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Method Development and Validation for the Determination of Pesticide Residues in Water by GC-NPD

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ABSTRACT: A multi-residue method was developed for the determination of organophosphorous pesticides and Herbicide by liquid-liquid extraction (LLE) and followed by gas chromatography-nitrogen-phosphorus detector (GC/NPD). The method was evaluated with respect to the limit of detection and quantification, linearity and accuracy (repeatability, reproducibility, recovery). The method is linear over the range 2.5 -25 μg L^{-1} for eleven pesticides and 5-25 μg L^{-1} for methamidophos. Correlation coefficients were higher or equal to 0.992. The limits of detection (LODs) were between 0.67 and 2.23 μg L^{-1}. The limits of quantification (LOQs) ranged from 2.24 and 7.45 μg L^{-1}. Recoveries of fortified water samples in two different concentration levels with 12 organophosphorous pesticides and herbicide were over 95% in high concentration and 80% in low concentration. For repeatability, relative standard deviation (RSD%) ranged between 2.79 and 10.99%, and for reproducibility (RSD%) ranged between 1.56 and 10.36 %. The developed method is suitable for routine application in water samples in accordance with the validation data and the parameter as the high sample throughput and cost effective.

Keywords: Environmental pollution, GC/NPD, method validation, multi-residue analysis, pesticide

Sudaki Pestisit Kalıntılarının Belirlenmesi için GC-NPD Kullanılarak Method Geliştirilmesi ve Validasyonu

ÖZET: Organik fosforlu pestisitlerin ve herbisitlerin sıvı-sıvı ekstraksiyonu (LLE) ve ardından gaz kromatografisi-azot-fosfor dedektörü (GC / NPD) ile belirlenmesi için bir çoklu kalıntı yöntemi geliştirildi. Metod; dedeksiyon ve miktar sınırı, doğrusallık ve doğruluk (tekrarlanabilirlik tekrarüretilebilirlik, geri kazanma) limitine göre değerlendirildi. Yöntem, on bir pestisit için 2.5-25 μg L^{-1} aralığında ve metamidofos için 5-25 μg L^{-1} aralığında doğrusaldır. Korelasyon katsayıları 0.992' ye eşit veya daha yüksektir. Dedeksiyon limitleri (LOD) 0.67 ve 2.23 μg L^{-1} arasındadır. Miktar sınırlamaları (LOQ) 2.24 ve 7.45 μg L^{-1} arasında değişmektedir. 12 organofosforlu pestisit ve herbisit ile iki farklı konsantrasyon seviyesinde zenginleştirilmiş su numunelerinin geri kazanımı, yüksek konsantrasyonda %95'in üzerinde ve düşük konsantrasyonda %80' in üzerindedir. Tekrarlanabilirlik için, relatif standart sapma (RSD%) 2.79 ile 10.99 arasında ve tekrarüretilebilirlik için (RSD%), 1.56 ile %10.36 arasında değişmektedir. Geliştirilen yöntem, validasyon verilerine ve yüksek numune akışı ile uygun maliyetli oluşu gibi parametrelere göre su numunelerinde rutin uygulama için uygundur.

Anahtar Kelimeler: Çevre kirliliği, çoklu kalıntı analizleri, GC/NPD, metod validasyonu, pestisit

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INTRODUCTION

Pesticides are chemical or biological products that was used to destroy the harmful effect to agriculture (Dömötörová and Matisová, 2008). It is one of the sources of water contamination with serious risks to human and animal health and leads to serious environmental consequences. Pesticides may cause acute anaemia, bone structure disorders, teratogenic and embryologic disease and affect nervous system or endocrine system in the body (Castilho et al., 2000). Additionally, it causes changes in the ecosystem with harmful consequences for the environment and agriculture, because of long-term effects on living organisms, the emergence and spread of new pests and disease with consequent increasing in the need for using more pesticides (Costa et al., 2008). Due to the intensive use of pesticides and the persistence of these compounds, residue of pesticides is getting into the environment, including groundwater and surface water (Komatsu and Vaz, 2004).

