Method Validation of Pesticide Residues in Water By Gas Liquid Chromatography

Sanaa A.M. El-Sawi, Abir A. El-Gohary and Aly A. Mahmoud

Central Lab. of Analysis of Pesticide and Heavy Metals Residues in Foods, Agricultural Research Center, Dokki, Giza, Egypt

ABSTRACT

An applicable gas chromatographic (GC) method was found to be specified to determine the residues of certain organochlorine, organonitrogen and organophosphorous pesticides in several types of water (e.g. drinking water, ground water and irrigating water).The method performance was tested on 72 pesticides representing different types of pesticides. The average recovery of these pesticides using a concentration range 0.01-12.8 μg/l (ppb) varied between 73-119%. The reproducibility expressed as relative standard deviation was less than 15%. The method showed to be linear at least up to 12.8 μg/l except some compounds which showed to be linear up to 0.8 μg/l. The limit of quantitation (LOQ) in water samples was 0.01-0.2 μg/l. The measurement expressed as expanded uncertainty and in terms of relative standard deviation (at 95% confidence level) was found to be within the range of ±35.

INTRODUCTION

Pesticides are used for controlling fungi, weeds and insects. Chemical plant protection agents should be applied at specific concentrations according to agro technical needs. Misuse of pesticides can lead to excessive contamination of the environment, i.e. soil, water and air. Herbicides, fungicides, insecticides, fertilizers, molluscicides, food additives and synthetic dyes and other chemical pollutants are present in Egyptian environment. Accumulation of pesticides in the environment results in high levels of these dangerous chemicals in crops and animal feed, which ultimately leads to human exposure. Potential toxicity of pesticides is the main hazard associated with their agricultural use. Human population can be exposed to these toxic chemicals via the gastrointestinal tract, respiratory system, as well as through the skin. Occupation or accidental exposure to high doses of pesticides can result in life-threatening poisoning. However, long term environmental exposure also has a negative impact on health. This is particularly important

when human populations are exposed to pesticides by drinking contaminated water **(Badach et al., 2007)**.There are several sources of drinking water contamination by pesticides. The main source is pesticide leaching to ground water following application on agricultural fields. Another important factor is the inappropriate pesticide handling, storage and disposal. Dangerous could be also due to improper equipment cleaning practices, storage and disposal of expired pesticides in unsealed pits. Clearly, rural populations sustain much higher exposures to pesticides, particularly due to consumption of contaminated water, than urban populations which are exposed mainly by consumption of food containing pesticide residues. **El-Sebae and Abo- Elamayem (1978)** monitored the chlorinated insecticides in Alexandria city. Their data indicated that classical water treatment might reduce the organochlorine insecticides level, but still there is an appreciable level of these pollutants in the tap drinking water. Also, **Ernst et al., (1983)** reported that the detected organochlorine compound levels were low but still have the hazardous potential as source of continuous bioaccumulation and biomagnification in the food chain. Prolonged exposure to pesticides through consumption of contaminated water has been linked with increased risk of certain types of cancer **(Contor, 1997)**. Thus, contamination of drinking water by pesticides may have a damaging impact on public health and needs to be continuously monitored, sinc : cytotoxic effects were reported for number of pesticides **(El- Sebae et al., 1981)**.

MATERIAL AND METHODS
APPARATUS
Graduated cylinder 500 ml
Separatory funnel 1000 ml
Funnel 10 cm diameter
Round bottom flask
Rotary evaporator (Heidolph WB 2000),
Pippette 2 ml
Gas Chromatograph equipped with two electron capture detectors for organochlorine pesticides (HP 6890 series).
Gas Chromatograph equipped with two Nitrogen-Phosphorous detectors for organophosphorus and organonitrogen pesticides (HP 6890 series).

