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Multicomponent Determination of Pesticides in Mineral Water by Gas Chromatography-Mass Spectrometry

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Analytical procedures were developed for the identification and quantification of pesticides in natural and fruit flavoured mineral waters. The concentrations of pesticides in mineral waters are expected to be at below the ng/L level, which requires preconcentration of analytes and improved detection limits. Solid phase extraction and liquid-liquid extraction procedures were developed for preconcentration and detection was performed with large-volume injection gas chromatography-mass spectrometry by means of a programmable temperature vapourizer. The selectivity of the detection procedure was increased by using selective ion monitoring mode. Validation parameters such as linearity, linear range, accuracy, detection and quantification limits were evaluated. The mean percentage recoveries of pesticides by liquid-liquid extraction ranged from 72 ± 1 (aldrin) to 101 ± 3 % (4,4-DDT). The values using solid phase extraction procedure varied between 74 ± 1 (atrazine) and 102 ± 3 % (α endosulfan). The limits of detection for the pesticides ranged from 15 to 100 ng/L. The concentrations of pesticides ranged from 71 to 530 ng/L in samples extracted with solid phase extraction and from 66 to 1092 ng/L in samples extracted with liquid-liquid extraction procedure. Malathion was only determined in cherry aroma 1 at concentration of 385 ± 1 ng/L. Aldrin was only determined in cherry aroma 1, chlorpyrifos in mineral water 1 and bromopropylate in apple aroma at concentrations of 1092 ± 103 ng/L, 423 ± 7 ng/L and 638 ± 5 ng/L after liquid-liquid extraction.

Key Words: Mineral water, Large-volume injection, Extraction methods, Pesticides.

INTRODUCTION

Pesticides contamination of ground waters, surface waters and drinking waters from agricultural use has been well documented around the world. Pesticides are moved from agricultural fields to surface waters in surface run-off depending on the soil characteristics and environmental properties of individual pesticides. Pesticides can also be transported into the atmosphere by air currents and redeposited on water and land surface at considerable distances from their origin[1]. The important factors affecting chemical transport of the pesticides from the field to the ground waters and surface waters include water solubility of pesticides, vapour pressure,

organic carbon content/water partition coefficient and octanol-water partition coefficient of the soil. The pesticides having high water solubility and low soil adsorption will move easily to the ground water[2].

In order to limit human risks and environmental pollution, regulations for drinking and related waters are required. The European Union (EU) set the maximum admissible level to a concentration of 0.1 μg/L for a single pesticide compound and to a concentration of 0.5 μg/L for the sum of all pesticides in drinking water (Council Directive 98/83/EC)[3]. In Turkey, the regulation about maximum level of pesticide concentration in natural mineral water, for the sum of all pesticides[4] is 0.1 μg/L.

In water analysis, hazardous compounds are usually present at low concentrations and often masked by complex interfering compounds. Therefore, preconcentration and separation procedures are mandatory for the determination of contaminants at low concentrations. Several methods have been developed and applied for sample preparation, chromatographic separation and detection of pesticides. Common preconcentration methods of water samples include solid phase extraction (SPE)[5-9] and liquid-liquid extraction (LLE)[5,8,10]. Solid phase extraction is suited for the isolation of complex micropollutants from water and has become the method of choice in order to carry out the extraction of many pesticides in aqueous samples. The most widely used sorbents are C_8 and C_{18} commercially bonded to silica and polymeric resins[1,2,11]. Liquid-liquid extraction has been considered to give more reliable and repeatable data than solid phase extraction for sample preconcentration in water analysis. A variety of solvents such as dichloromethane, light petroleum and hexane have been evaluated for the determination of pesticides[10].