Water resources are affected from pesticides due to agriculture requires a water supply (Cabrera et al., 2008). For decades, the extensive use of organophosphorous pesticides in predominantly agricultural areas has been favoured over the more persistent organochlorine pesticides. Because the degradation rates of organophosphorous pesticides are more rapid than organochlorine pesticides (Driss et al., 1993). The spread using of these pesticides cause an increase in the environmental pollution especially in drinking waters (Beltran et al., 1998). Pesticides may leach down to the ground water, which may lead to extensive pollution of groundwater (EPA, 1990). Maximum permissible level is decided at 100 ng L^{-1} for single pesticide present in drinking water and 500 ng L^{-1} in the case of multiple pesticide residues by the European Union in its drinking water regulations. Increasing contamination of soil, water and sediment due to the intensive use of pesticides has led to the development of efficient analytical methods to detect the presence of pesticides (Park et al., 2011).

Therefore, continuous monitoring of pesticides residues in environmental samples is very important. However, it is necessary to develop a faster and more selective analytical methodologies that are less harmful to the environment and more sensitive to trace levels of pesticide residues in natural and drinking waters (Jin et al., 2012).

Determination of pesticides in environmental water samples were carried out by the complex chromatographic instrumentation. Although it requires the application of sample extraction procedures (usually with preconcentration steps) in order to isolate analytes, remove interferent substances and achieve the sensitivity required for drinking water pollution control (Beltran et al., 1998). There are many important techniques for extraction of pesticides such as supercritical fluid extraction, liquid-liquid extraction, solid phase extraction, solid phase micro extraction, matrix solid phase dispersion (Jin et al., 2012).

The analysis and detection of pesticides is mostly based on different chromatographic techniques such as high performance liquid chromatography (HPLC), liquid chromatography (LC) or gas chromatography (GC) (Rocha et al., 2012).

Different detectors are used to determine the compounds with gas chromatography. Organophosphorus compounds are determined with gas chromatography/nitrogen phosphorous detectors (GC-NPD) and gas chromatography/mass spectrometry (GC-MS) due to higher sensitivity. Organochlorine pesticides, pyrethroids and imidazoles compounds are detected from gas chromatography/electron capture detection (GC-ECD) with excellent sensitivity. Organophosphorus and organochlorine pesticides were detected simultaneously by GC–MS (Menezes Filho et al., 2010).

It must be able to measured residues at very low concentration levels and must also provided clear evidence to confirm both the identity and the magnitude of any residue detected with new developed method (Vidal et al., 2006). The method of pesticide residue analysis needs to be essentially

reliable and efficient as well as robust and simple. Validation of the methodology is extremely important as it confirms the analytical data (Suman and Singh, 2011).

The goal of this study is to develop a multi–residue method for determining the organophosphorus pesticides and herbicide which pollute the water by GC –NPD. In the laboratory, a method should be validated to constitute whether it is suitable for the purpose for which it is to be used (Bempelou and Liapis, 2006). Hence, validation of the method according to the parameters of linearity, reproducibility, repeatability, recovery, limits of quantification (LOQs) and limits of detection (LODs) is also aimed.

MATERIAL AND METHOD

Chemicals and Reagents

Some organophosphorus pesticides (OPPs) standards (chlorpyrifos methyl, chlorpyrifos ethyl, methamidofos, atrazine and simazine) were purchased from Dr. Ehrenstorfer GmbH 1000 ng μl^{-1} in acetone. Other OPPs pesticide standards (demeton, diazinon, ethion, disulfoton, malathion, parathion methyl and parathion ethyl) were purchased from AccuStandard M614, 1000 μg ml^{-1} in acetone/hekzane and stored in the freezer at –10 °C the dark at 20 °C. Dichloromethane, acetone and sodium sulphate were obtained from Merck for gas chromatography. Organic solvents are pesticide grade. Other chemicals are analytical grade (Sigma), and water was double distilled.

Apparatus

The Turbovap evaporation system was used at the last stage of extractions. Extractions were carried out using a 2 L separation funnel. Separation and detection of pesticides were performed by a Perkin Elmer GC equipped with a split/splitless injector, with a nitrogen phosphor detector (NPD). The GC-NPD detector investigations were carried out using a Perkin Elmer type Clarus 500 gas chromatograph. A 30 m elite-5 MS fused-silica capillary column (0.25 mm i.d. and 0.25 μm film thickness) was utilized for separation of pesticides. Helium (purity 99.999%) was used as the carrier gas at the constant flow rate of 2 mL min^{-1}. 2 mm focus liner was used as liner. The temperatures of injector and detector were set at 250 and 325 °C , respectively. The injection port was operated at splitless mode. Oven temperature program was: 70 °C for 1 minute, increased to 230 °C at 20 °C min^{-1} and held at 230 °C for 20 minutes, then increased to 325 °C at 45 °C min^{-1}, and held at 325 °C for 10 minutes.