Reagents
Dichloromethane (DCM) (Lab-scan), (Pestiscan), or similar quality
Sodium Chloride, (Reagent Grade), or similar quality

Anhydrous Sodium Sulphate, granular, (Reagent Grade), or similar quality

Preparation of standard solutions

The standard solutions were prepared according to the **Pesticide Analytical Manual (1994).**

Method of Analysis

Extraction and Partitioning

- Take 500 ml of the water sample into 1000 ml separatory funnel; add 5 g of Sodium sulphate anhydrous and around 5 g of sodium chloride.
- Transfer 50 ml dichloromethane (DCM) to the separatory funnel and extract the sample by vigorously shaking for a minute with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for 10 minutes.
- Filter the organic layer through 10cm funnel system fitted with a piece of cotton and packed with about 20 g of sodium sulphate anhydrous, into a round bottom flask.
- Add a second 50 ml of DCM to the separatory funnel (aqueous layer) and repeat the extraction procedure for the second time, combining the extracts on the same flask.
- Repeat the same step for the third time.

If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or other physical methods.

- Rinse Sodium sulphate anhydrous with about 25 ml DCM.
- Evaporate till dryness with Rotary evaporator at 40°C.
- Add 2 ml of injection standard then inject the sample on different GC systems **(AOAC, 2003).**

GC measurements

1-Parameters of ECD

HP 6890 gas chromatograph instrument was used at the following conditions:

Injector temperature = 225°C   Detector temperature = 300°C

Capillary columns:

A) Hewlett Packard PAS-5 (ECD tested Ultra 2 Silicone)	B) Hewlett Packard PAS-1701 (ECD Tested 1701 Silicone)
Column ID: 0.32 mm	Column ID: 0.32 um
Film thickness: 0.52 um	Film thickness: 0.25 um
Column length: 25 m	Column length: 30 m
Flow rate of nitrogen: 1 5 ml/min carrier, total flow (carrier + makeup) 55 ml/min	Flow rate of nitrogen: 1.3 ml/min carrier, total flow (carrier + makeup): 55 ml/min

Septum purge: 3 ml/min, purge flow 50 ml/min, purge time 0.7 min

Oven program:

initial temp: 90°C   Initial time: 2 min.

Level	Rate (°C/min)	Temp (°C)	Time (min)
(1)	20	150	0
(2)	6	270	15

2- Parameters of NPD

Adjust the gas chromatography instrument for:

Injector temp = 225°C   Detector temp A = 280°C

Detector temp B = 280°C

Capillary columns:

A) Hewlett Packard PAS-5 (Cross linked 5% PH ME Silicone)	B) Hewlett Packard PAS-1701
Column ID: 0.32 mm	Column ID 0.32 um
Film thickness: 0.25 um	Film thickness. 0.25 um
Column length: 25 m	Column length: 30 m
Flow rate of nitrogen: 1 5 ml/min carrier, total flow (carrier + makeup): 55 ml/min	Flow rate of nitrogen: 1.3 ml/min carrier

Septum purge: 5 ml/min, splitless time 0 75 min, purge flow: 34 ml/min.

Oven program:

Initial temp: 90°C

Initial time: 2 min

Level	Rate (°C/min)	Temp (°C)	Time (min)
(1)	20	150	0
(2)	6	270	15

Air flow 60 ml /min

Carrier gas Nitrogen

Detecor A gas (N_2) flow rate = 8 ml/min, H_2 flow rate = 4 5 ml/min

Detector B gas (N_2) flow rate = 6 ml/min, H_2 flow rate = 4 8 ml/min

Calculation of the results
Calculate the analyte concentration in sample Cs (µg/l) by the following equation:

$$Cs = \frac{As/Ais}{Ast/Aist} \times Cst \times \frac{Vf}{Va}$$

Where:
A_s = Peak area of analyte in sample
A_{is} = Peak area of injection standard in sample
Ast = Peak area of analyte in standard run
Aist = Peak area of injection standard in standard run
Cst = Amount of the analyte in sample
Vf = final volume (2 ml)
Va = Sample volume (500ml)

Quality Control
Spiked Samples:
    The performance of the method is continuously tested with tested standard solution of pesticides at different concentrations according to the pesticide type. Blank sample is fortified with 100 µl of   standard solution and analyzed as normal samples. The spiked sample must be analyzed with each set of samples.

