

Gas Chromatography-Mass Spectrometric Method for Simultaneous Separation and Determination of Several Pops with Health Hazards Effects

Nagwa ABO EL-Maali* and Asmaa Yehia Wahman

Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt

Abstract

The hazards effect of persistent organic pollutants, POPs, on the human health has lead us to modify the ASTM method D-5175 to enhance both sensitivity and selectivity of their simultaneous separation. As their separation is difficult- due to the similarity in their chemical and physical properties- that lead to co-elution in extraction, we proposed a validated method for their simultaneous determination using liquid/liquid microextraction followed by GC/MS in the SIM mode. The method is advantageous since the time needed for the chromatographic analysis of all analytes is less than 17 min. Method Detection Limits (MDLs) and Limit of Detection (LODs) reached sub- ppb levels and in many cases are lower than those achieved in the standard test method ASTM D-5175 for many analytes. Besides, three pesticides namely: Hexachlorocyclopentadiene, p,p'-DDE and trifluralin have been added to the method with good accuracy and precision. Application to several environmental samples has been successfully assessed and supported by proficiency testing samples provided from Absolute Standards®, Inc.

Keywords: GC-MS; POPs; Validation; Application to environmental matrices

Introduction

The importance of the Persistent Organic Pollutants (POPs) with their health effects has lead to looking for accurate and reliable methods for their determinations [1-6] using chromatographic techniques in many matrices viz. ground water [2], human serum [3,4] water and drinking water [5,6], fruits and vegetables [1,7] and tap water [8].

Organochlorines (OCs) are a lipophilic class of chemicals that include OC pesticides and other persistent organic pollutants, such as Polychlorinated Biphenyls (PCBs). It is well known that environmental and/ or dietary exposure to OCs results in the bioaccumulation of these chemicals in the human body especially, in adipose tissue, serum and breast milk [9,10].

Despite of the long-term adverse effects on humans, animals and environment [11], recent studies in East-Asian countries have reported elevated concentration of OCPs in various environmental media suggesting that same OCPs are still being used [12]. OC-exposure has been linked with a number of children diseases such as asthma, abnormalities of the productive tract, diabetes, and growth and neurobehavioral disorders [13,14]. In Spain [15,16], the level of chemical contamination by OCs of the population of the canary Island has been evaluated although they're banned in Spain in the late 1970s. In US, PCBs exposures are encountered by the general public by eating contaminated food or living near a previously operating PCB factory hazardous waste site [17], although they are banned in the United States in 1977. PCBs have been classified as probable human carcinogenic and are listed in the top 10% of EPA's most toxic chemical [18]. Of the 209 PCBs congeners four non-ortho and eight mono-ortho congeners are currently recognized by the World Health Organization (WHO) as "dioxin like" in their toxic effects [19]. Routine analysis of OCs in environmental in different matrices has been achieved through GC/MS and different extraction techniques [20-23].

Therefore, the aim of the present work is to validate and enhance the sensitivity of the ASTM method D5175 for the determination of OCPs viz. Alachlor, Aldrin, Dieldrin, Endrin, Heptachlor, Heptachlorepoxyde, Hexachlorobenzene, lindane, Methoxychlor, PCBs congeners namely: PCB 28, 52,118,138, and 180 cited in Table 1 in the presence of the new analytes viz. Hexachlorocyclopentadiene,

p,p'-DDE and the organofluorine pesticides trifluralin in other matrices viz. waste water and transformer oils with new levels lower than those cited in the literature.

Experimental

Chemicals and reagents

Organochlorine pesticides: Alachlor, aldrin, dieldrin, endrin, heptachlor, heptachlorepoxyde, hexachlorobenzene, hexachlorocyclopentadiene, lindane, methoxychlor, p,p'-DDE and the organofluorine one- trifluralin -with purity higher than 96.0% and PCBs 28, 52, 118, 138 and 180 with purity higher the 96.0% were acquired from Sigma, reference standards are acquired from AccuStandards®, Inc Lot # 209111013 and AbsoluteStandards®, Inc Lot # 032409. Proficiency testing samples are from AbsoluteStandards®, Inc Lot # 091608. Sodium chloride, Sigma, sodium thiosulfate, Merck. Methanol, Hexane and acetone (HPLC grade) were from Sigma. Ultrapure water used was from Milli-Q system model: Milli-Q Gradient A10, Elix 3UV and Tank 60L, Serial NO: F7AN24007K F7BN90274I, USA.

Preparation of standards

Standard solution, Stock: These solutions prepared from pure standard materials of each PCBs and Pesticides (1000 µg/ml).

- By accurately weighting about 1.0 mg of pure material. Dissolve the material in 1 ml of methanol absolute in 1.5 ml vials; the weight is used without correction to calculate the concentration of the stock.

*Corresponding author: Nagwa ABO EL-Maali, Department of Chemistry, Faculty of Science, Assiut University, 71516-Assiut, Egypt, Tel: 0020-882-080-799; E-mail: nelmaali@live.com

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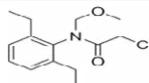
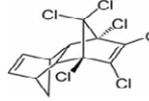
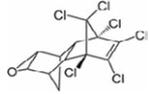
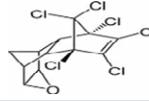
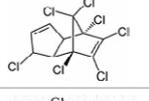
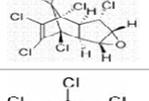
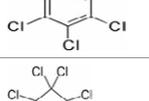
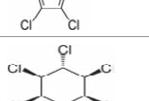
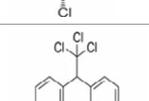
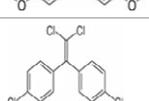
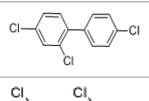
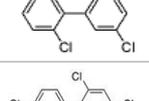
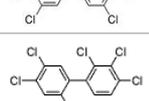
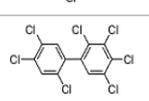
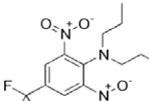
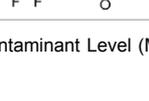
Analyte Name	Chemical structure	MCL, μgL^{-1} , EPA	Health effect
Alachlor		2.000	Eye, liver, kidney or spleen problems; anemia; increased risk of cancer
Aldrin		0.030*	Both aldrin and dieldrin are highly toxic to humans, the target organs being the central nervous system and the liver. Severe cases of both accidental and occupational poisoning and a number of fatalities have been reported
Dieldrin		0.030*	
Endrin		2.000	Liver problems
Heptachlor		0.400	Liver damage; increased risk of cancer
Heptachlor epoxide		0.200	Liver damage; increased risk of cancer
Hexachlorobenzene		1.000	Liver or kidney problems; reproductive difficulties; increased risk of cancer
Hexachlorocyclopentadiene		50.000	Kidney or stomach problems
Lindane		0.200	Liver or kidney problems
Methoxychlor		40.000	Reproductive difficulties
p,p'-DDE		1.000*	Exposure to technical-grade DDT, an increased risk for pancreatic cancer could not be excluded. Pesticide applicators are exposed primarily to p,p'-DDT, whereas it is the p,p'-DDE metabolite to which the general population is exposed in the diet or drinking-water.
PCB 28		0.500	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer
PCB 52			
PCB 118			
PCB 138			
PCB 180			
Trifluralin		20.000*	In a study in the USA, the use of trifluralin was associated with an increased risk for non-Hodgkin lymphoma. In contrast, a study of ovarian cancer in Italy did not suggest an association with trifluralin exposure. In both studies, the numbers of exposed subjects were small. A larger study in the USA showed no association with leukaemia (20). IARC concluded that there is inadequate evidence in humans for the carcinogenicity of trifluralin (20).