Gas chromatography (GC) is a powerful separation technique in multicomponent determination of pesticides at trace level in drinking and related waters. The determination of pesticide residues have been widely carried out by GC with highly sensitive and selective detectors such as electron-capture detection (ECD)[1,6,10], nitrogen-phosphorous detection (NPD)[12,13], flame photometric detection (FPD)[5] and coupled with mass spectrometry (GC-MS)[14,15]. GC-MS can quantify and confirm the compounds by its full scan or selected ion monitoring (SIM) spectra. The full scan often does not provide enough sensitivity in real samples but SIM improves sensitivity and reduces considerably the qualitative information. The selectivity of the detection procedure can be increased by combination of GC with tandem mass spectrometry (MS-MS) instead of SIM. This technique reduces the influence of matrix, increases selectivity and lowers the limit of detection[16].

Large volume injections *via* a programmable temperature vapourizer (PTV) have been applied to increase sensitivity in trace analysis. This injection technique was fist developed by Vogt *et al.*[17,18]. The analytes are enriched in the inlet of the GC-MS during large volume injection. During the first step of large volume injection the solvent is removed when the split valve is open. Programmable temperature

vapourizer method has been reported for the analysis of pesticides residue in environmental analysis. The optimization of PTV parameters on peak areas and peak shapes of pesticides were investigated in drinking water. The important aspects of PTV injections with respect to trace analysis of pesticides including reproducibility, linearity of peak areas and limits of detection were discussed[19-21]. The maximum sample volume that can be injected in PTV depends on the diameter of the liner and the amount vacuum applied during sample running. The best results were obtained using empty liners with relatively large diameters. Higher capacity of turbo molecular pump is required if the sample volume is needed to inject more than 20 μL. The injection of large sample volumes not only enables significant improvements of sensitivity of the method but also makes the PTV injector applicable for the elimination of matrix effects. Programmable temperature vapourizer injection was compared with other GC injection techniques in terms of long-term stability of responses and the extent of matrix-induced response enhancement[22].

Natural mineral water is considered as high quality water for human consumption. The ingredients of mineral waters are sugar, carbon dioxide, sodium benzoate and citric acid. Fruit flavoured mineral waters has been in the market in recent years and contains a variety of flavours in addition to ingredients of natural waters such as cherry, lemon, strawberry, apple, peach and watermelon-strawberry flavours.

The aim this work is to determine the occurrence of the selected pesticides in natural and flavoured mineral waters produced in Turkey by GCMS-PTV. The selection of the pesticides studied was based on their use in agricultural practice in Bursa region. The work focused on SPE and LLE followed by large volume injection in the trace level analysis of various pesticides in mineral waters

EXPERIMENTAL

Pesticide standards were purchased from Dr. Ehrenstorfer (Ausburg, Germany). The pesticides studied were as follows: atrazine, aldrin, malathion, chlorpyrifos, α-endosulfan, dieldrin, 2,4-DDT, β-endosulfan, 4,4-DDT and bromopropylate. Stock solutions of each pesticide were prepared in acetonitrile at 10 ng μL^{-1}. Hydrochloric acid, sodium chloride, anhydrous sodium sulfate, methanol, ethyl acetate, dichloromethane and hexane were obtained from Merck (Darmstadt, Germany).

Pesticide analysis was carried out on a Shimadzu QP 5000 gas chromatography-mass spectrometry. The gas chromatograph is fitted to a split/splitless programmed-temperature Vapourizer injector operated in the large volume injection mode. Compounds were separated on optima δ-3 (Düren, Germany) fused silica capillary columns (30 m × 0.25 mm × 0.25 μm film thickness).

Analytical procedure

Solid-phase extraction: Solid-phase extraction was carried out using glass columns packed with 100 mg of highly cross-linked styrene-divinylbenzene copolymer (Bond Elute ENV). The SPE column was obtained from Varian (Middelburg, The Netherlands).

SPE vacuum manifold (J.T. Baker, Deventer, Holland) was used for extraction of samples. The extraction column was previously conditioned by passing 5 mL of methanol followed by 10 mL deionized water through the column. 100 mL volume of mineral water sample was passed over the conditioned sorbent. During the conditioning and sample loading steps the sorbent should not to be allowed to dry. The extraction column was dried gently by nitrogen for 10 min. The analytes retained on the cartridge were eluted with 2 mL of hexane. The organic phase was evaporated to complete dryness with nitrogen. The dry extract was dissolved in 200 µL ethyl acetate and 8 µL were injected into GC-MS.

