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Assessment of Pesticide Residues in Some Fruits Using Gas Chromatography Coupled with Micro Electron Capture Detector

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Abstract

A very sensitive analytical method for the determination of 26 pesticides in some fruits based on solid phase extraction (SPE) cleanup was developed using gas chromatography (GC) coupled with micro electron capture detector (μECD). The identity of the pesticides was confirmed by gas chromatography mass spectroscopy (GC-MS) using selected ion monitoring (SIM) mode. Ethyl acetate was used as a solvent for the extraction of pesticide residues with assistance of sonication. For cleanup an octadecyl, C18 SPE column was used. A linear response of μECD was observed for all pesticides with good correlation coefficients (>0.9992). Proposed method was successfully applied for the determination of pesticide residues in the orange, apple, and grape fruits. Average recoveries achieved for all of the pesticides at fortification levels of 0.05, 1.0 and 2.0 μg g^{-1} in analyzed fruits were above 90% with relative standard deviations (RSD) less than 6%.

Keywords: Fruits; pesticide residues; solid-phase extraction; GC-μECD.

Introduction

Variety of pesticides is used in current agricultural practice to manage pests and infections that spoil crops. Pesticides help to increase both yield and quality of fruits [1, 2]. The application of these chemicals to handle pests is being adept in Pakistan since centuries; but, agrochemicals have acquired in 1954 with 254 metric tons of formulation [3]. The residues resulting from the inappropriate use of pesticides on fruits and vegetables is a most important concern in many countries as well as in Pakistan. Agriculture is the main support of Pakistan's economy. In a country like Pakistan, the application of pesticides has become inevitable to uphold and improve existing stage of harvest production by shielding the crop from pests. The climate of Pakistan as being a sub-tropical countryside, observes varying temperatures and humidity profile throughout the year, which brings a vast array of pests to be tackled. A number of pests are found to assault multiple objects (various crops) and have been attained resistance from prolong application of common pesticides. Presently, it is estimated that almost 45% of the world's crop has been destroyed by plant pests and diseases. Therefore, to meet the demand, it is essential to apply the pesticides to protect the crops, both during development and their consequent storage and transportation. Probably 2.5 million tons of pesticides are being applied globally each year and keep on rising with the passage of time [4, 5]. On the other hand, due to their persistency in the environment, the majority of these pesticides are no longer permissible to be use in many countries including Pakistan, but some developing countries still allow their use in agriculture and public health. Besides their positive effect, pesticides pose health-risk to consumers when retained in residue form in fruits [6]. Pesticide residues maybe found in processed products such as fruit juices, which are widely

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consumed as soft drinks, predominantly by children. Therefore, pesticides should be controlled at optimum level due to their high toxicity to the environment and human health [7]. Hence, international organizations and governments have launched maximum residue levels (MRLs), to control the quantity of pesticide residues in foodstuffs. MRL for residues of pesticide represents the maximum concentration of that residue (expressed in mg/kg) that is legally permitted in an appropriate food item. The founding of MRL is based on excellent non violating agricultural practice data on food derived from commodities [8].

There are several methods used to extract and clean-up pesticides, e.g. ultrasonication, soxhlet, pressurized liquid extraction, supercritical fluid extraction etc. Clean-up methods contain SPE, column chromatography, liquid-liquid partition. Methods which are mainly utilized to find out pesticide in fruits rooted in liquid-liquid partitioning by means of organic solvents such as dichloromethane and ethyl acetate [9, 10]. Technique which are commonly used for the investigation of pesticide residues inside fruits is gas chromatography with the variety of choosy detectors for instance flame photometric (FPD) [11], pulsed flame photometric detector (PFPD) [12], nitrogen phosphorus detector (NPD) [13], and electron capture detectors (ECD) [14, 15]. Many methods are reported in the literature in which gas chromatography coupled with mass spectrometric detectors (GC-MSD) employed [16, 17], because of the confirmation of pesticides distinctiveness in samples.

The main aim of the present work was to develop a very simple and effective method for the assessment of 26 pesticide residues in some fruits using gas chromatography coupled with micro-electron capture detector (GC-μECD), and its validation by applying for the monitoring of pesticide residues in some real fruit samples sold in the local fruit markets of Hyderabad region, Pakistan.

Material and Methods

Reagents

Reference standards of pesticides (99.9% purity) were bought from Sigma-Aldrich (Seelze, Germany). Methanol, acetonitrile, ethyl acetate, hexane and anhydrous sodium sulfate were purchased from Scharlau (Barcelona, Spain). Individual pesticide stock solutions (500 μg ml^{-1}) were prepared in ethyl acetate and kept in cold storage. A mixture of stock solution holds all of the pesticides at 5 μg ml^{-1} were prepared. From each stock solution 1 ml was transferred to a volumetric flask of 100 ml capacity and diluted to the mark by ethyl acetate. To acquire linear response of the detector and for the fortification of samples, standard working solutions of different concentrations were prepared with appropriate dilutions by ethyl acetate and then stored at 4 °C.