Control Chart
    The results of the spiked samples are collected into the control charts. In case of individual control point which lies outside, the specifications immediate action must be taken to discover the reason of the deviation and to make required corrections. If the reason has obviously affected the analysis of real samples, also these results should be corrected (usually by repeating analysis).

Blank samples
    Injection of blank matrix (samples not treated with pesticides) may be used to detect possible matrix interference. In routine analysis of large number of same commodities, the importance of blank analysis is relatively small if most of the samples are negative. However, if the same pesticide is found in several subsequent samples, the reason of contamination should

be studied if an interfering peak higher than limit of determination appears at retention time of any pesticide.

RESULTS AND DISCUSSION

As water pollution by pesticides can affect many biological systems, the widespread use of potentially harmful pesticides has recently come under scrutiny in Africa (**Kaminska et al., 2004 and Thrupp, 1996**). Once contaminated, the groundwater may take a long time to clear (**Prenazzi and Ziglio, 1995**) and there is always the danger of bioaccumulation. This method is used to detect very little amount of organochlorines, organonitrogene and organophosphorus pesticides at the concentration of µg/l. The recoveries of 72 pesticides are ranged between 73-119%. Typical validation characteristics for impurity tests {accuracy (trueness and precision) and linearity} were obtained by carrying out a simple method, to determine pesticide residues in water using Gas Liquid Chromatography (GLC).

Accuracy:

Accuracy expresses the closeness of a result to a true value. Accuracy is expressed in terms of two components: "Trueness" and "Precision".

1. Trueness:

The trueness of a method is an expression of how close the mean of a set of results (produced by the method) is to the true value. To check trueness of the method, spiked samples are used at different levels. Bias expressed as absolute relative difference percent (RD %) must not exceed 20 %.

2. Precision:

Precision is a measure of how close results are to one another. The two most common precision measures are (repeatability) and (reproducibility).

2.1. Repeatability:

Qualitatively is the closeness of agreement between successive results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory and short intervals of time).

The repeatability experiments were performed with ten replicates of spiked samples by same operator, same apparatus, same method and short intervals of time. The relative standard deviation (CV %) was ≤ 15 %.

2.2. Reproducibility:

Reproducibility is the precision under reproducibility conditions, i.e. conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment. In this study intra-laboratory reproducibility will only be considered, water samples fortified at spiking level are analyzed by different analysts on several days. The relative standard deviation (CV %) was ≤ 14 %.

Linearity:

Method linearity was checked by making recovery tests at different levels limit of quantification (LOQ), spiking level and high concentration for 72 compounds. The method found to be linear from LOQ up to high level. The correlation coefficient was found not less than 0.9992. Data in Tables 1-4 illustrate that the mean recoveries for the tested pesticides in spiking level ranged between 73-119% for fortified levels ≤ 2µg/l.

Table 1 shows the average recoveries % and the coefficient of variation (CV%) for the organophosphorus compounds residue in fortified water. Table 2 shows the studied parameters for the organonitrogenous residue levels and Table 3 shows those of the organoclorines, while Table 4 illustrates the data of the other tested residue level of different compound.

The limit of quantification (LOQ) was ranged between 0.01 to 0.2µg/l with a general recovery ranged between 89-114% which means how much this method is accurate. The coefficient of variation (CV) of the data reflects how much the results are close to each other that gives a good idea about the efficiency of this method (<14).

The recovery tests for 72 compounds prepared in 12 mixtures were fortified in water on different concentration levels. The average relative standard deviation on each level was calculated.

Table (1): The average recoveries % and the coefficient of variation (CV %) for organophosphorus compounds residues levels in fortified water.