Liquid-liquid extraction: 100 mL volume of mineral water samples were acidified with hydrochloric acid and pH was adjusted to 3.2. The mineral water sample was saturated using 2 g of sodium chloride. Then 40 mL of dichloromethane/ethyl acetate (4:1) solvent was added to the sample. The mixture was poured into a 200 mL-volume separator funnel and then shaken several times over 10 min. The organic layer was allowed to separate from the mineral water phase for at least 15 min. The same procedure was applied using 10 mL of solvent mixture and 2 fractions were combined together. The extract was dried over anhydrous sodium sulfate and concentrated to a volume of 2 mL by using a Kuderna Danish evaporator at 80 ºC. 2 mL of extract was evaporated to complete dryness with nitrogen. The dry extract was dissolved in 200 µL ethyl acetate and 8 µL were injected into GC-MS.

Instrumental conditions: The injector temperature was programmed from 65 ºC (hold 2 min) to 270 ºC at 250 ºC min^{-1} (hold 5 min). Cold splitless injection mode was used. The split valve was initially closed then opened to transfer the analytes to the column at a 3 min sampling time. The oven temperature was initially 80 ºC for 3 min, ramped at 50 ºC min^{-1} to 150 ºC (hold 1 min), then 1 ºC min^{-1} to 160 ºC (hold 1 min) and finally 250 ºC at 5 ºC min^{-1} (hold 12.6 min). Total time for the GC analysis was 47 min. The carrier gas was helium at a constant flow of 1.5 mL min^{-1}. The electronic impact ionization mode was used at 70 eV of ionization energy and ion source temperature was set to 280 ºC. Four ions for each pesticide were chosen for analysis in selected ion monitoring (SIM) mode.

RESULTS AND DISCUSSION

GC-MS analysis: GC-MS with PTV injection was performed for the separation of a mixture of 10 pesticide standards. PTV cold splitless mode was used to introduce large volume of samples. The sample is introduced at a temperature at which solvents evaporates and is discharged *via* the split outlet while the higher-boiling analytes are retained in the liner. The moment of closing the split vent is important to minimize losses of analytes during the elimination of the solvent. The chromatogram of the mixture of 10 pesticide standards in SIM mode is shown in Fig. 1. All the pesticides are well resolved and eluted within an acceptable time of about 44 min. Four quantification ions are selected for each pesticide and retention times are shown in Table-1.

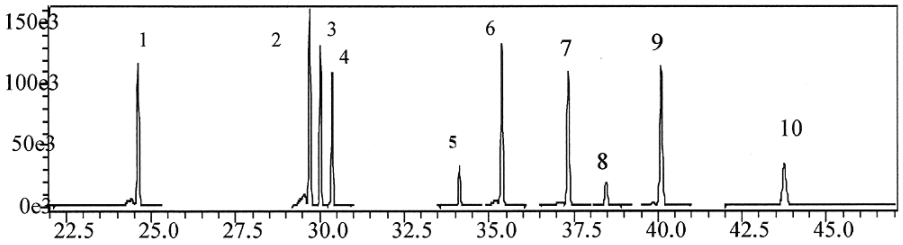

Fig. 1. SIM chromatograms of standard pesticides. Peaks: (1) Atrazine; (2) Aldrin; (3) Malathion; (4) Chlorpyrifos; (5) α-Endosulfan; (6) Dieldrin; (7) 2,4-DDT; (8) β-Endosulfan; (9) 4,4-DDT; (10) Bromopropylate

TABLE-1
RETENTION TIMES AND QUANTIFICATION IONS OF THE SELECTED PESTICIDES

Pesticide	Retention time (min)	Quantitation ions (m/z)
Atrazine	24.7	68, 173, 200, 215
Aldrin	29.8	66, 79, 91, 263
Malathion	30.1	93, 125, 127, 173
Chlorpyrifos	30.4	97, 197, 258, 314
α-Endosulfan	34.2	102, 195, 237, 241
Dieldrin	35.5	79, 81, 263, 277
2,4-DDT	37.4	165, 199, 235, 237
β-Endosulfan	38.6	102, 159,195, 241
4,4-DDT	40.2	165, 199, 235, 237
Bromopropylate	43.9	155, 183, 185, 341