Instruments

Agilent (CA, USA) model 7890 A GC system coupled with micro Electron Capture Detector (μECD), with automatic split–splitless injector model Agilent 7683 B and 7683 Agilent autosampler was employed for the determination of pesticides. A HP-5 capillary column (30 m × 0.32 mm × i.d., 0.25μm film thickness), supplied by Agilent Technologies, was engaged.

GC-MS confirmation was carried out with an Agilent Technologies 6890N network GC system equipped with a 5975 inert MSD run in Electron Impact ionization mode (EI), and Agilent 7683 automatic split-splitless injector. HP-5MS capillary column (30 m × 0.25 mm × i.d., 0.25μm film width) provided by Agilent Technologies, was engaged. The carrier gas used was helium with (99.9993%) purity. A rotary evaporator model R-210 Büchi, (Flawil, Switzerland) and an ultrasonic bath Raypa, (Barcelona, Spain) were used for solvent evaporation and sonication, respectively.

Instrumental conditions

The operating conditions for GC-μECD were as described: The temperature of injection port was 250 °C, injection volume 2μl in split ratio 50:1 and split flow 60 ml/min. The detector temperature was 310 °C. Column temperature was programmed as, the first temperature 70 °C for 0 min, after that increased at a rate of 30 °C/min to 210 °C and seized for 2 min, then from 210 °C to 250 °C at a rate of 25 °C/min with held for 2 min, then increased upto to 290 °C with the rate of 30

°C/min and finally held for 5 min. The carrier gas, Nitrogen (purity 99.99%) at a flow rate of 1.2 ml/min was used. The whole analysis time was less than 17 min, and the time for the equilibration of the system was 0.5 min.

For GC-MS confirmation the working conditions were as: The temperature for injector port was 250 °C, volume of injection was 2µl in splitless manner, helium (99.99%) used as carrier gas at 1.2 ml/min flow rate. For column the temperature program was the same as in GC-µECD. The MSD was run in electron impact ionization manner (I.E = 70 eV) scanning as from *m*/*z* 50 to 550 at 4.4 scan/s. Temperatures of ionization source and quadrupole were adjusted at 230 °C and 150 °C, respectively.

Fruit samples

Fruit samples such as orange, apple and grape were purchased from the local fruit markets of Hyderabad region, situated in the province of Sindh, Pakistan. Samples were investigated following the method described underneath and those samples with concentrations of pesticides below the detection limits were used as blank fruit samples for recovery study.

Extraction procedure

Whole, unwashed fruit samples were chopped and homogenized. An aliquot from each sample (10 g) was weighed and extracted two times by means of 20 ml ethyl acetate. For recovery studies, samples were fortified with different concentrations of prepared pesticide standards. Extracts were kept in a sonicator for 2 min at 40 ± 2 °C. After sonication, the extracts filtered through a filter paper by means of suction pump. Residues were washed with ethyl acetate (10 ml) and extracts were shifted to the separatory funnel. The aqueous part of the combined extracts was thrown away while organic part was passed all the way through anhydrous sodium sulfate and vanished to dryness in a vacuum rotary evaporator. Residues were dissolved in ethyl acetate (5 ml) and cleaned-up on solid phase extraction column containing 1 g of C_{18} preconditioned by means of acetonitrile (3 ml) and water (5 ml). The extracted residues were shifted to the column and eluted two times with 5 ml of ethyl acetate-hexane (1:1, v/v). The eluate shifted to a tube where it gets concentrated under a gentle flow of nitrogen to a suitable quantity. An aliquot of the final extract was examined by GC-µECD.

Results and discussion

Gas chromatographic determination

To overcome the matrix effect and to get improvement of the chromatographic response, blank samples of fruits were spiked with the pesticides of known concentration. As shown in (Fig. 1a) chromatogram of a blank fruit sample extract, and (Fig. 1b) a blank sample spiked with the mixture of pesticide standards at concentration 1 µg g^{-1}. The figure shows that blank fruit sample chromatogram showing lack of interferences at the retention time of the targeted pesticides. So, the quantification has been conceded by preparing standards with blank fruit samples. According to previous workings, separation of these pesticides usually takes about 50–60 min. In order to get shorten analysis time with best separation and resolution of chromatogram, optimization of appropriate temperature programming was made. To get the absolute separation and best resolution of peaks, a multistep temperature program was found to be more suitable. All of the targeted pesticides get monitored in less than 17 min. It indicates a 4-fold gain in investigation time saved compared to usual GC schemes. (Fig. 2) shows the representative chromatogram of standards mixture with good separation and resolution.