Table 1: Structure, Maximum Contaminant Level (MCL) and health effects for Pesticides (OCP, OFP) and polychlorinated biphenyls (PCBs) under investigation. *MCL from WHO.

- Store standard solution in freezer and protect from light. Stock standard solution should be checked frequently for assign degradation or evaporation, especially prior to preparation calibration standard from them.
- Store standard solution must be replaced if comparison with checked standard indicates a problem.

Standard solution, secondary dilution: Use the stock standard solution to prepare secondary dilution standard solution in methanol and check frequently for singe of degradation evaporation especially just before preparing calibration standard.

Sample preparation and collection

- When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 ml/min and collect samples from the flowing stream.
- When sampling drinking, surface, well , and waste water a sampling water apparatus model Easy-Load[®] Masterflex[®] USE 15, 24 TUBING Model:7518-12 part No: 4,813,855 Assembled in USA is used.

Sample preservation and storage

In 1 L empty bottle, add 8 mL of 1 M sodium thiosulfate just prior to sample collection. The samples must be chilled to 4°C at the time of collection and maintained at that temperature until the analyst is prepared for the extraction process. Store samples and extracts at 4°C until analysis has been completed. Extract all samples as soon as possible after collection. Results of holding time studies suggest that all analytes were stable for 14 days when stored under these conditions.

Instrumentation

GC separation was performed using Gas Chromatograph from Agilent Technologies Model 7890A equipped with temperature programming capability, splitless injector, capillary column, and Mass Quadrupole Spectrometry detector Model 5975B. A computer data system is MSD Chem Station E.0201.1177 used for measuring peak areas and heights.

Gas chromatograph parameters

The analytical columns used were DB-1701P (30 m × 0.25 mm × 0.25 μm), Agilent Part No.122-7732 as a primary column and DB-5ms (30 m × 0.25 mm × 0.25 μm), Agilent Part No.122-5532 as a secondary one, the oven temperature was set at 60°C for 0.50 min, increased to 140°C at 120°C/min, 260°C at 11°C/min then to 260°C for 5.5 min. The volume of the injected sample was 1 μL in split less mode. The injector temperature was set at 250°C. Helium (99.999%, purity) was used as carrier constant flow, 1 mLmin⁻¹.

Mass spectrometer parameter

The mass spectrometer was operated in electron impact (70 eV of ion energy), with 4.0 min solvent delay, SIM acquisition mode, mass quadruple and mass source kept at 150°C and 230°C.

Data analysis

Analysis of data is done using Microsoft[®] Office Excel 2003 (11.5612.5606) Part of Microsoft Office Professional Edition 2003, Product ID: 73931-640-0000106-75603.

Extraction procedure

Stored samples are removed from the fridge and allow to equilibrate to room temperature. To 35 ml of each sample, add 6 g NaCl in the separating funnel. Recap and dissolve the NaCl by inverting and shaking several times (approximately 30 sec). Remove the cap, add 2 ml of n-hexane recap and shake vigorously by hand for 2 min, inverting the separating funnel while shaking. Stand the separating funnels upright and allows the water and hexane phases to separate. Transfer 0.5 ml of hexane layer into an auto sampler vial; inject 1 μl portions into the gas chromatograph for analysis.

For transformer oil samples, solid phase extraction procedure using AccuBOND II FLORISIL Cartridges provided from Agilent Part No. 188-2460 was applied using the following method: weigh 0.2 gm of the transformer oil sample, pass through the FLORISIL Cartridges followed by flush five times with 2 mL aliquots of n-Hexane, the eluent was collected in a 10 mL volumetric flask then completed to the mark and mix thoroughly prior to the GC/MS analysis.

Results and Discussion

GC-MS separation

To confirm the retention times of the POPs – under investigation- OCPs, OFP and PCBs, a mass range of 50-500 m/z was scanned. Thereafter the SIM mode was applied to monitor the mixture. The selected ions (m/z) used for confirmation and quantification are cited in Table 2. POPs- under investigation- are eluted from the column in the following order: Hexachlorocyclopentadiene, Hexachlorobenzene, Trifluralin, lindane, PCB 28, Heptachlor, PCB 52, Aldrin, Alachlor, Heptachlorepoxide, p,p'-DDE, Dieldrin, PCB 118, PCB 138, Endrin, PCB180 and Methoxychlor (Figure 1). It is worthy to mention that the time needed for the chromatographic analysis is less than 17 min.

Optimization of the extraction procedure

In order to achieve the highest recoveries for the compounds under investigation, different organic solvents have been tried for this purpose, among them hexane and dichloromethane. With hexane only 2 ml for 2 min gave rise to best recovery all the analytes under investigation while using dichloromethane it needs 6.3 ml for 6 min is required.

Analyte	Primary Ion	Secondary Ion(s)
Alachlor	45.0	146.1, 160.1, 188.1, 224.1
Aldrin	66.0	44.0, 79.0, 91.0, 262.0
Dieldrin	79.0	44.0, 108.1, 262.9, 276.9
Endrin	81.0	67.0, 263.0, 79.0, 53.0, 261.0, 265.0
Heptachlor	100.0	272.0, 65.0, 237.0, 102.0
Heptachlorepoxide	81.0	44.0, 236.8, 262.9, 352.9
Hexachlorobenzene	284.0	286.0, 282.0, 249.0, 288.0
Hexachlorocyclopentadiene	237.0	239.0, 235.0, 272.0, 95.0
Lindane	181.0	183.0, 111.0, 219.0, 109.0
Methoxychlor	227.1	44.0, 113.7, 152.1, 212.1
p,p'-DDE	246.0	105.0, 176.0, 210.0, 318.0
PCB 28	256.0	257.0, 258.0, 259.0, 260.0
PCB 52	292.0	255.0, 257.0, 290.0, 294.0
PCB 118	325.9	254.0, 256.0, 323.9, 327.9
PCB 138	359.9	287.9, 289.9, 357.9, 361.9
PCB 180	393.9	323.9, 395.9, 397.9
Trifluralin	306.0	43.0, 264.0, 248.1, 290.0

Table 2: Characteristic ions for the investigated pesticides and PCBs.