Compound	Uses	spiking level (µg/l)	n	Average Recovery (%)	CV (%)
.Malathion	I	0.06	6	91	7.98
		0.60	6	88	4.62
		4.80	6	100	4.50
Dimethoate	I	0.06	6	92	7.44
		0.60	6	99	1.15
		4.80	6	114	5.63
Chlorpyrifos	I	0.06	6	97	8.31
		0.60	6	89	6.82
		4.80	6	101	3.35
Pirimiphos-methyl	I	0.06	6	93	5.53
		0.60	6	88	8.32
		4.80	6	104	4.43
Profenofos	I	0.06	6	93	5.53
		0.60	6	94	6.34
		4.80	6	100	3.83
Fenitrothion	I	0.06	6	97	3.52
		0.60	6	91	4.00
		4.80	6	108	4.97
Parathion-methyl	I	0.06	6	106	3.75
		0.60	6	93	4.64
		4.80	6	106	4.23
Diazinon	I	0.06	6	92	13.85
		0.60	6	79	4.53
		4.80	6	110	3.22
Triazophos	I,A	0.06	6	101	8.12
		0.60	6	88	8.53
		4.80	6	105	7.30
Chlorpyrifos-methyl	I	0.06	6	99	5.16
		0.60	6	91	5.44
		4.80	6	105	4.85

I = Insecticide, A = Acaricide

Table (1) continued

Compound	Uses	spiking level (µg/l)	n	Average Recovery (%)	CV (%)
Cyanophos	I	0.20	6	100	5.48
		2.00	6	102	5.61
		16.00	6	105	1.76
Prothiophos	I	0.06	6	99	4.60
		0.60	6	93	5.59
		4.80	6	99	5.18
Fenthion	I	0.06	6	94	6.01
		0.60	6	93	5.56
		4.80	6	106	4.66
Pyrazophos	F	0.06	6	95	3.39
		0.60	6	96	3.81
		4.80	6	99	3.06
Tolclophos-methyl	F	0.06	6	98	4.78
		0.60	6	89	4.03
		4.80	6	110	4.76
Parathion-ethyl	I	0.06	6	98	3.94
		0.60	6	93	3.78
		4.80	6	103	2.35
Phosalone	I,A	0.06	6	94	5.10
		0.60	6	95	4.43
		4.80	6	92	7.15
Pirimiphos-ethyl	I	0.06	6	99	4.20
		0.60	6	92	4.17
		4.80	6	107	2.35
Phosphamidon	I	0.10	6	106	6.98
		1.00	6	96	1.77
		8.00	6	90	2.52
Phenthoate	I	0.10	6	109	8.88
		1.00	6	87	6.07
		8.00	6	100	2.36
Ethion	I,A	0.08	6	104	4.13
		0.80	6	89	3.00
		6.40	6	91	3.69
Ethoprophos	N	0.08	6	101	3.07
		0.80	6	98	4.87
		6.40	6	96	5.07

I = Insecticide, A = Acaricide, N = Nematocide I = Insecticide,   F = Fungicide

Table (2): The average recoveries % and the coefficient of variation (CV %) for organonitrogenous compounds residues levels in fortified water.

Compound	Uses	spiking level (µg/l)	n	Average Recovery (%)	CV (%)
Pirimicarb	I	0.06	6	93	5.69
		0.60	6	102	4.48
		4.80	6	99	4.66
Bupirimate	F	0.06	6	99	5.78
		0.60	6	109	2.33
		4.80	6	98	4.95
Bendiocarb	I	0.20	6	103	8.42
		2.00	6	97	6.49
		16.00	6	92	3.29
Metalaxyl	F	0.20	6	103	2.14
		2.00	6	99	5.13
		16.00	6	92	1.63
Procymidone	F	0.06	6	101	6.51
		0.60	6	110	4.94
		4.80	6	105	2.16
Carbosulfan	I	0.06	6	91	8.89
		0.60	6	90	7.92
		4.80	6	99	2.56
Atrazine	H	0.06	6	91	2.22
		0.60	6	99	1.63
		4.80	6	108	2.20