Optimization of extraction procedure

Solvents used in many pesticide residues determination methods for the extraction purpose in fruits were usually acetone, dichloromethane, acetonitrile and ethyl acetate. For best possible extraction, solvents like acetone, dichloromethane, and ethyl acetate used individually and in combination with different ratios to extract the targeted analytes. The result shows that ethyl acetate gave superior results in comparison to the other solvents. Therefore, ethyl acetate was selected for the extraction of samples for residue determination. In addition to the solvent selection, the effect of sonication was also studied in the optimization process of the extraction method.

Pesticide recoveries ranged from 70% to 80% without sonication, but extraction assisted with sonication gave enhancement in recoveries as shown in (Fig. 3), particularly in orange as compare to the apple and grape, which may be as a consequence of the thinner nature of apple and grape sample matrices. Hence, the extraction of pesticides from samples in the proposed method was carried out assisted by sonication.

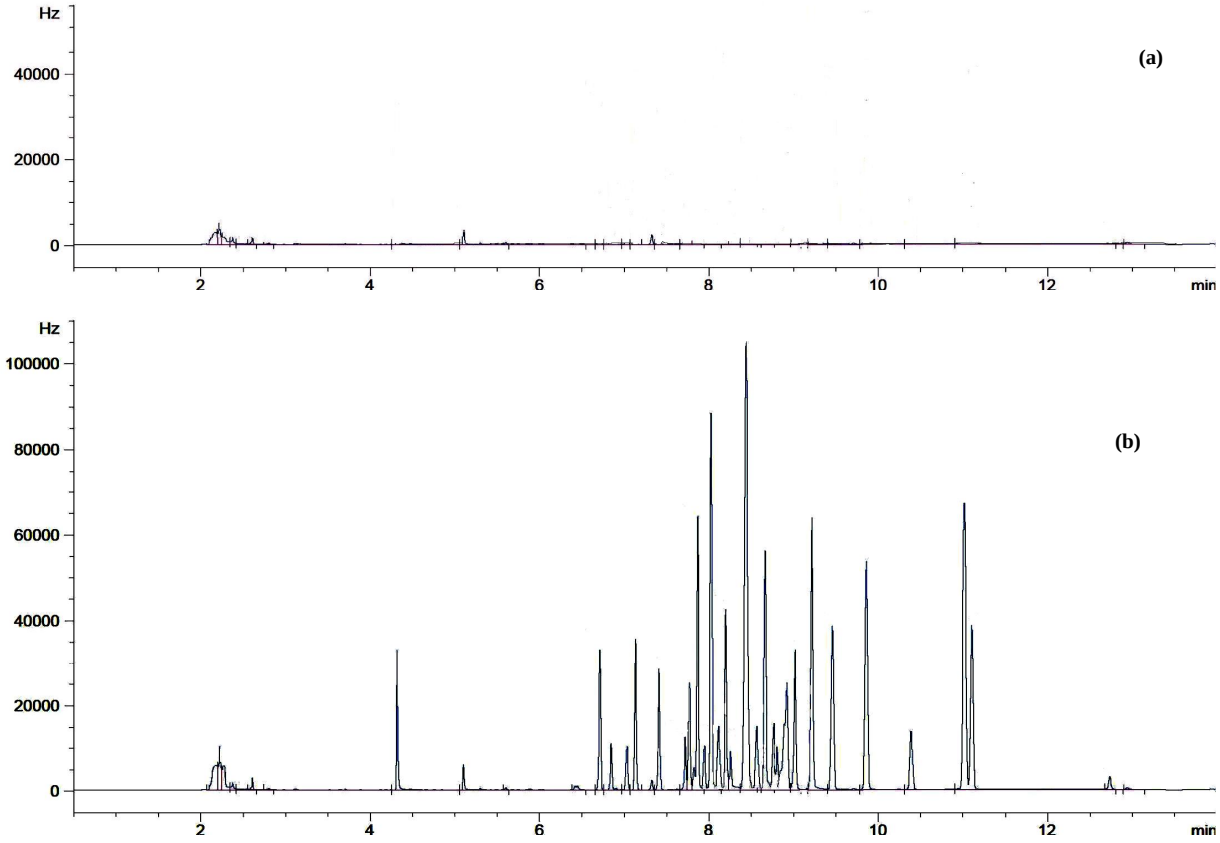

Figure 1. **(a) GC-µECD chromatogram of the blank sample extract.**
(b) GC-µECD chromatogram of standard mixture in blank spiked sample of the same concentration in ethyl acetate (1 µg g^{-1}).