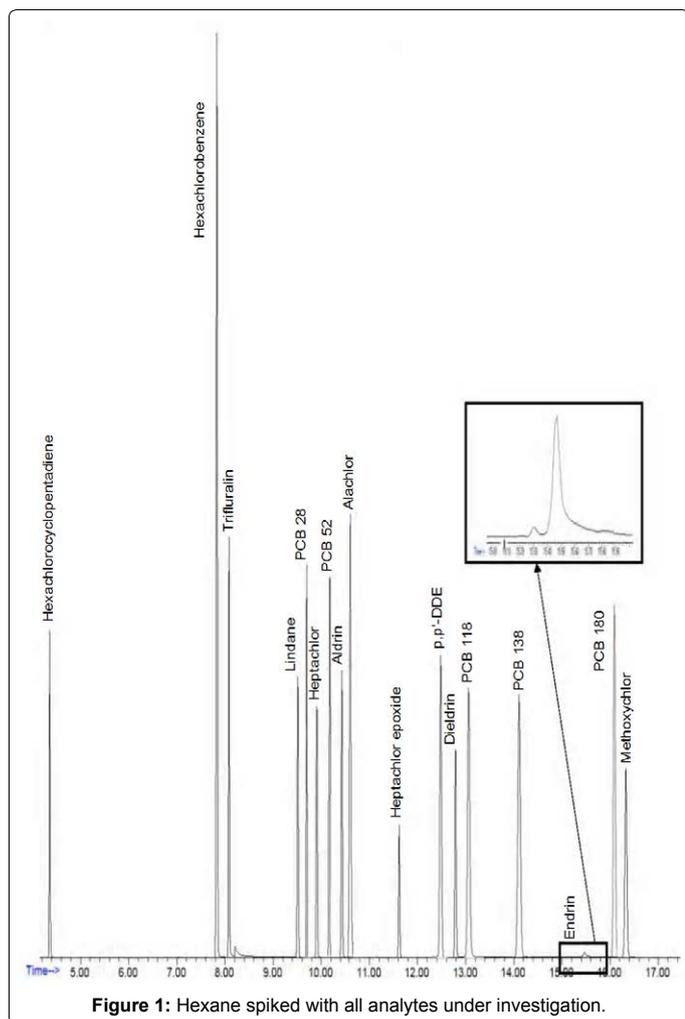


Figure 1: Hexane spiked with all analytes under investigation.

Method validation

Method validation is performed to provide evidence that the method is fit for the purpose for which it is used. Since the key challenges in the validated methods is that only well-characterized reference materials with well documented purities should be used during method validation activities, all steps are validated using reference materials, this includes specificity, accuracy, linearity, precision, range, detection limit, quantitation limit and robustness.

In order to assess these parameters, the method was therefore tested for Linearity, range Table 3. The analytical method demonstrated initial and extended validation as being capable of providing mean recovery values at each spiking level within the range 70-120%, spiked recovery experiments are performed (Figure 2), In order to check the precision of the proposed method, a minimum of 5 replicates is performed Table 4 summarizes these data.

Method Detection Limit (MDL) and Limit of Detection (LOD) - for the analytes under investigation - are cited in Table 5. Under normal conditions, reproducibility of data is tested in order to be sure that the method is robust. By changing the pH of the extract and the oven temperature, laboratory reproducibility as RSD% was found to be $\leq 20\%$, for all compounds indicating that the method is robust.

Quality control

Validation are supported and extended by method performance

verification during analysis through analytical quality control AQC. AQC data are used to validate the extension of the method to new analytes viz Hexachlorocyclopentadiene, p,p'-DDE and trifluralin, new matrices viz. waste water and transformer oils and also to new concentration levels. Minimum quality control requirements are checked for POPs determination these include.

Analysis of laboratory reagent blanks (LRB)

All glassware and reagent interferences are taken under control by checking the extract and the reagent for any source of contamination within the retention time window of all analytes under investigation.

Initial demonstration of capability

This has been checked at different spiking levels which have been selected at a concentration level about ten times the estimate detection limit or at the maximum contaminant level for each analyte. For all aliquots analyzed, the recovery value for each analyte falls in the range 70-120%.

Analysis of laboratory fortified blanks (LFB)

Table 6 illustrates the spiking concentration of each analyte in the LFB sample with the calculated accuracy as percent recovery (%R). The recovery of all analytes under investigation fall inside the control limits ($X \pm 3S$); where X is the mean percent recovery and S is the standard deviation of the percent recovery.

Analysis of laboratory fortified sample matrix (LFM)

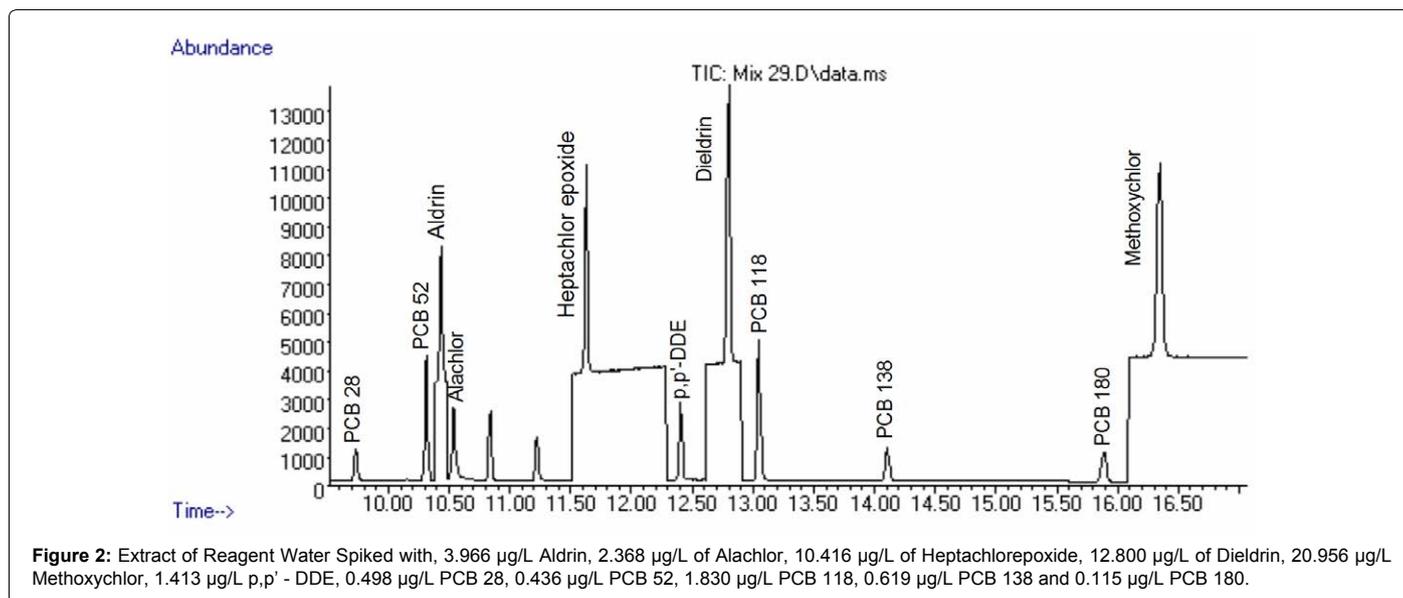
To assess analytes recovery, a known spike of Aldrin, Alachlor, Heptachlorepoxyde, Dieldrin, Methoxychlor, p,p'-DDE, PCB 28, PCB 52, PCB 118, PCB 138 and PCB 180 is added to waste water matrix as shown in Figure 3.