Validation of the method

Linearity: The linearity of all the pesticides was evaluated by the calculation of 5 point linear plot, based on linear regression and correlation coefficient. Correlation coefficients of all the studied pesticides ranged from 0.9907 to 0.9982 for 5 point calibration curves. For quantification purposes 5 point calibration curves based on peak area data in SIM mode were constructed in the concentration range 1 to 100 μg/L.

Accuracy: Analysis of standard mixture of pesticides at 15 μg/L concentration was performed to evaluate the accuracy of the PTV-GC-MS method. The concentrations of each pesticide were calculated from calibration curves and the results are shown in Table-2. The accuracy of pesticides is in the range of standard deviation. The deviation from true value may be the result of decomposition or retaining of pesticides in liner during the evaporation step.

Repeatability: The precision of the chromatographic method was evaluated in terms of relative standard deviation (RSDs) of a standard solution at 5 μg/L. The standard mixture of pesticides was injected 6 times and the results are presented in Table-2. RSDs of the 10 pesticides ranged from 1 to 2 %. The RSD data obtained from the PTV-GC-MS were acceptable.

TABLE-2
VALIDATION PARAMETERS OF THE SELECTED PESTICIDES

Pesticide	Linearity	Linear range (μg/L)	Accuracy (μg/L)	LOD (ng/L)	LOQ (ng/L)	% RSD
Atrazine	0.9997	1-1000	15 ± 2	50	160	1
Aldrin	0.9993	1-1000	16 ± 1	20	70	2
Malathion	0.9992	1-1000	14 ± 2	80	270	2
Chlorpyrifos	0.9993	1-1000	16 ± 2	100	300	2
α-Endosulfan	0.9997	1-1000	16 ± 1	20	70	1
Dieldrin	0.9996	1-1000	14 ± 1	80	270	1
2,4-DDT	0.9980	1-1000	15 ± 1	100	200	1
β-Endosulfan	0.9995	1-1000	15 ± 2	15	56	1
4,4-DDT	0.9969	1-1000	14 ± 1	40	120	1
Bromopropylate	0.9996	1-1000	16 ± 2	30	100	1

Recovery: The extraction efficiency of the 10 pesticides standards from deionized water by LLE and SPE is presented in Table-3. The recovery studies were carried out by spiking the mixture of standard pesticides at a 0.5 mg/L of concentration to deionized water following the LLE and SPE procedure. The mean percentage recoveries of pesticides by LLE ranged from 72 ± 1 (aldrin) to 101 ± 3 % (4,4-DDT). The values using SPE procedure varied between 74 ± 1 (atrazine) and 102 ± 1 % (α-endosulfan). LLE gave better recoveries for 6 pesticides than SPE procedure. The lower recovery of SPE for more polar pesticides of atrazine aldrin and malation is due to low polarity of the elution solvent (hexane). Less polar pesticides were extracted using hexane with high recovery, but more polar pesticides retained in the column and lowered the recovery. Although, comparatively better recoveries were obtained for less polar pesticides by SPE, more polar pesticides can be extracted by both procedures.

TABLE-3
RECOVERIES ± SD* OF PESTICIDES STANDARDS ADDED TO DEIONIZED WATER BY SPE AND LLE

Pesticide	Recovery (%)	
	SPE	LLE
Atrazine	74 ± 1	76 ± 5
Aldrin	75 ± 3	72 ± 1
Malathion	74 ± 2	75 ± 4
Chlorpyrifos	76 ± 2	84 ± 5
α-Endosulfan	102 ± 1	75 ± 1
Dieldrin	101 ± 3	80 ± 1
2,4-DDT	78 ± 1	83 ± 3
β-Endosulfan	102 ± 3	75 ± 6
4,4-DDT	78 ± 1	101 ± 3
Bromopropylate	74 ± 2	93 ± 3

*Values are mean of triplicate analysis.