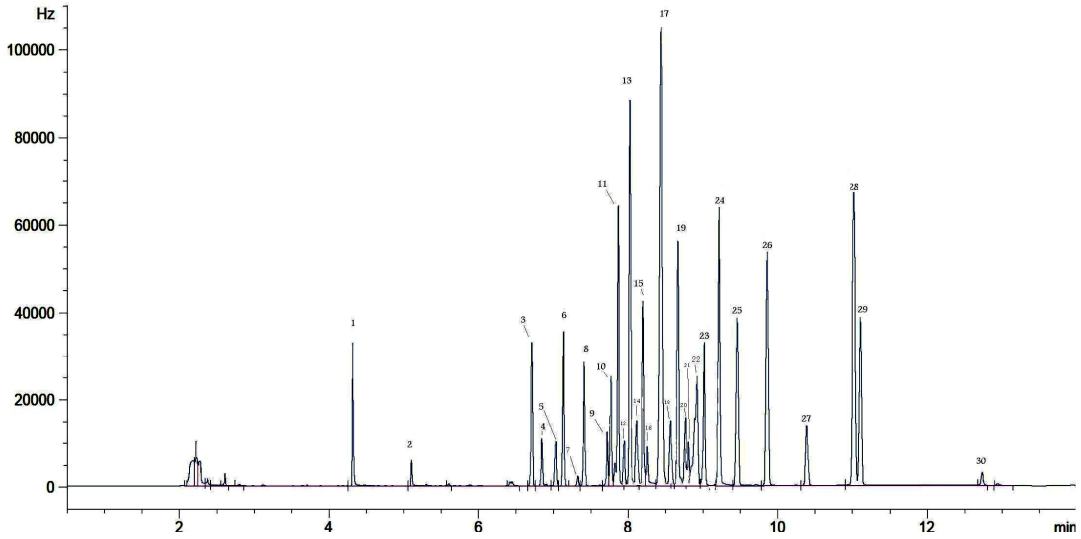

Figure 2. **GC-µECD chromatogram of a standard mixture. Peak numbers are named in the order of increasing t_R in Table 1.**

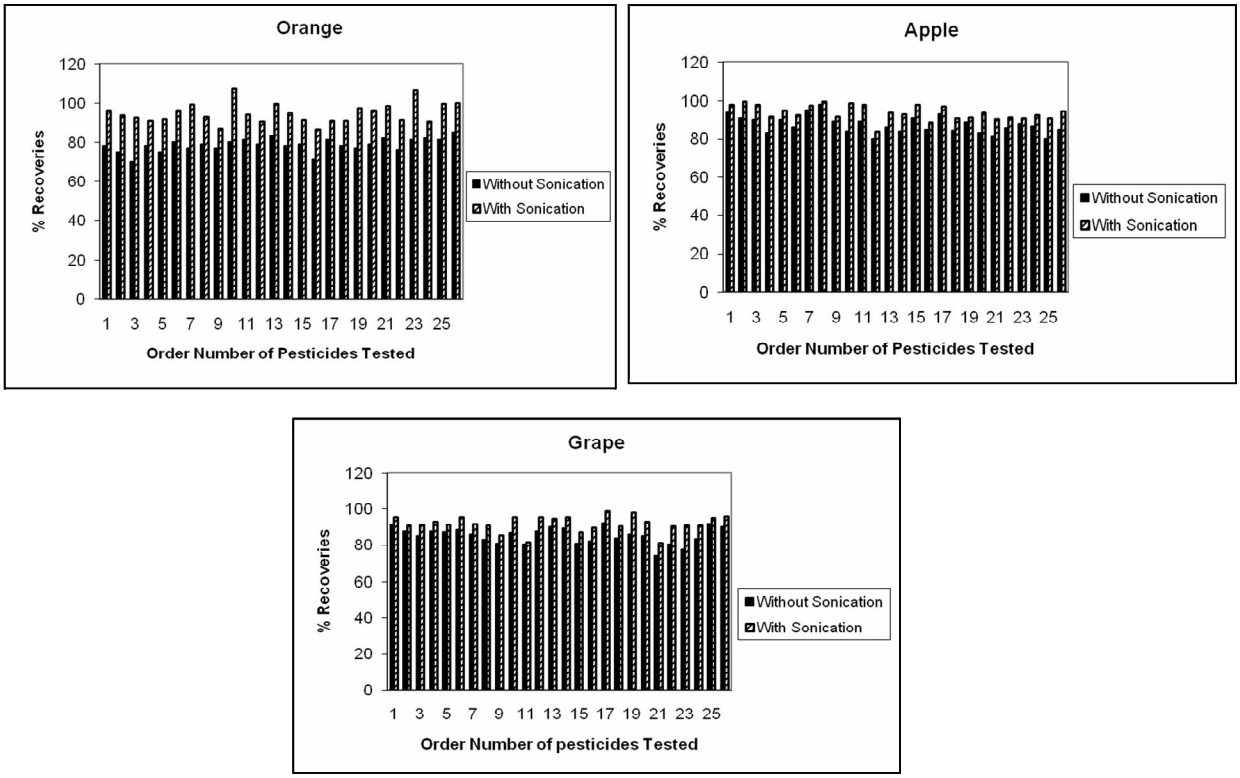

Figure 3. **Effect of sonication on pesticide recovery in the extraction procedure samples were fortified at 1.0 µg g^{-1}.**

Method Validation

Linearity

Those samples which were initially analyzed with pesticide concentrations below detection limits were fortified at different concentration levels 50, 100, 500, 2000 and 5000 µg kg^{-1} for the determination of linearity of the proposed method. The response given by the detector was tremendous and linear in the series of concentrations studied with excellent values of determination coefficient (>0.9992) for each of the pesticide. Summarized data of calibration and validation for the pesticides studied shown in Table 1.