Analysis of reference materials (QCS) and proficiency testing

In order to assure the correct execution of the whole procedure for each individual sample and the correct injection of each final sample extract in the GC system, the use of one or more quality control (QC-) standards is utilized. These compounds are added at different steps of the procedure e.g., to the samples prior to extraction as surrogate standard or to the final sample extract just before injection as instrument internal standards. Analysis of QC samples provided from

Analyte	Calibration Equation	R ²
Alachlor	y=945.77x	0.999
Aldrin	y=1281.3x-1279.1	0.993
Dieldrin	y=841.31x-840.35	0.993
Endrin	y=15.60x-21.671	0.986
Heptachlor	y=901.89x-3608.8	0.989
Heptachlor epoxide	y=876.49x-4385.6	0.994
Hexachlorobenzene	y=6065.70x-23753	0.995
Hexachlorocyclopentadiene	y=2341.40x-64838	0.963
Lindane	y=1086.50x-607.36	0.993
Methoxychlor	y=1392.8x-27039	0.995
p,p'-DDE	y=2547.7x	0.998
PCB 28	y=3235.3x	0.997
PCB 52	y=8424.3x	0.995
PCB 118	y=2480.7x	0.997
PCB 138	y=2034.4x	0.996
PCB 180	y=939.48x	0.997
Trifluralin	y=550.82x-415.15	0.991

Table 3: Calibration equation and R² for pesticides and polychlorinated biphenyls.



Analyte	MDL, µg/L			PQL, µg/L		
	Reagent Water	Tap Water	Waste Water	Reagent Water	Tap Water	Waste Water
Alachlor	0.017	No ^	No ^	0.053	No ^	No ^
Aldrin	0.079	0.029	0.132	0.169	0.093	0.421
Dieldrin	0.109	0.030	0.139	0.346	0.096	0.443
Endrin	1.003	No ^	No ^	2.006	No ^	No ^
Heptachlor	0.759	No ^	No ^	2.416	No ^	No ^
Heptachlor epoxide	0.107	0.099	0.163	0.342	0.316	0.521
Hexachlorobenzene	0.010	No ^	No ^	0.0201	No ^	No ^
Hexachlorocyclopentadiene	3.762	No ^	No ^	7.523	No ^	No ^
Lindane	0.081	No ^	No ^	0.161	No ^	No ^
Methoxychlor	5.000	No ^	No ^	10.000	No ^	No ^
p,p'-DDE	0.006	0.005	0.012	0.019	0.017	0.037
PCB 28	0.020	0.007	0.061	0.056	0.021	0.194
PCB 52	0.013	0.006	0.029	0.042	0.020	0.092
PCB 118	0.014	0.008	0.031	0.045	0.025	0.099
PCB 138	0.012	0.008	0.077	0.038	0.027	0.245
PCB 180	0.010	0.006	0.025	0.031	0.018	0.081
Trifluralin	1.007	No ^	1.078	2.014	No ^	No ^
^No analysis conducted.						
^Analytes Provided from Sigma-Aldrich.						
^Analytes Provided from Absolute Standard Lot # 032409						

Table 4: Accuracy and Precision for Pesticides and PCBs in reagent, tap and waste water.

Analyte	MDL, µg/L			PQL, µg/L		
	Reagent Water	Tap Water	Waste Water	Reagent Water	Tap Water	Waste Water
Alachlor	0.017	No ^	No ^	0.053	No ^	No ^
Aldrin	0.079	0.029	0.132	0.169	0.093	0.421
Dieldrin	0.109	0.030	0.139	0.346	0.096	0.443
Endrin	1.003	No ^	No ^	2.006	No ^	No ^
Heptachlor	0.759	No ^	No ^	2.416	No ^	No ^
Heptachlor epoxide	0.107	0.099	0.163	0.342	0.316	0.521
Hexachlorobenzene	0.010	No ^	No ^	0.0201	No ^	No ^
Hexachlorocyclopentadiene	3.762	No ^	No ^	7.523	No ^	No ^
Lindane	0.081	No ^	No ^	0.161	No ^	No ^
Methoxychlor	5.000	No ^	No ^	10.000	No ^	No ^
p,p'-DDE	0.006	0.005	0.012	0.019	0.017	0.037
PCB 28	0.020	0.007	0.061	0.056	0.021	0.194
PCB 52	0.013	0.006	0.029	0.042	0.020	0.092
PCB 118	0.014	0.008	0.031	0.045	0.025	0.099
PCB 138	0.012	0.008	0.077	0.038	0.027	0.245
PCB 180	0.010	0.006	0.025	0.031	0.018	0.081
Trifluralin	1.007	No ^	1.078	2.014	No ^	No ^
^No analysis conducted						

Table 5: Method detection limit (MDL) and practical quantitation limit (PQL).

Accu Standard[®], and Absolute Standards[®] Inc., are shown in Figure 4 and Table 7 respectively. In addition sharing in a proficiency testing program provided from Absolute Standards[®], Inc., was successfully achieved as shown in Figure 5 and Table 8 indicating that our results meet the performance criteria for the provided QC sample datasheets.

Qualifying results with uncertainty data

Measurement uncertainty is a quantitative indicator of the confidence in the analytical data and describes the range around a reported or experimental result within which the true value can be expected to lie within a defined probability (confidence level). Uncertainty ranges must take into consideration all sources of error. To determine the uncertainty associated with analytical results, the available sufficient data derived from method validation /verification, inter-laboratory studies (e.g., proficiency

tests provided from Absolute Standards[®], Inc proficiency testing provider) and in-house quality control tests provided from Accu Standard[®] are applied to estimate the uncertainties. Uncertainty associated with repeatability of measurements for these true samples in the main elements of the uncertainty budget. The expanded uncertainty is calculated and cited in Table 9 as follows:

