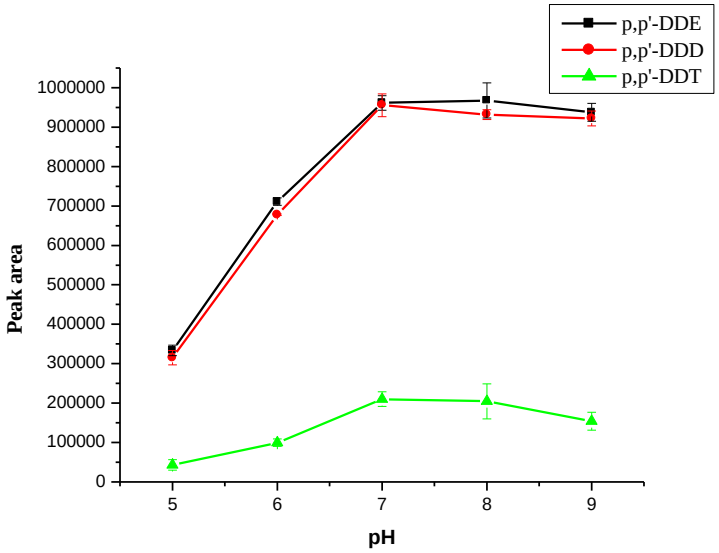

Figure 2: Effect of pH. Experimental conditions: sample size, 1 g; extraction solvent, 3 mL acetonitrile; volume of water added, 5 mL; amount of salts added 2.2 g $(NH_4)_2SO_4$ and 1 g NaCl; spiking level,0.15 mg/kg for p,p'-DDE, p,p'- DDD and 0.3 mg/kg for p,p'-DDT.

Table 1: Statistical and performance characteristics of the proposed method

Analyte	Cabbage			*Khat*		
	Recovery	Repeatability	Reproducibility	Recovery	Repeatability	Reproducibility
p,p'-DDE	99.42	6.63	7.40	72.17	5.74	8.29
p,p'-DDD	107.99	5.88	5.26	82.64	8.58	5.11
p,p'-DDT	97.16	8.22	7.89	90.55	7.35	9.01

Table 2: Recovery (%) and precision (%RSD) of the proposed method for the spiked cabbage and *Khat* samples

Analyte	Linear range (mg/kg)	Cabbage					*Khat*				
		R^2	LOD (10^{-3} mg/kg)	LOQ (10^{-3} mg/kg)	Regression equation	Amount found (mg/kg)	R^2	LOD (10^{-3} mg/kg)	LOQ (10^{-3} mg/kg)	Regression equation	Amount found (mg/kg)
,p'-DDE	0.05–1.60	0.998	0.03	0.09	y = 89849x – 36725	0.004	0.995	0.02	0.07	y = 2e+06x – 11817	0.01
p,p'-DDD	0.05–1.60	0.996	0.04	0.14	y = 61955x – 15518	0.01	0.994	0.03	0.1	y = 2e+06x – 13021	0.03
p,p'-DDT	0.1–3.2	0.993	0.04	0.13	y = 20095x – 7425	0.01	0.992	0.06	0.2	y = 31974x – 49806	0.07