Repeatability

To inspect the repeatability, a blank sample fortified at 10 µg g^{-1} has performed. The sample inserted 10 times by means of an auto injector. Result shows a fine repeatability attained in the term of relative standard deviation (RSDs) have achieved for peak areas and retention times with values < 4% and 0.05, respectively as shown in (Table 1).

Recovery

Those samples which were initially analyzed to make sure the nonexistence of pesticides studied were fortified at 0.05, 1.0 and 2.0 µg g^{-1} earlier than extraction and analyzed for recovery study of the proposed method by GC-µECD. The average recoveries achieved are exposed in (Table 2). The recoveries gained for all pesticides ranged as of 90 to 107.5% with RSDs of <6%.

Detection and quantification limits

Blank samples were used for the determination of detection and quantification limits of each pesticide. By taking into consideration a value 3 times of the background noise attained for blank samples limit of detection (LOD) of the proposed method has been determined, and the LOQs were established considering a value 10 times the background noise. A summarized data for LODs and LOQs obtained for the individual pesticides in the different samples are shown in (Table 3).

Table 1. **Retention times (t_R), calibration data, and repeatability of the pesticides analyzed by GC-μECD.**

#	Pesticide	t_R, min	Calibration Data		Repeatability[a] (RSD, %)	
			Equation	R^2	t_R	peak area
01	Dichlorvos	4.29	y = 9.5753x + 1.6977	0.9998	0.02	1.4
02	Phosdrin	5.08	$y = 6.1418x + 5\times10^{-3}$	0.9995	0.03	1.5
03	α -HCH	6.68	y = 5.075x + 2.5952	0.9997	0.04	1.8
04	Dimethoate	6.82	y = 11.388x + 1.682	0.9994	0.01	1.2
05	β-HCH	7.00	y = 1.5534x + 1.1034	0.9998	0.02	2.8
06	γ -HCH	7.10	y = 5.1582x + 3.3399	0.99	0.01	2.2
07	Disulfoton	7.30	$y = 4.3971x + 4\times10^{-4}$	0.99	0.01	1.9
08	δ -HCH	7.38	y = 4.2158x + 2.7238	0.9996	0.02	2.7
09	Chlorpyrifos Methyl	7.65	y = 14.759x + 4.8829	0.9999	0.03	2.3
10	Propanil	7.69	y = 10.92x + 2.4567	0.9998	0.03	1.4
11	Metribuzin	7.74	y = 6.7901x + 2.8332	0.9993	0.02	2.5
12	Parathion Methyl	7.85	y = 13.005x + 2.8897	0.9994	0.01	2.3
13	Heptachlor	7.99	y = 16.436x + 9.1816	0.999	0.03	3.1
14	Bromacil	8.18	y = 15.081x + 4.8706	0.9999	0.02	2.3
15	Malathion	8.24	y = 10.136x + 1.5545	0.9997	0.04	1.2
16	Parathion	8.39	y = 6.1765x + 4.3059	0.9997	0.01	3.5
17	Aldrin	8.40	y = 15.002x + 11.291	0.9997	0.01	1.6
18	Chlorpyrifos	8.41	y = 9.4448x + 2.3975	0.9998	0.04	1.4
19	Triademofen	8.44	y = 8.8255x + 7.165	0.9998	0.02	2.7
20	Bromophos Methyl	8.65	y = 16.011x + 4.3919	0.9998	0.04	1.8
21	Allethrin	8.86	y = 13.786x + 5.9197	0.9996	0.02	1.0
22	Tolyfluanid	8.89	y = 16.603x + 9.4754	0.9999	0.03	3.0
23	Captan	8.98	y = 8.4931x + 4.1676	0.9997	0.02	3.1
24	Bromophos Ethyl	9.19	y = 16.509x + 6.0949	0.9998	0.01	2.2
25	α-Endosulfan	9.44	y = 10.839x + 6.6558	0.9995	0.03	2.3
26	Dieldrin	9.83	$y = 2.6265x - 6\times10^{-4}$	0.9997	0.02	1.7
27	β -Endosulfan	10.37	y = 4.5629x + 3.1647	0.9996	0.02	2.9
28	DDT	11.00	y = 15.357x + 7.3635	0.9997	0.02	1.8
29	Endosulfan sulfate	11.01	y = 14.443x + 7.7363	0.9998	0.01	3.7
30	Dialifos	12.73	$y = 5.5514x + 4\times10^{-4}$	0.9994	0.03	1.3