Detection and quantification limits: Limits of detection (LOD) and limits of quantification (LOQ) were determined in deionized water. The sample containing 5 μg/L of each pesticide was analyzed 6 times by GC-MS. The quantification and confirmatory ion were observed at this concentration. The LOD was calculated from the analysis of 6 replicate samples as:

$$LOD\ (\mu g/L) = 3s/m$$

where s is the sample standard deviation for the 6 replicate analyses, m is the slope of calibration curve. Similarly, the LOQ is calculated as:

$$LOQ\ (\mu g/L) = 10s/m$$

Table-2 summarized the LODs and LOQs for the pesticides. The detection and quantification limits were improved by introducing large volume sample by means of PTV. LOD ranged from 15 to 100 ng/L and LOQ ranged from 56 to 300 ng/L for 10 pesticides.

Analysis of mineral water samples: Analysis of commercial mineral waters was carried out using the developed SPE and LLE procedures. Mineral waters of different brands were purchased in local supermarkets. Mineral water 1, cherry aroma 1 and other fruit supplement mineral waters have the same brands. Mineral water 2, cherry aroma 2 and mineral water 3 samples have different brands. Figs. 2 and 3 show representative SIM chromatograms of pesticides in mineral water extracts obtained by SPE and LLE methods, respectively. The identities of the pesticides in samples extracts were confirmed by comparing their retention times with those of the pesticides standards and the presence of all 4 ions (Table-1) in the correct ratio. The relative SIM responses of each of the ions monitored for the analyte should correspond to those obtained from a standard where no interference observed. The peaks in the chromatograms were considered to be above S/N ratio of 5 at significant masses for identification. For example, the S/N ratio is 24 at m/z 127 for malathion in cherry aroma 1 (Fig. 2C), S/N ratio 13 at m/z 241 for α-endosulfan in mineral water 1 (Fig. 2D), S/N ratio 15 at m/z 241 for α-endosulfan in mineral water 2 (Fig. 2E), S/N ratio 6 at m/z 241 for β-endosulfan in mineral water 1 (Fig. 2F). The chromatograms show that the sample preparation methods give different results for the determination of pesticides in mineral water samples. α-Endosulfan and β-endosulfan were determined in mineral water 1 by SPE and LLE but chlorpyrifos was determined by LLE. Aldrin and α-endosulfan were determined in cherry aroma 1 by both procedures but malathion was determined by SPE and β-endosulfan was determined by LLE. β-Endosulfan was determined in lemon aroma by both procedures but aldrin was determined by SPE and α-endosulfan was determined by LLE. α-Endosulfan and β-endosulfan were determined in strawberry aroma by both procedures but aldrin was determined by SPE. α-Endosulfan was determined in apple aroma by both procedures, but aldrin was determined by SPE and β-endosulfan and bromopropylate were determined by LLE. Aldrin was determined in peach aroma by SPE, α-endosulfan and β-endosulfan were determined by LLE. α-Endosulfan and β-endosulfan were determined in watermelon-strawberry aroma but no pesticide was determined by SPE.