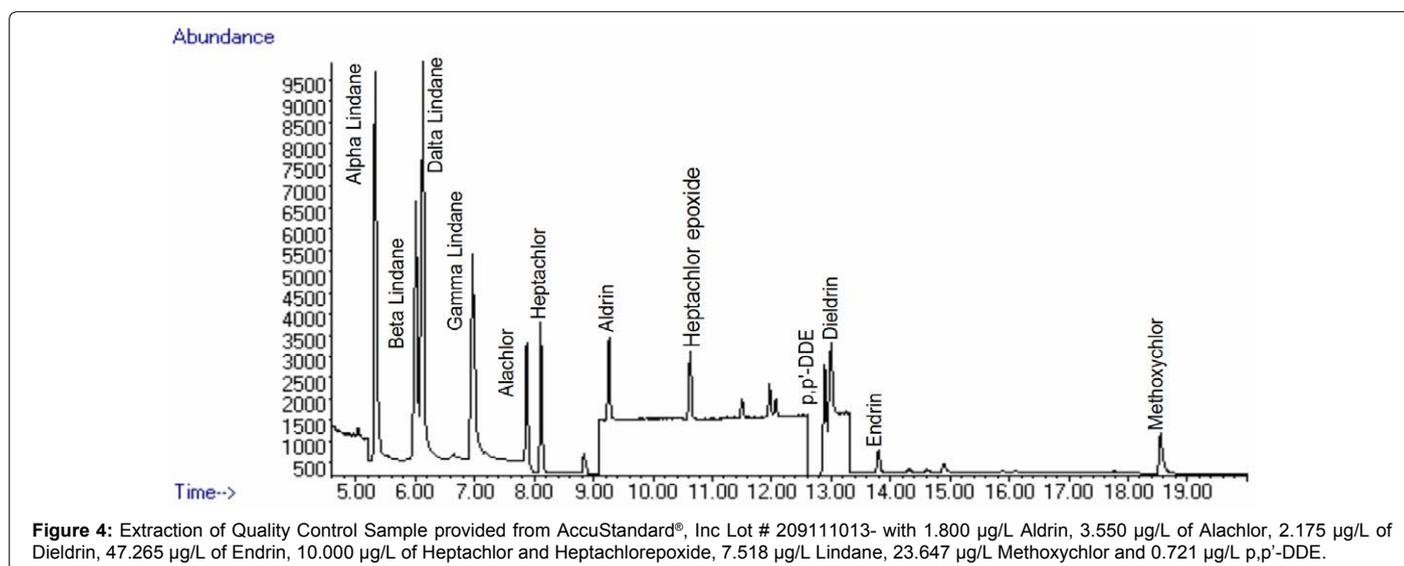
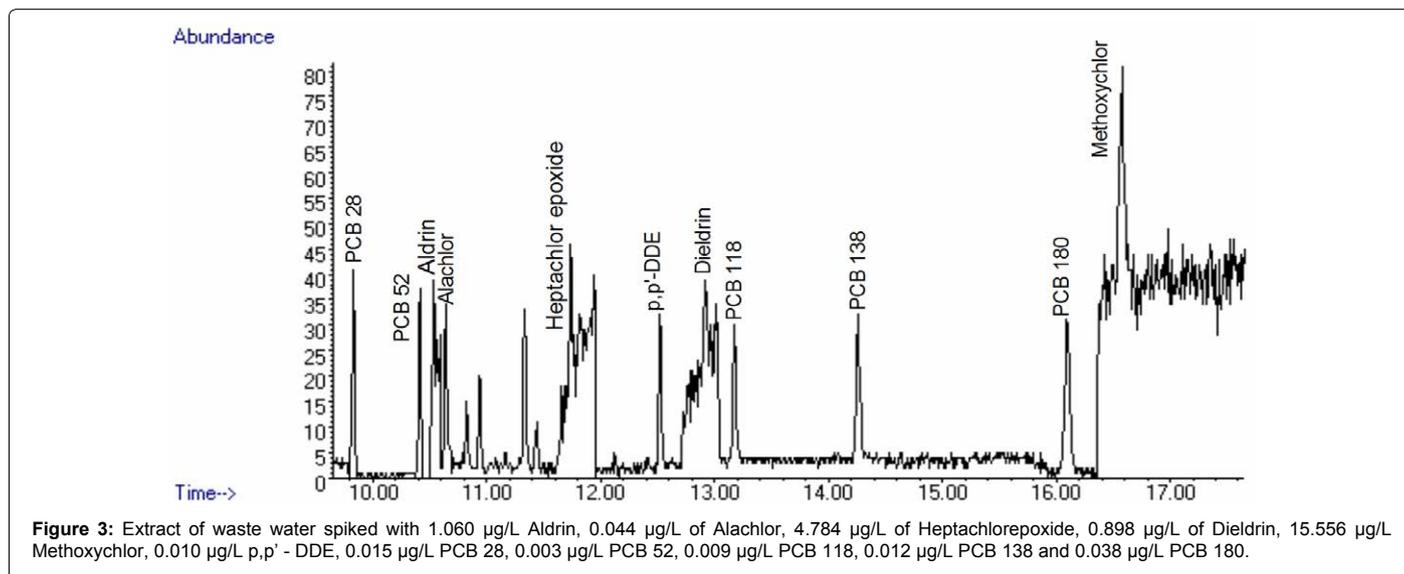
$$u = K \frac{SD}{\sqrt{n}}$$

Where K: is the coverage factor (it has a value of 2 at 95% confidence level); SD: is the standard deviations; n: is the number of measurements.

Since uncertainty tends to be greater at lower levels, especially as the LOQ is approached. It was therefore necessary to generate

Analyte	Spiking Level, ppb	Recovery (%R) Relative Standard Deviation	
		R%	RSD%
Alachlor	0.800	77.318	55.902
Aldrin	7.500	74.915	0.982
Dieldrin	5.000	78.802	0.533
Endrin	7.500	92.003	2.627
Heptachlor	10.000	98.948	0.719
Heptachlorepoide	15.000	75.746	2.428
Hexachlorobenzene	15.000	92.125	0.570
Hexachlorocyclopentadiene	20.00	115.899	0.550
Lindane	10.000	91.890	3.293
Methoxychlor	20.000	104.355	0.477
p,p'-DDE	0.020	70.775	13.402
PCB 28	1.500	69.283	22.619
PCB 52	2.048	99.953	25.132
PCB 118	0.027	75.892	21.876
PCB 138	0.014	118.874	20.267
PCB 180	0.020	109.254	14.171
Trifluralin	5.000	97.896	0.210

Table 6: Laboratory fortified blank for pesticides and polychlorinated biphenyls.



Analyte	True Concentration, ppb	Observed Concentration, ppb	Accuracy	
			%R	%Bias
Aldrin	2.000	2.218	110.887	10.887
Dieldrin	5.000	3.940	78.802	-21.198
Endrin	7.500	6.900	92.003	-7.997
Heptachlor	7.500	7.222	96.287	-3.713
Heptachlor epoxide	15.000	11.362	75.746	-24.254
Hexachlorobenzene	15.000	13.819	92.125	-7.875
Hexachlorocyclopentadiene	40.000	35.119	87.798	-12.202
Lindane	5.000	4.416	88.327	-11.673
Methoxychlor	20.000	20.871	104.355	4.355
Trifluralin	10.000	9.628	96.277	-3.723

Table 7: Quality control sample for pesticides provided from AbsoluteStandards®, Inc., Lot # 032409.