Table 2. **Recovery of pesticides from spiked samples.**

Pesticide	Fortification level (µg g^{-1})	Mean recovery ± RSD[b] (%)[a]		
		Orange	Apple	Grape
Aldrin	0.05	100.2 ± 4.0	92.7 ± 4.9	90.1 ± 3.2
	1.0	96.1 ± 5.2	97.6 ± 2.7	95.3 ± 2.9
	2.0	90.3 ± 3.9	90.4 ± 4.3	89.1 ± 1.7
Allethrin	0.05	96.2 ± 2.0	90.7 ± 3.9	91.6 ± 1.2
	1.0	93.1 ± 4.2	99.3 ± 1.7	90.6 ± 2.4
	2.0	91.3 ± 1.9	88.4 ± 2.3	89.1 ± 2.8
Bromacil	0.05	90.9 ± 3.0	100.7 ± 2.9	98.1 ± 3.7
	1.0	92.1 ± 1.2	97.8 ± 3.7	91.2 ± 2.3
	2.0	98.3 ± 2.0	95.4 ± 1.9	89.9 ± 2.7
Bromophos Methyl	0.05	87.2 ± 4.9	90.4 ± 4.9	88.9 ± 2.6
	1.0	90.7 ± 2.8	91.4 ± 1.9	92.7 ± 2.2
	2.0	92.6 ± 1.9	93.7 ± 1.7	89.8 ± 1.9
Bromophos Ethyl	0.05	98.9 ± 1.1	97.3 ± 2.4	88.1 ± 2.0
	1.0	91.2 ± 3.9	94.8 ± 1.3	91.2 ± 3.3
	2.0	93.8 ± 2.5	89.8 ± 2.4	89.3 ± 3.1
Captan	0.05	85.2 ± 2.5	88.4 ± 3.4	97.9 ± 2.8
	1.0	96.1 ± 2.2	92.3 ± 1.2	95.4 ± 3.9
	2.0	94.8 ± 2.9	96.9 ± 3.3	99.1 ±2.6
Chlorpyrifos	0.05	94.8 ± 2.3	104.0 ± 2.7	97.8 ± 3.6
	1.0	99.0 ± 1.7	97.3 ± 1.7	91.4 ± 4.3
	2.0	92.3 ± 0.9	96.2 ± 2.3	98.6± 3.9
Chlorpyrifos Methyl	0.05	90.4 ± 4.3	90.3 ± 3.9	92.1 ± 1.7
	1.0	92.6 ± 4.5	99.4 ± 3.8	90.7 ± 3.0
	2.0	93.8 ± 3.7	93.5 ± 3.6	97.3 ± 2.9
Dialifos	0.05	94.1 ± 3.8	92.5 ± 489	79.9 ± 4.2
	1.0	86.5 ± 4.5	91.6 ± 1.7	85.3 ± 2.9
	2.0	87.4 ± 3.6	92.4 ± 3.3	89.1 ± 3.7
Dichlorvos	0.05	115.0 ± 3.9	93.0 ± 3.1	94.8 ± 3.2
	1.0	107.5 ± 3.0	98.6 ± 4.1	95.3 ± 1.9
	2.0	93.8 ± 3.7	94.4 ± 4.0	90.1 ± 2.7
Dieldrin	0.05	107.5 ± 3.0	90.7 ± 3.9	84.5 ± 3.9
	1.0	93.8 ± 3.7	97.6 ± 1.7	81.4 ± 3.7
	2.0	93.0± 3.1	95.2 ± 3.3	80.8 ± 3.0
Dimethoate	0.05	90.4 ± 4.3	91.6 ± 1.5	86.3 ± 3.9
	1.0	90.0 ± 5.2	83.9 ± 3.9	95.2 ± 5.2
	2.0	92.6 ± 4.5	86.3 ± 3.9	91.7 ± 4.6
Disulfoton	0.05	93.4 ± 2.5	83.4 ± 1.5	84.1 ± 1.9
	1.0	99.5 ± 4.9	93.4 ± 2.4	94.4 ± 4.6
	2.0	97.5 ± 4.8	90.6 ± 4.8	81.5 ± 2.4