I = Insecticide, F = Fungicide, H = Herbicide

Table (2): Continued

Compound	Uses	spiking level (µg/l)	n	Average Recovery (%)	CV (%)
Buprofezin	I	0.20	6	105	3.65
		2.00	6	96	3.27
		16.00	6	99	1.38
Thiobencarb	H	0.20	6	101	5.87
		2.00	6	99	2.15
		16.00	6	100	0.62
Vinclozolin	F	0.01	6	98	8.56
		0.10	6	96	5.56
		0.80	6	95	6.32
Iprodione	F	0.10	6	82	8.20
		1.00	6	78	3.36
		8.00	6	116	4.20
Trifluralin	H	0.02	6	113	6.42
		0.20	6	104	6.99
		1.60	6	95	12.66
Dichlofluanid	F	0.02	6	97	6.97
		0.20	6	104	4.60
		1.60	6	107	4.12
Triadimefon	F	0.02	6	105	2.13
		0.20	6	113	4.65
		1.60	6	104	4.46
Oxadiazon	H	0.06	6	102	4.46
		0.60	6	107	5.21
		4.80	6	93	8.42
Pendimethalin	H	0.06	6	99	6.71
		0.60	6	102	6.25
		4.80	6	87	3.94
Metribuzin	H	0.06	6	111	2.90
		0.60	6	101	2.31
		4.80	6	105	0.83

I = Insecticide, F = Fungicide, H = Herbicide

Table (2): Continued

Compound	Uses	spiking level (µg/l)	n	Average Recovery (%)	CV (%)
Chlorfenpyr	I,A	0.04	6	114	5.50
		0.40	6	107	11.19
		3.20	6	95	9.53
Fenarimol	F	0.04	6	97	7.19
		0.40	6	97	7.02
		3.20	6	97	3.00
Diniconazol	F	0.04	6	98	8.56
		0.40	6	96	5.56
		3.20	6	95	6.32
Propiconazole	F	0.06	6	108	9.39
		0.60	6	96	2.59
		4.80	6	110	3.16
*Imazalil	F	2.00	6	102	6.70
		16.00	6	100	4.28

*out of scope I = Insecticide, ⁻ = Fungicide, A = Acaricide

Table (3): The average recoveries % and the coefficient of variation (CV%) for organochlorine (chlorinated hydrocarbons) compounds residues levels in fortified water.

Compound	Uses	spiking level (µg/l)	n	Average Recovery (%)	CV (%)
Flusilazole	F	0.20	6	101	2.64
		2.00	6	99	6.32
		16.00	6	103	7.87
Lindane	I	0.01	6	91	6.32
		0.10	6	85	7.87
		0.80	6	107	3.92
Bromopropylate	A	0.02	6	101	8.02
		0.20	6	104	4.43
		1.60	6	95	5.38
Tetradifon	A	0.02	6	98	9.47
		0.20	6	108	5.42
		1.60	6	100	5.81
δ-HCH	-	0.02	6	94	6.32
		0.20	6	97	7.87
		1.60	6	100	3.92
DDE-p,p	-	0.01	6	94	4.07
		0.10	6	83	6.36
		0.80	6	103	3.21
β-HCH	-	0.01	6	89	5.60
		0.10	6	84	8.88
		0.80	6	91	8.29
Heptachlor	I	0.01	6	99	7.37
		0.10	6	81	13.81
		0.80	6	112	4.28
α-Endosulfan	I	0.01	6	100	6.68
		0.10	6	86	6.82
		0.80	6	111	3.24
β-Endosulfan	I	0.01	6	100	11.02
		0.10	6	87	5.49
		0.80	6	110	5.21