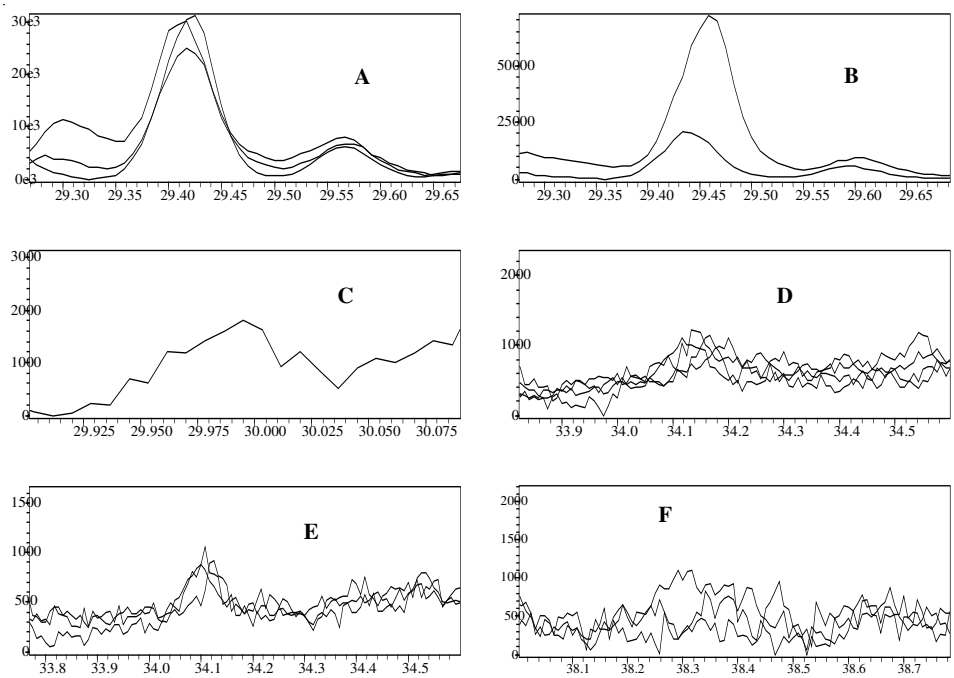

Fig. 2. SIM chromatograms of pesticides in mineral water samples after SPE: (**A**) Aldrin in; cherry aroma 1 (t_R: 29.567), strawberry aroma (t_R: 29.558), peach aroma (t_R: 29.592); (**B**) Aldrin in; apple aroma (t_R: 29.600), lemon aroma (t_R: 29.608); (**C**) Malathion in; cherry aroma 1 (t_R: 29.995); (**D**) α-Endosulfan in; mineral water 1 (t_R: 34.125), cherry aroma 1 (t_R: 34.150), strawberry aroma (t_R: 34.167), apple aroma (t_R: 34.183); (**E**) α-Endosulfan in; mineral water 2 (t_R: 34.100), mineral water 3 (t_R: 34.108), cherry aroma 2 (t_R: 34.125); (**F**)) β-Endosulfan in; mineral water 1 (t_R: 38.475), strawberry aroma (t_R: 38.383), lemon aroma (t_R: 38.308)

The concentrations of pesticides were determined in various types of mineral water samples after SPE and LLE procedures are shown in Tables 4 and 5. The pesticides concentration ranged from 71 to 530 ng/L in samples extracted with SPE and from 66 to 1092 ng/L in samples extracted with LLE procedure. Aldrin was determined at highest concentration in cherry aroma 1 sample with both extraction procedures. Malathion was only found in cherry aroma 1 with SPE (Table-4). The malathion level in other water samples was below the detection limit. Chlorpyrifos was only found in mineral water 1 sample with LLE and its level in other samples was below the detection limit. Bromopropylate was only found in apple aroma sample with LLE and its level in other samples was below the detection limit (Table-5). The higher concentrations of pesticides were determined with LLE procedure. The recoveries were also better by about 20 % for LLE. Quantification of these pesticides by using SPE procedure is difficult as their concentrations are close to or below the LOD of the method.