Endosulfan (α - β)	0.05	90.9 ± 2.0	82.7 ± 4.0	90.1 ± 3.2
	1.0	94.9 ± 3.2	92.8 ± 2.5	95.3 ± 2.9
	2.0	89.8 ± 1.9	97.9 ± 2.3	89.1 ± 1.7
Endosulfan sulfate	0.05	98.9 ± 3.0	94.1 ± 1.9	93.1 ± 4.2
	1.0	90.9 ± 12	97.8 ± 4.7	96.6 ± 3.7
	2.0	92.7 ± 2.4	97.3 ± 1.3	99.7 ± 2.1
HCH Isomers (α – β – γ – δ)	0.05	98.6 ± 2.1	93.4 ± 2.1	95.8 ± 3.4
	1.0	96.1 ± 1.2	98.6 ± 1.5	99.3 ± 2.0
	2.0	93.1 ± 4.4	92.4 ± 3.8	90.6 ± 3.7
Heptachlor	0.05	91.4 ± 3.3	107.5 ± 3.0	101.1 ± 3.2
	1.0	90.7 ± 2.2	97.0 ± 3.7	98.6 ± 2.3
	2.0	98.5 ± 1.9	100.4 ± 4.0	93.1 ± 3.7
Malathion	0.05	96.7 ± 3.2	98.7 ± 2.9	92.7 ± 1.2
	1.0	90.7 ± 1.8	90.6 ± 4.4	90.2 ± 3.6
	2.0	96.9 ± 1.0	94.9 ± 1.3	97.5 ± 2.6
Metribuzin	0.05	103.9 ± 2.1	97.7 ± 2.0	98.3 ± 1.2
	1.0	96.9 ± 3.0	91.2 ± 4.0	97.7 ± 3.4
	2.0	93.9 ± 1.0	96.7 ± 1.3	94.1 ± 2.7
Parathion Methyl	0.05	90.1 ± 3.6	90.1 ± 3.9	97.9 ± 1.9
	1.0	95.9 ± 1.5	93.7 ± 1.6	92.7 ± 4.1
	2.0	99.8 ± 3.7	98.9 ± 3.0	99.6 ± 2.1
Parathion	0.05	105.7 ± 2.8	82.5 ± 3.0	93.0± 3.1
	1.0	98.2 ± 4.1	90.1 ± 3.8	80.7 ± 4.9
	2.0	90.5 ± 1.8	89.7 ± 1.7	88.5 ± 2.6
Propanil	0.05	94.8 ± 2.1	92.5 ± 1.6	90.5 ± 2.0
	1.0	90.8 ± 3.1	90.9 ± 1.9	90.3 ± 1.9
	2.0	98.5 ± 2.1	97.3 ± 2.8	99.2 ± 4.1
Tolyfluanid	0.05	90.4 ± 2.8	93.7 ± 3.9	98.3 ± 4.2
	1.0	106.9 ± 2.9	90.7 ± 2.3	90.8 ± 1.0
	2.0	94.1 ± 1.6	92.7 ± 1.3	95.7 ± 2.6
Triademofen	0.05	90.3 ± 3.9	90.5 ± 3.5	99.3 ± 1.3
	1.0	90.1 ± 2.2	92.4 ± 1.9	90.6 ± 1.3
	2.0	97.2 ± 4.0	97.8 ± 2.1	92.0 ± 2.5
DDT	0.05	107.3 ± 1.2	96.5 ± 3.2	92.8 ± 2.0
	1.0	99.3 ± 1.0	90.4 ± 1.4	95.0 ± 3.0
	2.0	97.5 ± 3.7	90.7 ± 2.1	97.3 ± 4.8
Phosdrin	0.05	90.9 ± 3.1	90.3 ± 1.4	90.7 ± 4.9
	1.0	99.9 ± 4.8	94.6 ± 1.8	95.6 ± 3.9
	2.0	104.9 ± 1.5	98.0 ± 3.0	94.3 ± 3.0

[a]n = 5.
[b]Relative standard deviation.

Table 3. **Limits of detection (LOD, µg kg^{-1}) and limits of quantification (LOQ µg kg^{-1}) of pesticides assayed by GC-µECD.**

Pesticide	Limits of detection (LOD, µg kg^{-1})			Limits of quantification (LOQ, µg kg^{-1})		
	Oranges	*Apple*	*Grapes*	*Oranges*	*Apple*	*Grapes*
Aldrin	0.3	0.3	0.3	1.0	1.1	1.0
Allethrin	0.5	0.4	0.6	1.7	1.7	1.8
Bromacil	0.5	0.5	0.4	1.9	1.7	1.9
Bromophos Methyl	0.6	0.6	0.6	2.0	2.1	1.9
Bromophos Ethyl	0.6	0.5	0.4	2.2	1.8	2.0
Captan	0.6	0.4	0.6	2.1	2.0	2.1
Chlorpyrifos	1.8	2.1	2.0	6.2	6.0	6.1
Chlorpyrifos Methyl	0.6	0.5	0.6	2.3	2.2	2.0
Dialifos	7.9	7.5	7.0	26.3	26.0	26.3
Dichlorvos	1.5	1.5	1.4	5.0	4.9	5.1
Dieldrin	19.3	19.3	191	64.4	64.0	64.4
Dimethoate	1.7	1.7	1.7	5.9	5.8	5.9
Disulfoton	12.8	12.7	12.4	42.7	42.8	42.1
Endosulfan (α - β)	0.4 0.7	0.3 0.8	0.4 0.9	1.4 2.4	1.1 2.0	1.5 2.4
Endosulfan sulfate	0.3	0.4	0.3	1.0	1.2	1.0
HCH Isomers (α – β – γ – δ)	0.9 2.5 1.2 1.0	1.1 2.3 1.2 1.1	0.9 2.4 1.2 1.0	3.2 8.5 4.1 3.3	3.0 8.1 4.2 3.2	3.0 8.3 4.0 3.3
Heptachlor	0.2	0.2	0.2	0.8	0.8	0.8
Malathion	1.7	1.7	1.9	5.9	6.0	5.8
Metribuzin	0.8	0.6	0.7	2.7	2.9	2.9
Parathion Methyl	0.8	1.0	0.8	2.8	3.0	2.7
Parathion	0.7	0.8	0.7	2.6	2.4	2.5
Propanil	1.9	1.4	1.7	6.5	6.9	6.5
Tolyfluanid	0.2	0.5	0.2	0.8	0.7	0.8
Triademofen	7.4	7.0	7.1	24.8	20.1	24.5
DDT	3.7	4.0	3.9	12.6	13.0	12.6
Phosdrin	42.4	42.9	42.8	141.2	140.1	141.0