I = Insecticide, F = Fungicide, A = Acaricide

Table (3): Continued

Compound	Uses	spiking level (μg/l)	n	Average Recover y (%)	CV (%)
α-HCH	-	0.01	6	100	7.34
		0.10	6	95	8.83
		0.80	6	101	10.95
Chlorothalonil	F	0.01	6	100	7.17
		0.10	6	83	4.31
		0.80	6	113	3.32
Dieldrin	I	0.01	6	99	7.14
		0.10	6	92	8.39
		0.80	6	92	4.24
DDT-O,P	-	0.01	6	102	6.99
		0.10	6	107	12.66
		0.80	6	110	3.54
Hept.Exo epoxide	-	0.01	6	107	2.02
		0.10	6	108	9.22
		0.80	6	111	2.24
Endrin	I	0.01	6	99	5.78
		0.10	6	105	6.43
		0.80	6	93	3.62
DDD-P,P	I	0.01	6	95	10.65
		0.10	6	98	11.97
		0.80	6	95	5.23
HCB	F	0.01	6	104	8.83
		0.10	6	92	6.87
		0.80	6	73	11.73
Endosulfan Sulfate	I	0.04	6	107	11.09
		0.40	6	113	6.00
		3.20	6	94	4.79

I = Insecticide, F = Fungicide

Table (4): The average recoveries % and the coefficient of variation (CV %) for the other tested residue levels in fortified water.

Compound	Uses	spiking level (µg/l)	n	Average Recovery (%)	CV (%)
Fenvalerate	I	0.02	6	106	8 14
		0.20	6	97	7.36
		1.60	6	103	2.55
Cypermethrin	I	0.10	6	105	11.92
		1.00	6	87	5.86
		8.00	6	103	8.62
Permithrin	I	0.02	6	94	6.59
		0.20	6	107	3.04
		1.60	6	100	5.07
Cyfluthrin	I	0.20	6	92	7.03
		2.00	6	109	11.01
		16.00	6	88	5.92
L-Cyhalothrin	I	0.06	6	96	5.94
		0.60	6	107	6.98
		4.80	6	98	4.83
Esfenvalerate	I	0.04	6	100	6.50
		0.40	6	110	10.16
		3.20	6	96	6.81
Fenopropathrin	I	0.04	6	108	8.58
		0.40	6	119	5.53
		3.20	6	93	9.01
Tau-Fluvalenate	I	0.16	6	100	1.69
		1.60	6	98	7.79
		12.80	6	100	4.19
Deltamethrin	I	0.10	6	98	9.31
		1.00	6	98	1.03
		8.00	6	99	5.64

I = Insecticide. F = Fungicide, A = Acaricide

CONCLUSION

A simple procedure using gas chromatography (GC) was found to be very efficient in determination of different pesticide residues in water.

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الملخص العربى

طريقة لتقدير متبقيات المبيدات فى المياه بواسطة أجهزة الكروماتوجرافى الغازى

سناء عبد القادر الصاوى و ربيع أحمد الجوهرى و على على محمود

المعمل المركزى لتحليل متبقيات المبيدات والعناصر الثقيلة – الدقى – الجيزة

تم تقدير متبقيات المبيدات بواسطة طريقة عملية متخصصة يستخدم فيها أجهزة الكروماتوجراف الغازى يمكن تطبيقها لتحليل متبقيات المبيدات الكلورينية والفوسفورية والنيتروجينية فى أنواع المختلفة من المياه   (مياه الشرب والمياه الجوفية ومياه الرى) . تم إختبار كفاءة الطريقة على ٧٢ مبيد ممثلة لأنواع مختلفة من المبيدات وكان متوسط معدل الإسترجاع لهذه المبيدات بتركيز يتراوح بين ٠,٠١ - ١٢,٨ ميكروجرام لكل لتر ٧٣) كما فى مركب اسكهكلوروبنزين من مجموعة الكلورين العضوية من مجموعة البيريثرويدات] العضوية %١١٩) كما فى مركب فينيتروبيونثرين [وكانت متبقيات المبيدات بعض اعداد لكل لتر ميكرجرام ١٢,٨ بتركيز حتى خطية أنها الطريقة أظهرت). المختلفة] وحتى تركيز ٠,٨ ميكروجرام لكل لتر . تحت أقل كمية من متبقيات المبيدات المستخدمة والتى يمكن تقديرها بين ٠,٠١ - ٠,٢ ميكروجرام لكل لتر (جزء فى البليون لكل لتر). وقد تراوح الإنحراف القياسى المقدر (CV%) ما بين ١,٠٣ - ١٤,٠٥ %.