Calibration Solutions

A stock solution containing 12 pesticides at 100 ppb in acetone was prepared from individual pesticide stock solutions. The solutions were prepared at four different concentrations (2.5-5-10-25 µg L^{-1}) using this stock solution and pesticide-free water. Pesticide-free water was employed in calibration and validation studies to exclude further studies on matrix effects. This water was tested for absence of pesticides by GC/NPD.

Methodology

For liquid-liquid extraction, one litre of water sample was put into a 2 L separatory funnel, spiked (in acetone) with organophosphate compounds (for optimization and validation studies), mixed and allowed to equilibrate to room temperature. Samples were extracted with three 100 ml portions of dichloromethane (DCM). The separatory funnel was mixed intensely for a few minutes with periodic venting to release excess pressure and was left to separate the organic layer. Seperated phase was collected into an erlenmeyer flask. The combined extract was percolated through an anhydrous sodium sulphate column. The combined extract was evaporated using Turbovap evaporator at 35 °C then evaporated to dryness with nitrogen gas. The residue was dissolved with 1 mL acetone. Optimization of GC/NPD parameters was based on sequential injections extracted water samples. 5 μL were injected into the GC/NPD in the split-less mode. Fig. 1 shows the chromatogram of the spiked pesticides in water at 10 µg L^{-1} obtained by GC–NPD