Confirmation by GC-MS

Identity of the targeted pesticides was verified by GC-MS by means of SIM mode. A solution of standard mixture was previously run to obtain a total ion chromatogram for the determination of their main ions and retention times. In (Table 4) retention times and main ions for the pesticide studied are shown. All of these pesticides can easily be identified by their main ions by searching in the MS PEST library.

Evaluation of method

Proposed method applied to the real fruit samples to determine pesticide residue levels, purchased from local markets. Pesticide levels encountered in the collected samples (apple, grape, and orange), their ranges, frequencies and averages all are summarized in (Table 5).

Table 4. **Selected ions from MS of the studied pesticides.**

Pesticide	**t_R, min**	**MS**
		Selected ions (m/z)
Aldrin	8.40	293, 263, 221
Allethrin	8.86	91,123, 136
Bromacil	8.18	207, 205, 231
Bromophos Methyl	8.65	331, 125
Bromophos Ethyl	9.19	303, 359, 331
Captan	8.98	79, 264, 299
Chlorpyrifos	8.41	197, 199, 258, 314
Chlorpyrifos Methyl	7.65	208, 288, 286
Dialifos	12.73	76, 181, 357
Dichlorvos	4.29	145, 141
Dieldrin	9.83	277, 345
Dimethoate	6.82	199, 230
Disulfoton	7.30	109, 157
Endosulfan (α - β)	9.44	195, 241, 339
	10.37	195, 241, 339
Endosulfan sulfate	11.01	272, 387, 420
HCH Isomers (α – β – γ – δ)	6.68	111,181, 219
	7.00	111,181, 219
	7.10	111,181, 219
	7.38	111,181, 219
Heptachlor	7.99	100, 272
Malathion	8.24	127, 158, 173
Metribuzin	7.74	198, 144, 182
Parathion Methyl	7.85	109, 263, 125
Parathion	8.39	125, 291
Propanil	7.69	161, 217
Tolyfluanid	8.89	137, 238, 106, 63
Triademofen	8.44	208, 128, 181
DDT	11.00	165, 235, 237
Phosdrin	5.08	109, 127, 192

Table 5. **Summarized results of pesticide residues found in monitoring study of fruits.**

Fruits	No. of samples collect	Contaminated	Violating MRL	Pesticides found	Frequency	Range (min:max) (µg kg^{-1})	Average (µg kg^{-1})
Apple	20	08	03	Dieldrin	03	05-196	100.5
				Disulfoton	04	98-298	198
				Endosulfan sulfate	03	43-110	76.5
				Parathion	05	256-681	468.5
				Chlorpyrifos	07	278-530	404
Orange	18	05	02	Dieldrin	02	90-187	138.5
				Disulfoton	02	08-280	179
				Endosulfan sulfate	02	2.8-10	6.4
				Parathion	03	340-149	244.5
				Triadimefon	03	14-710	362
				Chlorpyrifos	04	280-570	425
Grape	15	04	01	Disulfoton	03	45-280	162.5
				Endosulfan sulfate	01	0.9	0.9
				Parathion	02	59-150	104.5
				Chlorpyrifos	04	60-680	370

Conclusions

A simple, effective and quick method based on determination of 26 pesticides in fruits using GC-µECD with extraction assisted by sonication and SPE clean-up has been developed. The confirmations of these pesticides have been performed by GC-MS with SIM mode. With the proposed method requirement of organic solvents for the extraction procedure reduced as the sonication endow with improved extraction, which could be very obliging into reducing the danger for human health and the environment with short time consuming as well. The good reproducibility, accuracy and low detection and quantification limits of the proposed method allow its application for the accurate determination of pesticide residues in fruits. Investigation of real fruit samples illustrated the validity of method used, which permitted the determination and recognition of pesticides present in the samples.

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