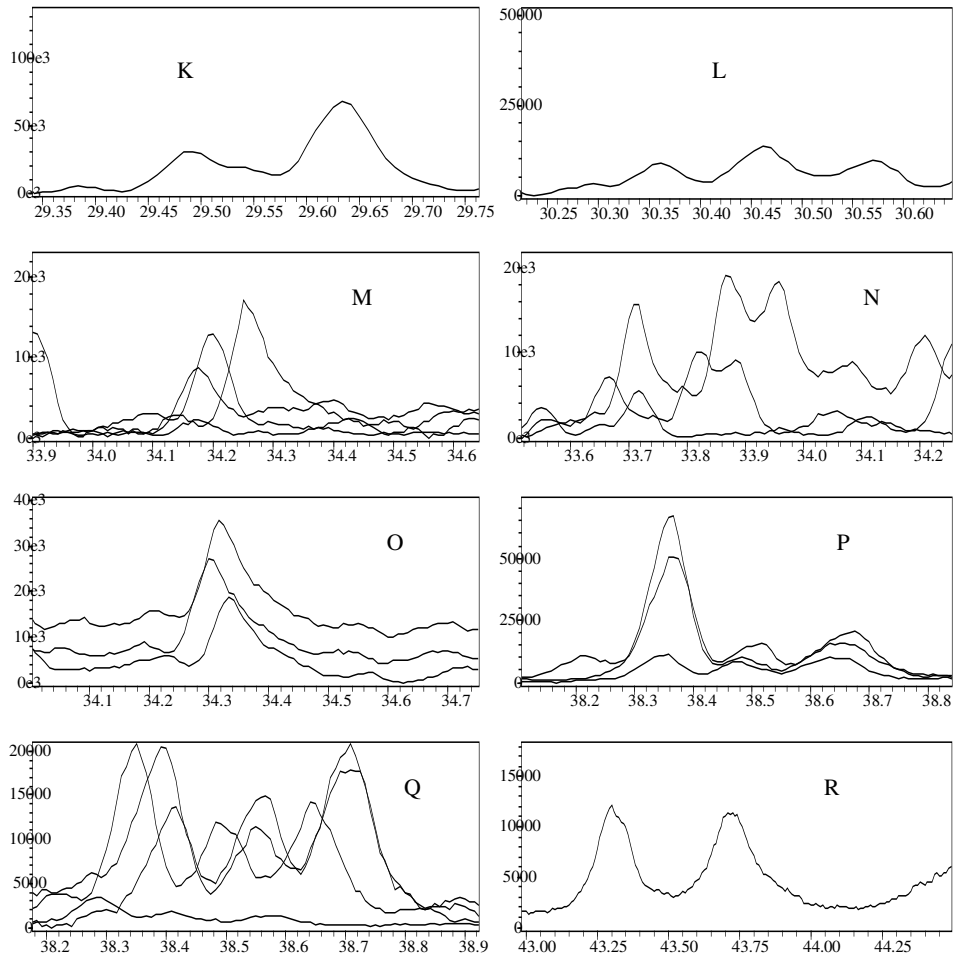

Fig. 3. SIM chromatograms of pesticides in mineral water samples after LLE: (**K**) Aldrin in cherry aroma 1 (t_R: 29.633); (**L**) Chlorpyrifos in mineral water 1 (t_R: 30.362); (**M**) α-Endosulfan in; strawberry-watermelon aroma (t_R: 34.142), apple aroma (t_R: 34.175), strawberry aroma (t_R: 34.150), cherry aroma 1 (t_R: 34.175); (**N**) α-Endosulfan in; peach aroma (t_R: 34.050), mineral water 1 (t_R: 34.108), lemon aroma (t_R: 34.092); (**O**) α-Endosulfan in; mineral water 2 (t_R: 34.200), mineral water 3 (34.192), cherry aroma 2 (t_R: 34.233); (**P**) β-Endosulfan in; apple aroma (t_R: 38.483), strawberry aroma (t_R: 38.492), cherry aroma 1 (t_R: 38.517); (**Q**) β-Endosulfan in; lemon aroma (t_R: 38.567), peach aroma (t_R: 38.483), strawberry-watermelon aroma (t_R: 38.542), mineral water 1 (t_R: 38.583); (**R**) Bromopropylate in apple aroma (t_R: 43.725)

There is no literature on determination of pesticide residues in natural and fruit flavoured mineral waters. A few insecticides and fungicides have been detected in fruit juices by other authors[23,24] and the levels found are of the same order of those encountered in present study. However, the detected levels are higher than the LODs established for these pesticides in natural and fruit flavoured mineral waters.