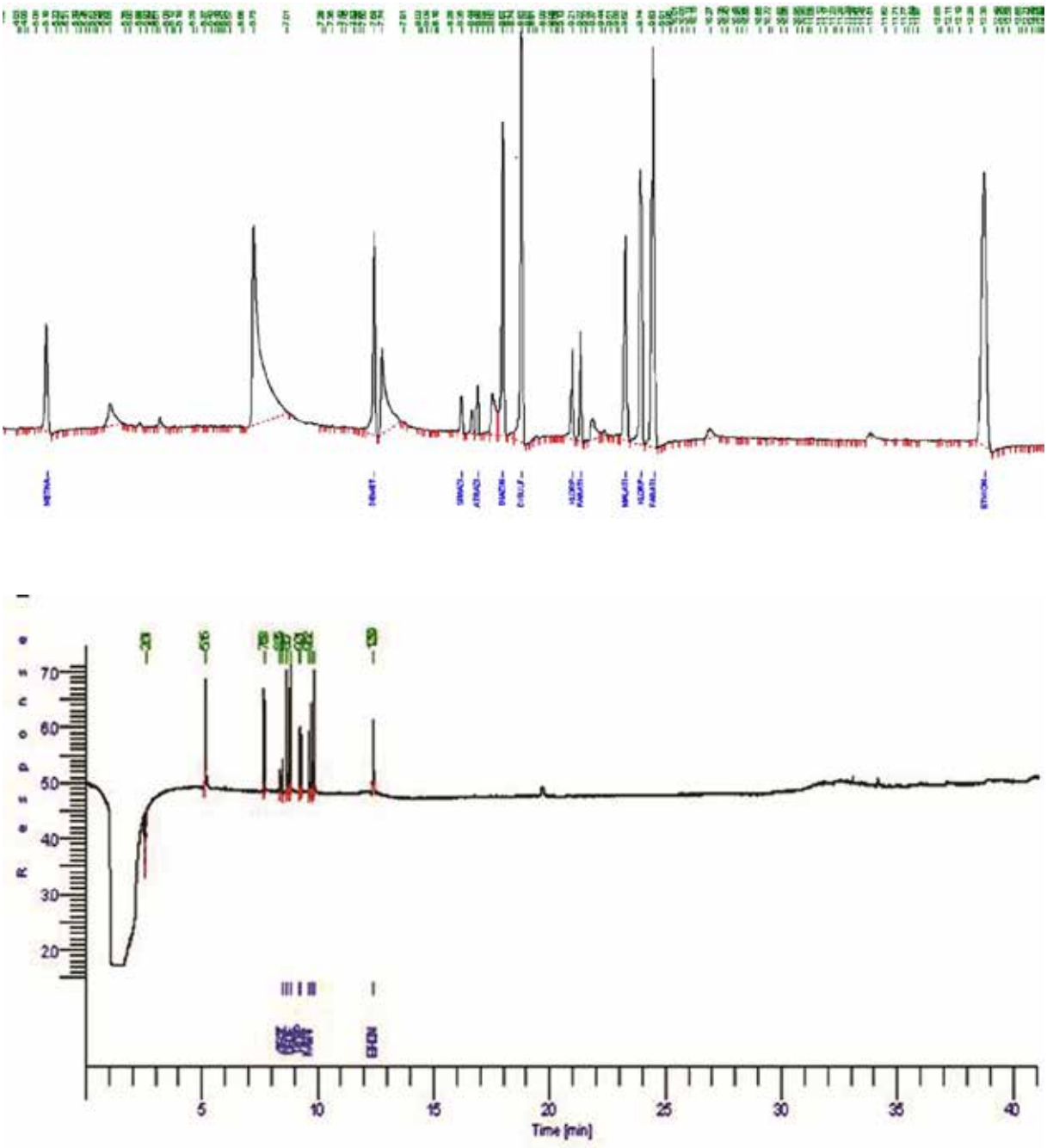

Figure 1. Chromatogram of GC-NPD analysis of pesticides for 10 µg L^{-1}. Target compounds are numbered as follows: methamidofos, simazine, diazinon, disulfoton, chlorpyrifos methyl, parathion methyl, malation, chlorpyrifos ethyl, parathion ethyl, ethion

RESULTS AND DISCUSSION

The performance characteristics of the method were identified by the evaluation of linearity, accuracy, limits of detection and quantification with standard solutions, sample blanks and spiked samples. Validation studies are carried out with varied pesticide concentrations in spiked pesticide water samples before extraction.

Linearity

For GC/NPD; the linearity of the calibration curve was determined by the analysis of each of the 11 pesticides at 4 calibration levels (2.5, 5, 10 and 25 µg L^{-1}). For only methamidofos, its curve was graphed at 3 calibration levels because it was not determined at 2.5 µg L^{-1}. The calibration curves were prepared for each

compound from the spiked water by plotting relative responses versus the analyse concentration and linear regression method was used.

The majority of the correlation coefficients (R) were higher or equal to 0.992.

Accuracy

Accuracy is defined with recovery, repeatability and reproducibility. For repeatability; six (6+6=12) analyses of one concentration (25 µg L^{-1}) were performed in the same day (Table 1).

Table 1. For repeatability; Mean, SD, RSD, and r values of pesticides analyzed at 25 µg L^{-1}.

		Mean	SD	RSD	RSD%	r
methamidofos	1	20.207	0.820	0.041	4.056	2.319
	2	21.020	1.467	0.070	6.977	4.151
demeton	1	20.623	1.894	0.092	9.185	5.361
	2	20.875	1.458	0.070	6.985	4.126
simazine	1	19.957	1.210	0.061	6.063	3.424
	2	19.653	0.903	0.046	4.593	2.555
atrazine	1	21.812	0.759	0.035	3.481	2.149
	2	21.941	0.749	0.034	3.413	2.119
diazinon	1	23.335	0.719	0.031	3.083	2.036
	2	23.428	1.127	0.048	4.811	3.190
disulfoton	1	23.393	0.820	0.035	3.506	2.321
	2	22.798	1.800	0.079	7.897	5.095
chlorpyrifos methyl	1	20.447	1.830	0.089	8.950	5.179
	2	21.105	2.321	0.110	10.998	6.569
parathion methyl	1	20.865	1.835	0.088	8.792	5.192
	2	20.747	2.225	0.107	10.725	6.297
malathion	1	25.002	0.988	0.040	3.951	2.795
	2	25.312	0.708	0.028	2.796	2.003
chlorpyrifos ethyl	1	23.172	0.978	0.042	4.221	2.768
	2	23.553	1.134	0.048	4.814	3.209
parathion ethyl	1	21.775	0.949	0.044	4.357	2.685
	2	22.348	0.993	0.044	4.445	2.811
ethion	1	21.828	1.168	0.054	5.351	3.305
	2	22.287	1.571	0.070	7.050	4.446

For reproducibility; analyses of nine (9+9=18) different samples of one concentration (10 µg L^{-1}) were performed in 3 different days (Table 2). Reproducibility relative standard deviation (RSDr) , Reproducibility (R) and Repeatability (r) were calculated in

$$\mathbf{RSD_r} = \sqrt{\frac{\sum[(a_i - b_i)/\bar{x}_i]^2}{2n}} \ ,$$

r=Standard Deviation (SD)*2.83 and

R=SD*2.8.