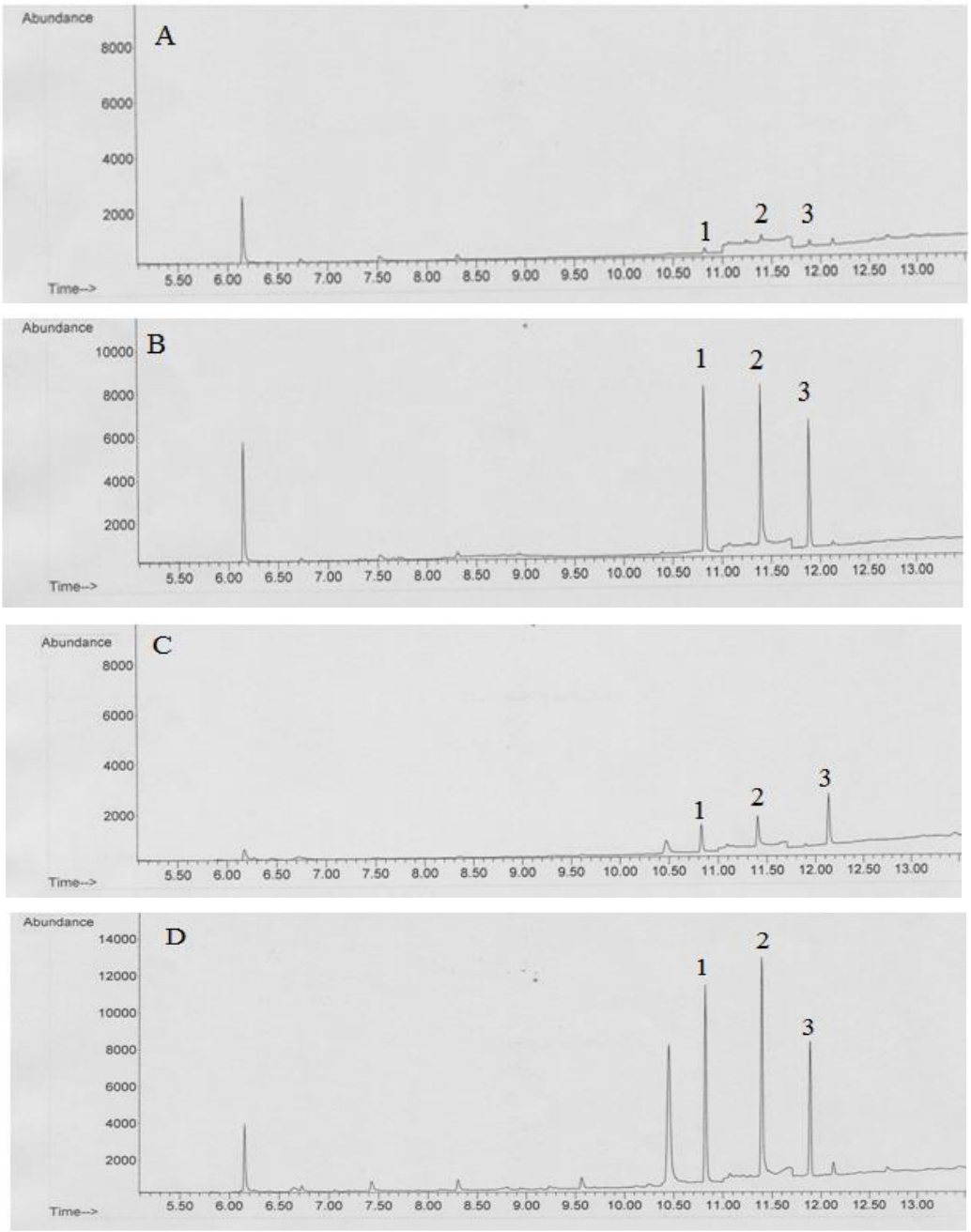

Figure 3: Representative chromatograms for unspiked (A) and spiked (B) cabbage; and unspiked (C) and spiked (D) *Khat* samples; Peaks: 1, p,p'-DDE; 2, p,p'-DDD; 3, p,p'-DDT. Spiking level, 0.15 mg/kg for p,p'-DDE, p,p'-DDD and 0.3 mg/kg for p,p'-DDT.

Table 3: Comparison of the proposed QuEChERS method with other methods

Method	Linear range (mg/L)	LOD	LOQ (mg/kg)	Recovery (%)	Volume of organic solvent (ACN) used for extraction, mL	References
SPE-GC	0.002–0.3	0.002–0.004 mg/L	-	72.4–112.9	-	Zhou et al.; 2013
QuEChERS-GC-MS	0.03–0.36	-	0.02–0.1	80–115	10	Nguyen et al.; 2008
QuEChERS-GC-MS	0.002–1.0	-	0.001–0.13	70–120	10	Cies´lik et al.; 2011
QuEChERS-GC-MS	0.05–3.2	$2x10^{-5}$–$6x10^{-5}$ mg/kg	$7x10^{-5}$–$19x10^{-5}$	72.1–107.99	3	This study

3.3. Comparison of the proposed method with other reported methods

Table 3 shows comparison of the proposed QuEChERS method with other methods reported so far. The values in the table indicate that the method proposed by our group uses smaller volume of acetonitrile for extraction than the other methods indicating its less deleterious effect on the analyst as well as the environment. The values in Table 3 also show that the proposed method has comparable LOD, LOQ and recovery with other reported methods. Thus, the proposed method can be used for efficient and selective extraction of the selected pesticides in cabbage and *Khat* sample matrices.

4. Conclusion

Sample preparation is always the major bottleneck in any analytical procedure for the determination of pesticide residues in food products. The QuEChERS multiresidue procedure simplifies and reduces the time taken to complete the extraction and clean-up processes. Analytical methods based on a fast GC-MS methodology were developed and validated for determination of DDT and its metabolites in cabbage and *Khat* samples using QuEChERS sample preparation method. The method provided wide linear range, good reproducibility and repeatability over the studied concentration ranges for both cabbage and *Khat* samples. The method also offered low LOD and LOQ for all pesticides under study which demonstrate its usefulness for the determination of the analytes in the samples. The developed method was successfully applied to cabbage and *Khat* samples. The results obtained indicates that the cabbage sample was found to contain p,p'-DDE, p,p'-DDD and p,p'-DDT at concentration level of 0.004, 0.01 and 0.01 mg/kg, respectively. The p,p'-DDE, p,p'-DDD and p,p'-DDT were also found in *Khat* sample at concentration level of 0.01, 0.03 and 0.07 mg/kg, respectively. The amounts of pesticides detected in both cabbage and *Khat* samples were below the EU maximum residue limits. Even though the use of DDT was banned in Ethiopia for agriculture purposes, detectable levels are still being observed. The results of the study necessitate the need for awareness creation of the community and continuous monitoring of such pesticides residues in cabbage and *Khat* samples.

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