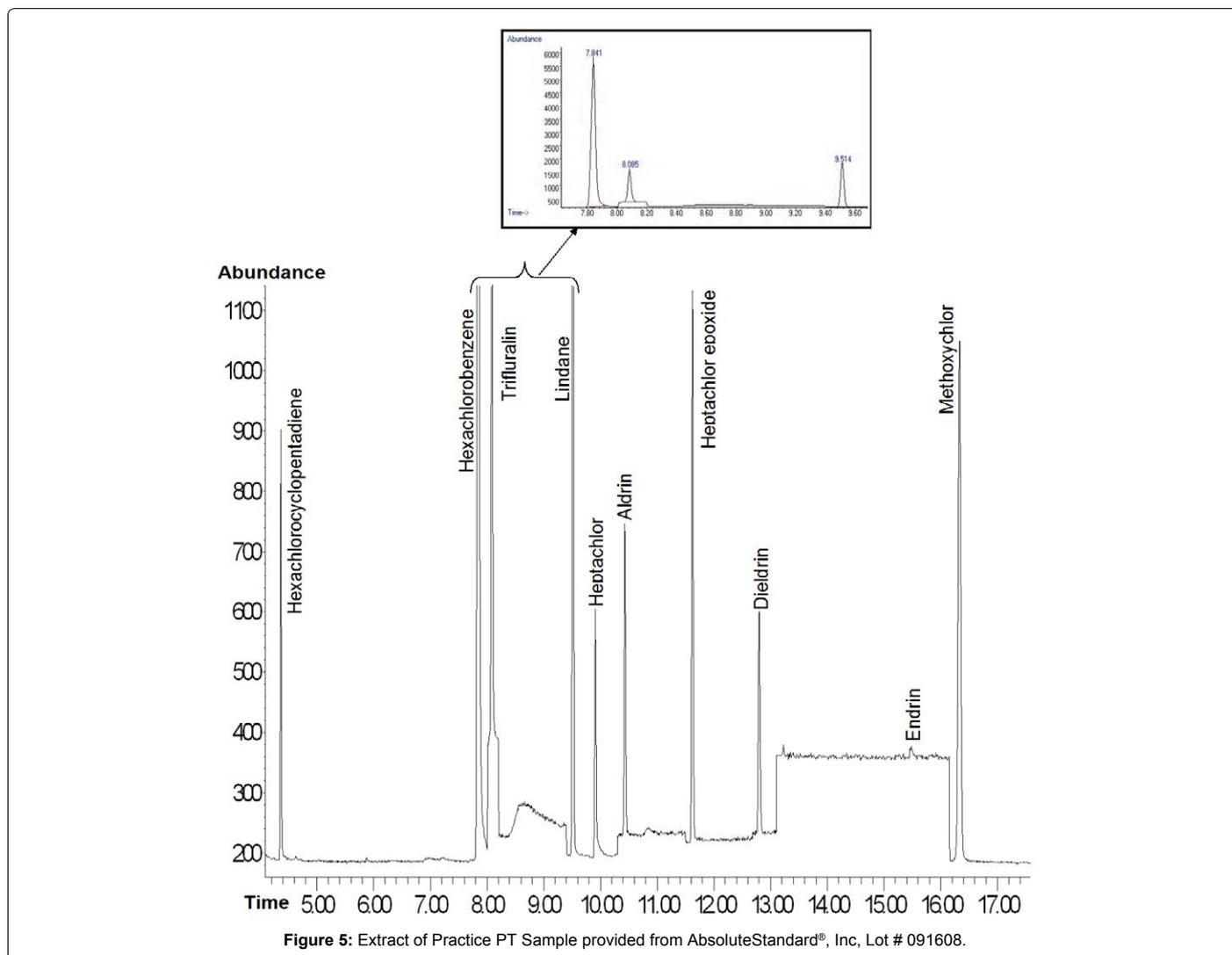


Figure 5: Extract of Practice PT Sample provided from AbsoluteStandard®, Inc, Lot # 091608.

uncertainty data for a range of concentrations if typical uncertainty is to be provided for a wide range of analytes data.

Real samples analysis

Nile River water (Assiut, Egypt), ground water (Assiut), waste water (Zenar, Assiut), tap water from our laboratory and Transformer oils (Cemex, Assiut) were analyzed using the proposed method. Chromatograms are shown in Figure 6 and data are cited in Table 10.

According to the MCL for water provided in Table 1 and the International permissible concentration of PCB's in Transformer oil as cited in the Environmental Protection Agency, EPA, USA regulations that is: >50 ppm= Non-PCB transformer, 50-500 ppm = PCB-contaminated transformer and ≥ 500 ppm= Repeat the reclassification process until the transformer can be classified as to non-PCB or a PCB-contaminated status; or remove the transformer from service, it is clear that for water samples a contamination with Aldrin and Dieldrin is noticeable while some of the transformer oils are to be considered as PCB-contaminated transformers.

Component	Method	Reported value	Assign Value	Accepted limits	
				Low	High
Aldrin	Modified ASTM D 5175-03	1.241	1.75	0.743	2.20
Dieldrin	Modified ASTM D 5175-03	1.330	1.40	0.874	1.85
Endrin	Modified ASTM D 5175-03	2.254	2.30	1.610	2.99
Heptachlor	Modified ASTM D 5175-03	3.644	3.36	1.850	4.87
Heptachlor epoxide	Modified ASTM D 5175-03	5.915	4.75	2.610	6.89
Hexachlorobenzene	Modified ASTM D 5175-03	4.697	3.81	1.750	4.81
Hexachlorocyclopentadiene	Modified ASTM D 5175-03	27.726	22.6	4.280	31.80
Lindane	Modified ASTM D 5175-03	2.070	2.40	1.320	3.48
Methoxychlor	Modified ASTM D 5175-03	19.654	25.0	13.80	36.30
Propachlor	Modified ASTM D 5175-03	-----	2.60	1.510	3.58
Trifluralin	Modified ASTM D 5175-03	2.280	4.00	2.120	5.02

Table 8: Proficiency Testing Evaluation Report for Organochlorine Pesticides mixture in water supply provided from Absolute Standard[®], Inc., USA.

Analyte	Conc., ppb	Reagent Water		Tap Water		Waste Water	
		n ^A	u ^B	n ^A	u ^B	n ^A	u ^B
Alachlor	0.089	6	± 0.004	7	± 0.002	7	± 0.007
	6.375	4	± 2.361	4	± 0.213	7	± 0.311
	12.800	7	± 3.311	4	± 0.213	7	± 1.296
Aldrin	0.160	6	± 0.014	5	± 0.008	7	± 0.032
	10.200	4	± 0.588	4	± 1.120	7	± 0.460
	20.480	3	± 0.803	7	± 1.947	7	± 0.865
Dieldrin	0.293	7	± 0.026	7	± 0.007	7	± 0.033
	12.750	4	± 1.190	4	± 4.809	5	± 1.737
	25.600	5	± 2.967	No ^c	No ^c	5	± 3.584
Endrin	2.000	5	± 0.065	No ^c	No ^c	No ^c	No ^c
Heptachlor	5.020	6	± 0.369	No ^c	No ^c	No ^c	No ^c
Heptachlor epoxide	0.280	7	± 0.026	7	± 0.024	7	± 0.039
	12.750	4	± 1.511	7	± 0.553	7	± 1.208
	25.600	5	± 5.871	5	± 1.671	7	± 4.738
Hexachlorobenzene	5.00	5	± 0.041	No ^c	No ^c	No ^c	No ^c
Hexachlorocyclopentadiene	20.060	7	± 0.228	No ^c	No ^c	No ^c	No ^c
Lindane	2.010	7	± 0.051	No ^c	No ^c	No ^c	No ^c
Methoxychlor	15.008	7	± 2.518	7	± 1.518	5	± 1.156
p,p'-DDE	0.020	7	± 0.001	4	± 0.002	7	± 0.003
	14.329	7	± 1.047	7	± 0.703	5	± 0.353
	28.672	5	± 1.397	7	± 5.992	7	± 1.194
PCB 28	0.009	7	± 0.021	7	± 0.001	7	± 0.015
	6.141	7	± 1.015	5	± 0.553	5	± 0.162
	12.288	7	± 3.162	7	± 2.894	5	± 0.541
PCB 52	0.008	6	± 0.003	7	± 0.001	7	± 0.007
	8.188	7	± 0.653	4	± 0.798	7	± 0.239
	16.384	7	± 0.972	5	± 1.144	4	± 0.799
PCB 118	0.027	7	± 0.003	5	± 0.002	7	± 0.008
	6.899	4	± 0.914	7	± 0.415	7	± 0.505
	13.824	5	± 2.015	7	± 2.222	7	± 0.878
PCB 138	0.014	5	± 0.003	5	± 0.003	7	± 0.019
	10.235	5	± 0.114	7	± 0.646	4	± 0.495
	20.480	7	± 0.895	7	± 3.514	7	± 0.564
PCB 180	0.020	6	± 0.003	7	± 0.002	7	± 0.006
	20.470	7	± 2.247	7	± 0.769	5	± 0.466
	40.960	5	± 2.491	7	± 13.262	7	± 1.256
Trifluralin	2.014	7	± 0.061	No ^c	No ^c	No ^c	No ^c