TABLE-4
CONCENTRATIONS OF PESTICIDES IN MINERAL WATER AFTER SPE SAMPLE PREPARATION METHOD

Sample	Pesticide concentration (ng/L)			
	Aldrin	Malathion	α-Endosulfan	β-Endosulfan
Mineral water 1	Nd*	nd	80 ± 2	75 ± 2
Mineral water 2	nd	nd	80 ± 2	nd
Mineral water 3	nd	nd	78 ± 2	nd
Cherry aroma 1	530 ± 80	385 ± 1	80 ± 2	nd
Cherry aroma 2	nd	nd	75 ± 2	nd
Lemon aroma	220 ± 10	nd	nd	77 ± 2
Strawberry aroma	400 ± 20	nd	78 ± 2	71 ± 2
Apple aroma	520 ± 60	nd	72 ± 2	nd
Peach aroma	470 ± 10	nd	nd	nd

nd* = Not detected.

TABLE-5
CONCENTRATIONS OF PESTICIDES IN MINERAL WATER AFTER LLE SAMPLE PREPARATION METHOD

Sample	Pesticide concentration (ng/L)				
	Aldrin	Chlorpyrifos	α-Endosulfan	β-Endosulfan	Bromopropylate
Mineral water 1	nd*	423 ± 7	102 ± 1	66 ± 4	nd
Mineral water 2	nd	nd	76 ± 4	nd	nd
Mineral water 3	nd	nd	74 ± 1	nd	nd
Cherry aroma 1	1092 ± 103	nd	201 ± 18	401 ± 2	nd
Cherry aroma 2	nd	nd	112 ± 3	nd	nd
Lemon aroma	nd	nd	166 ± 8	581 ± 27	nd
Strawberry aroma	nd	nd	364 ± 44	153 ± 2	nd
Apple aroma	nd	nd	254 ± 14	193 ± 3	638 ± 5
Peach aroma	nd	nd	138 ± 3	335 ± 21	nd
Watermelon-Strawberry aroma	nd	nd	213 ± 8	628 ± 12	nd

nd* = Not detected.

The sources of some of the pesticides in mineral water samples might be from diffuse sources such as run-off from agricultural lands[1]. There are high agricultural activities in the area of mineral water sources.

In conclusion, a GC-MS with PTV method is proposed after SPE and LLE for the identification and quantification of pesticides in natural and fruit flavoured mineral waters. The proposed method permitted the determination of selected pesticides at concentration levels of 0.1 μg L^{-1}, as demanded by current legislation for individual pesticides in drinking and related waters (Council Directive 98/83/EC and Official Journal, RG,18.10.1997;23144). Aldrin (1.092 μg L^{-1}) in cherry 1 sample

using LLE method is found above the limit of these legislations but the Council Directive is only related to drinking water and Official Journal[3,4] is related to natural mineral water. These 2 regulations do not contain any limit for pesticides in fruit flavoured mineral waters and there is also no literature on the determination of pesticides in this type of samples. Total pesticides concentration in cherry 1 sample is 0.995 μg L^{-1} determined by SPE method. The reason for high concentration of aldrin by LLE is that matrix compounds can also be extracted with solvents and they must be eliminated by SPE. When 2 extraction methods are compared, SPE is widely applied if sample contain high level of matrix interfering compounds[5-9]. The method of large volume injection can be successfully applied to increase the detection limit, accuracy of generated data and long-term stability of analytes responses on repetitive injections of real-life samples. The developed method was applied to determine pesticide residue levels in natural, cherry aroma, lemon aroma, strawberry aroma, peach aroma and watermelon-strawberry aroma mineral waters sold in Turkey and the residue levels were below the detection limits. Four pesticides were detected in several mineral water samples after SPE and five were detected after LLE. There are some differences between the pesticides determined with 2 extraction procedures. Malathion was only detected in cherry aroma 1 after SPE. Chlorpyrifos was only detected in mineral water 1 and bromopropylate in apple aroma after LLE. Higher concentrations of pesticides were obtained after LLE. The lower level of pesticides determined after SPE is due to evaporative losses during sample storage or to passage of too large a sample through the cartridge. When the cartridge was eluted under vacuum irreproducible losses of the solvent and analytes may occur.

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