Accuracy was expressed as the relative standard deviation (RSD%). RSD% was <6 for repeatability and was <15% for reproducibility for most pesticides.

Table 2. For reproducibility; Mean, SD, RSD, RSD_r values of pesticides examined at 10 µg L^{-1}.

	Repeat	**Mean**	**SD**	**RSD**	**RSD%**		**RSD_r**	**RSD_r%**	**R**
methamidofos	a	9.502	0.868	0.091	9.132	0.004	0.016	1.561	2.43
	b	9.57	0.88	0.09	9.16				2.45
demeton	a	11.11	1.47	0.13	13.27	0.154	0.093	9.260	4.13
	b	10.92	1.56	0.14	14.32				4.38
simazine	a	11.15	2.82	0.25	25.28	0.193	0.104	10.364	7.89
	b	11.03	2.44	0.22	22.14				6.84
atrazine	a	13.49	1.10	0.08	8.13	0.055	0.055	5.517	3.07
	b	13.54	1.14	0.08	8.40				3.19
diazinon	a	8.72	1.46	0.17	16.70	0.041	0.048	4.750	4.08
	b	8.67	1.13	0.13	13.03				3.16
disulfoton	a	10.54	1.56	0.15	14.84	0.085	0.069	6.852	4.38
	b	10.46	1.19	0.11	11.39				3.33
chlorpyrifos methyl	a	14.63	3.05	0.21	20.85	0.029	0.040	3.986	8.54
	b	14.47	3.27	0.23	22.62				9.17
parathion methyl	a	15.58	3.63	0.23	23.33	0.020	0.033	3.339	10.18
	b	15.49	3.31	0.21	21.39				9.28
malathion	a	10.33	1.95	0.19	18.92	0.070	0.062	6.225	5.47
	b	10.81	1.89	0.17	17.50				5.30
chlorpyrifos ethyl	a	13.31	1.67	0.13	12.51	0.018	0.031	3.121	4.66
	b	13.54	1.81	0.13	13.33				5.06
parathion ethyl	a	13.64	1.33	0.10	9.74	0.019	0.032	3.236	3.72
	b	13.75	1.51	0.11	10.96				4.22
ethion	a	13.28	1.25	0.09	9.42	0.053	0.054	5.405	3.50
	b	13.15	1.51	0.11	11.45				4.21

Recovery; Trueness has been calculated as the recovery of 12 spiked reference materials in water for two concentration levels. The recoveries for each of pesticides are given in (Table 3).

Table 3. Mean recoveries, SD, RSD fortified at two different concentration level

	Concentration (µg L^{-1})	**Mean recovery %**	**SD**	**RSD**	**RSD %**
methamidofos	5	80.023	0.35	0.004	0.436
	25	90.62	7.14	0.08	7.88
demeton	2.5	68.93	3.86	0.06	5.60
	25	90.10	8.73	0.10	9.69
simazine	2.5	71.53	1.67	0.02	2.33
	25	80.73	9.58	0.12	11.86
atrazine	2.5	93.67	10.08	0.11	10.76
	25	96.03	5.14	0.05	5.35
diazinon	2.5	102.40	1.04	0.01	1.02
	25	96.83	3.61	0.04	3.73
disulfoton	2.5	102.87	2.17	0.02	2.11
	25	97.92	3.84	0.04	3.92
chlorpyrifos methyl	2.5	65.07	4.65	0.07	7.14
	25	99.09	10.47	0.11	10.56
parathion methyl	2.5	87.20	2.70	0.03	3.10
	25	102.17	13.89	0.14	13.59
malathion	2.5	16.47	1.81	0.11	11.02
	25	98.49	16.26	0.17	16.51
chlorpyrifos ethyl	2.5	82.07	2.31	0.03	2.82
	25	95.49	9.25	0.10	9.69
parathion ethyl	2.5	103.20	2.53	0.02	2.45
	25	95.83	6.83	0.07	7.12
ethion	2.5	101.07	1.18	0.01	1.17
	25	99.11	3.48	0.04	3.51