^A Number of measurements

Table 9: Expanded uncertainty for pesticides and polychlorinated biphenyls in reagent, tap and waste water.

Conclusion

The validation and application of GC MS method in the Selected Ion Monitoring (SIM) mode for the simultaneous determination of

the pesticides and PCBs has been evaluated in this study. The optimal conditions of extraction techniques have been obtained. The established method can be applied to determine the concentration of the pesticides in real water samples and transformer oils. The recoveries in water are

Matrices/Analytes	Concentration, µg/L								
	Alachlor	Aldrin	Dieldrin	p,p'-DDE	PCB 28	PCB 52	PCB 118	PCB 138	PCB 180
Waste Water1	---	---	---	---	0.006	0.004	0.002	0.007	---
Waste Water2	---	---	---	0.003	---	0.001	---	---	---
Waste Water3 (Zennar)	---	0.071	---	---	0.038	---	---	---	---
Water Irrigation (Grape Residue)	---	0.453	---	---	---	---	---	---	---
Tap w ater	0.067	---	---	---	---	---	---	---	---
Ground water	0.052	---	---	---	---	---	---	---	---
El ibrahimia w ater	0.067	---	0.073	---	---	---	---	---	---
Naga Hammady water	0.046	---	---	---	---	---	---	---	---
Nile w ater1	0.055	---	0.294	---	---	---	---	---	---
Nile w ater2	0.035	---	---	---	---	---	---	---	---
Nile w ater3	0.026	---	---	---	---	---	---	---	---
Concentration, mg/L									
Transformer Oil-1	---	---	---	---	---	53.830	---	---	3.730
Transformer Oil-2	---	---	---	---	---	---	---	---	8.300
Transformer Oil-3	---	---	---	---	---	55.230	---	---	5.100
Transformer Oil-4	---	---	---	---	---	26.900	---	---	---
Transformer Oil-5	---	---	---	---	---	100.900	---	---	---
Transformer Oil-6	---	---	---	---	---	33.130	---	---	14.560
Transformer Oil-7	---	---	---	---	---	---	---	---	17.460
Transformer Oil-8	---	---	---	---	---	54.460	---	---	15.700
Transformer Oil-9	---	---	---	---	---	---	---	---	2.530
Transformer Oil-10	---	---	---	---	---	---	---	---	0.960
Transformer Oil-11	---	---	---	---	---	---	---	---	0.960
Transformer Oil-12	---	---	---	---	---	---	---	---	5.600
Transformer Oil-13	---	---	---	---	---	---	---	---	10.900
Transformer Oil-14	---	---	---	---	---	---	---	---	11.530
Transformer Oil-15	---	---	---	---	---	15.230	---	---	16.600
Transformer Oil-16	---	---	---	---	---	---	---	---	6.030

^{1,2,3} are different samples from different areas

Table 10: Application in different Matrices.

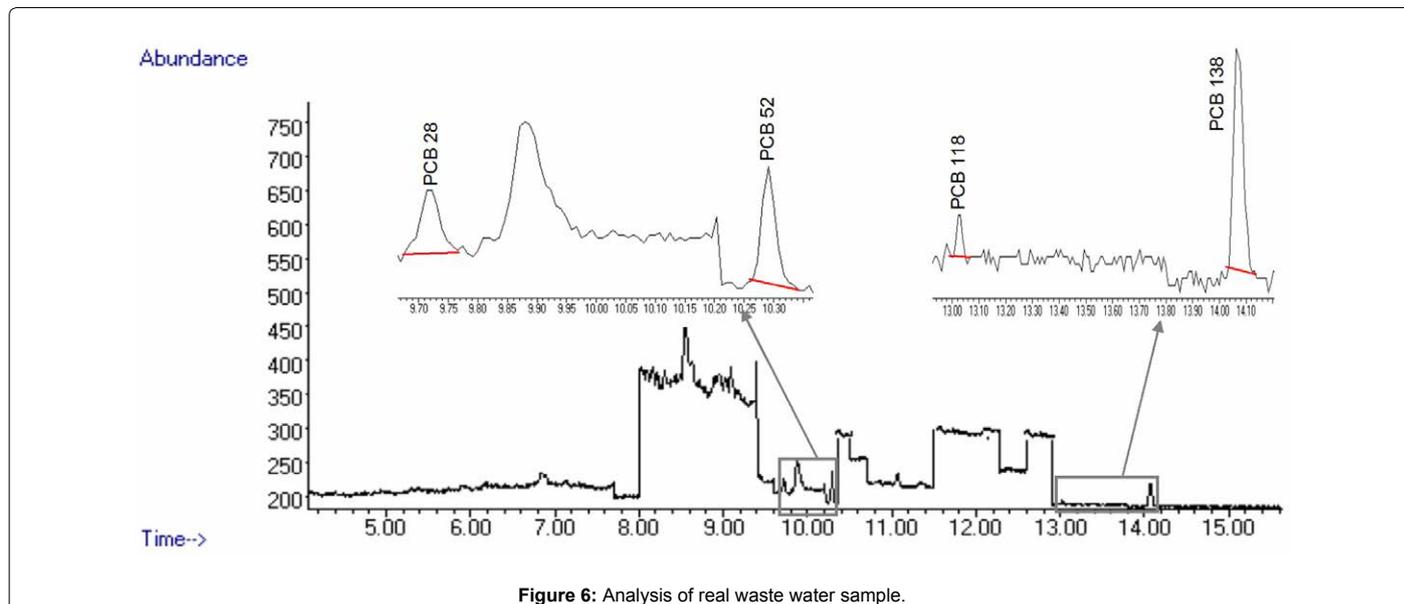


Figure 6: Analysis of real waste water sample.