The results of the present study (Table 3) showed that recovery of the most of 12 pesticides have existed in above 95% in high concentration and 80% in low concentration. None of mean recovery exceeds 103%. International guidelines indicate that for the validation of quantitative methods mean recovery should be within the range of 70–110%(SANCO, 2004). The results were in accordance with these guidelines. Dorea et al. detected organophosphate pesticide residues in fruits by GC-NPD detector. The lowest recoveries were 88.2% for diazinon, 89.5% for methylparation and 89.1% for malation. For similar pesticides (diazinon, parationmetil and malation), RSD and recovery values for grape and orange were found to be compatible with our results (Dorea et al., 1996). Tian et al. tried to determine six organophosphorus pesticides in water

with GC-NPD. They obtained the recoveries 97% for diazinon, 70.6% -91.2% for parationmethyl sand 86.7% -107.5% for were malation. These results are in compatible with our results (Tian et al., 2014). Canbay et al. analyzed pesticide residues in the lake and sediment with GC-ECD and NPD. %RSD, %recovery values are compatible with our results (Canbay et al., 2014). 2.5 µg L^{-1} was selected as low value for recoveries however recoveries of methamidophos was selected 5 µg L^{-1} because of the lowest calibration value. High recoveries were observed for most studied pesticides at the highest spiking concentration level of 25 µg L^{-1}. Variability in recoveries will be higher by approaching to concentrations near to LOQ. Table (3) shows the average recoveries %, Standard deviation (SD) and the relative standard deviation (RSD %) for pesticides compounds residue in water.

Limits of Detection (LODs) and Quantification (LOQs)

12 analyses were carried out at 5 µg L^{-1} for LODs and LOQs. The standard deviation was calculated for each pesticide and 3 and 10 times of these values was used for calculation of LODs and LOQs respectively. The LODs values ranged between 0.67 and 2.23 µg L^{-1} and the LOQs values ranged between 2.24 and 7.45 µg L^{-1} (Table 4). The relative standard deviation (RSD%) was <15% for most pesticides.

Table 4. LOD, LOQ, Mean, SD, RSD values at 5 µg L^{-1}.

	Retention Time	Mean	SD	RSD	RSD%	LOD	LOQ
methamidophos	5.17	4.125	0.272	0.066	6.600	0.817	2.722
demeton	7.68	3.871	0.372	0.096	9.610	1.116	3.720
simazine	8.35	5.343	0.639	0.120	11.963	1.918	6.392
atrazine	8.48	5.410	0.453	0.084	8.379	1.360	4.533
diazinon	8.67	4.499	0.232	0.052	5.161	0.697	2.322
disulfoton	8.82	4.946	0.225	0.045	4.544	0.674	2.247
chlorpyrifos methyl	9.21	5.200	0.667	0.128	12.836	2.002	6.674
parathion methyl	9.27	4.628	0.705	0.152	15.241	2.116	7.053
malathion	9.62	3.003	0.371	0.124	12.353	1.113	3.710
chlorpyrifos ethyl	9.74	5.198	0.745	0.143	14.332	2.235	7.449
parathion ethyl	9.83	5.175	0.448	0.086	8.650	1.343	4.476
ethion	12.39	5.213	0.288	0.055	5.521	0.863	2.878

CONCLUSION

In this work, a new multi-residue method to analyze for 12 pesticide residues in a single injection in water samples was developed. The instrumental analysis was carried out approximately 12 minutes by GC/NPD detector, however total analysis time was enlarged for cleanup of column in high temperature. The period of extraction is decrease with six cellular in Turbowap evaporator system for application in routine analysis where a high sample throughput is required. The method provides sensitivity, selectivity, detection limits in the parts-per-billion level and good repeatability for the simultaneous analysis of residue of pesticides belong to different chemical classes (two herbicides and ten organophosphate pesticides) in water samples. The developed method was validated in order to ensure the applicability of the method for routine analysis. Parameters such as linearity, trueness (recovery), precision (reproducibility and repeatability), LODs and LOQs were studied in the validation.

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