Analyte	Range, µg/L (proposed method)	Range, µg/L (ASTM method)	MCL, µg/L (EPA/WHO*)
Alachlor	0.050-12.800	0.500-37.500	2.000
Aldrin	0.080-40.000	0.040-1.420	0.03*
Dieldrin	0.040-40.000	0.100-7.500	0.03*
Endrin	2.006-15.045	0.100-7.500	2.00
Heptachlor	0.480-80.000	0.040-1.410	0.40
Heptachlorepoxide	0.040-320.000	0.040-1.420	0.20
Hexachlorobenzene	0.020-321.600	0.010-0.370	1.00
Hexachlorocyclopentadiene	7.523-320.960	----	50.00
Lindane	0.161-20.100	0.040-1.390	0.20
Methoxychlor	10.000-320.000	0.200-15.000	40.00
p,p'-DDE	0.014-28.672	----	1.00*
PCB 28	0.006-12.288	0.500-50.000	0.5
PCB 52	0.008-16.384		
PCB 118	0.027-13.824		
PCB 138	0.010-20.480		
PCB 180	0.020-40.960		
Trifluralin	2.014-20.140	----	20.00*

Table 11: Comparison between concentration range in the proposed method and ASTM D5175.

from 70% to 120%. Adequate repeatability, good linearity and the low detection limits prove the capability and credibility for the validation of method by analyzing proficiency testing samples provided from AbsoluteStandards, Inc.

Comparing the data produced from our proposed method, using the universal detector MS in the SIM mode, with those from the ASTM D 5175 method obtained with electron capture detector, Table 11 gave evidence that our proposed method may solve many environmental pollution problems for ultra-trace pollutants since it can reach sub-ppb and ppt levels.

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References

- Štěpán R, Hajšlová J, Kocourek V, Tichá J (2004) Uncertainties of gas chromatographic measurement of troublesome pesticide residues in apples employing conventional and mass spectrometric detectors. *Anal Chim Acta* 520: 245-255.
- Linsinger TP, Führer M, Kandler W, Schuhmacher R (2001) Determination of measurement uncertainty for the determination of triazines in groundwater from validation data. *Analyst* 126: 211-216.
- Moreno Frías M, Garrido Frenich A, Martínez Vidal JL, Mateu Sánchez M, Olea F, et al. (2001) Analyses of lindane, vinclozolin, aldrin, p,p'-DDE, o,p'-DDT and p,p'-DDT in human serum using gas chromatography with electron capture detection and tandem mass spectrometry. *J Chromatogr B Biomed Sci Appl* 760: 1-15.
- Martínez Vidal JL, Moreno Frías M, Garrido Frenich A, Olea-Serrano F, Olea N (2002) Determination of endocrine-disrupting pesticides and polychlorinated biphenyls in human serum by GC-ECD and GC-MS-MS and evaluation of contributions to the uncertainty of the results. *Anal Bioanal Chem* 372: 766-775.
- Ratola N, Santos L, Herbert P, Alves A (2006) Uncertainty associated to the analysis of organochlorine pesticides in water by solid-phase microextraction/gas chromatography-electron capture detection-evaluation using two different approaches. *Anal Chim Acta* 573-574: 202-208.
- Quintana J, Martí I, Ventura F (2001) Monitoring of pesticides in drinking and related waters in NE Spain with a multiresidue SPE-GC-MS method including an estimation of the uncertainty of the analytical results. *J Chromatogr A* 938: 3-13.
- Yenisoy-Karakaş S (2006) Validation and uncertainty assessment of rapid extraction and clean-up methods for the determination of 16 organochlorine pesticide residues in vegetables. *Anal Chim Acta* 571: 298-307.
- Picó Y, Rodríguez R, Mañes J (2003) Capillary electrophoresis for the determination of pesticide residues. *Trends Anal Chem* 22: 133-151.
- Luzardo OP, Mahtani V, Troyano JM, Alvarez de la Rosa M, Padilla-Pérez AI, et al. (2009) Determinants of organochlorine levels detectable in the amniotic fluid of women from Tenerife Island (Canary Islands, Spain). *Environ Res* 109: 607-613.
- Luzardo OP, Goethals M, Zumbado M, Alvarez-León EE, Cabrera F, et al. (2006) Increasing serum levels of non-DDT-derivative organochlorine pesticides in the younger population of the Canary Islands (Spain). *Sci Total Environ* 367: 129-138.
- Haraguchi K, Koizumi A, Inoue K, Harada KH, Hitomi T, et al. (2009) Levels and regional trends of persistent organochlorines and polybrominated diphenyl ethers in Asian breast milk demonstrate POPs signatures unique to individual countries. *Environ Int* 35: 1072-1079.
- Wong MH, Leung AO, Chan JK, Choi MP (2005) A review on the usage of POP pesticides in China, with emphasis on DDT loadings in human milk. *Chemosphere* 60: 740-752.
- Feeley M, Brouwer A (2000) Health risks to infants from exposure to PCBs, PCDDs and PCDFs. *Food Addit Contam* 17: 325-333.
- Ribas-Fito N, Gladen BC, Brock JW, Klebanoff MA, Longnecker MP (2006) Prenatal exposure to 1,1-dichloro-2,2-bis (p-chlorophenyl)ethylene (p,p'-DDE) in relation to child growth. *Int J Epidemiol* 35: 853-856.
- Boada LD, Lara PC, Alvarez-León EE, Losada A, Zumbado ML, et al. (2007) Serum levels of insulin-like growth factor-I in relation to organochlorine pesticides exposure. *Growth Horm IGF Res* 17: 506-511.
- Zumbado M, Goethals M, Alvarez-León EE, Luzardo OP, Cabrera F, et al. (2005) Inadvertent exposure to organochlorine pesticides DDT and derivatives in people from the Canary Islands (Spain). *Sci Total Environ* 339: 49-62.
- Hopf NB, Ruder AM, Succop P (2009) Background levels of polychlorinated biphenyls in the U.S. population. *Sci Total Environ* 407: 6109-6119.
- <http://www.epa.gov/epawaste/hazard/tsd/pcbs/index.htm>
- World Health Organization (2003) Polychlorinated Biphenyls: Human Health Aspects, Concise International Chemical Assessment Document 55.
- Seródio P, Nogueira JMF (2004) Multi-residue screening of endocrine disruptors chemicals in water samples by stir bar sorptive extraction-liquid desorption-capillary gas chromatography-mass spectrometry detection. *Anal Chim Acta* 517: 21-32.
- Muir D, Sverko E (2006) Analytical methods for PCBs and organochlorine pesticides in environmental monitoring and surveillance: a critical appraisal. *Anal Bioanal Chem* 386: 769-789.
- (1991) U. S. Environmental of Organic Compounds in Drinking Water, EPA 600/4-88/039, U. S. Government Printing Office, Washington, DC.
- (2011) Annual Book of ASTM Standards.