Chapter 6

Gas Chromatographic Determination of Pesticides Multi-residues in Soil and Groundwater

CONTENTS

1. Introduction

Pesticides are a valuable, indispensable tool and essential components of modern agriculture for the sustainable agricultural production. More than 700 pesticides and their formulations are registered for use in the world[1] to control pest injurious to crop, agricultural products and human health. However, after applications to crop and public health problem, the pesticides and their degradation products, which are often toxic chemicals, may cause contamination of soil, water, air and food affecting the environmental quality. Many international organizations and agencies such as European Union[2], Food Agriculture Organization (FAO)[3] and the United States Environment Protection Agency (US EPA)[4] have published tolerances or maximum residues limits (MRLs) of pesticides in/on raw agricultural commodities, food, feed and environmental samples. Therefore, analysis of pesticides at very low levels in water, food and soil samples has gained prime importance.

Several methods have been published for screening the multi-residues of organochlorine pesticides and pyrethroids in various environmental samples and raw agicultural commodities. Majority of the methods used, various organic solvents either for solid-liquid[5] / liquid-liquid[6,7] extraction to extract the pesticides from substrate or for elution in various preconcentration and clean-up procedures viz., solid phase extraction (SPE)[8-10], solid phase micro extraction (SPME)[11-12], gel permeation chromatography[13] or various columns containing silica gel, florisil or charcoal to remove interfering co-extractives prior to analysis. Therefore, extraction efficiencies of various organic solvents play a vital role to select the suitable solvent combination for efficient separation of various pesticides from different soil, water, air and environmental samples.

In the present study, an attempt was made to study the extraction efficiencies of various solvents to extract twenty commonly used chlorinated pesticides belonging to different classes viz., organochlorines, synthetic pyrethroids, fungicides and herbicides from different soils (red, black clay and sandy) and ground water samples to determine the most suitable solvent combination for extraction. A simple, fast and sensitive gas chromatographic method with electron capture detector (GC-ECD) was developed for simultaneous quantification of selected pesticides. A gas chromatographic mass spectrometric (GC-MS) method with electron impact ionization in scan mode, was also developed to confirm the identity of these pesticides, based on their molecular mass and fragmentation patterns.

2. Experimental Procedure

2.1 Materials and Methods

The certified reference standards (CRS) of selected pesticides (Organochlorines, synthetic pyrethroids, Fungicides and herbicide) were procured from various sources viz., Sigma- Aldrich, Supelco (Bellefonte, USA), Reidel-deHaen (Seelze, Germany) and Chem Service (West Chester, P A USA).

Four types of soils (red, black, clay and sandy) were collected from different regions of Gujarat and Maharashtra states of India and characterized (**Table 2**). Groundwater samples were collected from the campus of Jai Research foundation, Vapi, Gujarat.

Acetone, dichloromethane, ethyl acetate and n-hexane (AR grade) were procured from Qualigens Fine Chemicals, India. Anhydrous sodium sulphate, sodium chloride and sodium lauryl sulphate (AR grade) were procured from, s.d.fine-chem Limited, India.

Capillary columns viz., DB-5; 30 m x 0.25 mm (i.d.) x 0.25 µm film thickness from Supelco (Bellefonte, P A USA) for GC-ECD analysis and HP-5MS; 30 m x 0.25 mm (i.d.) x 0.25 µm film thickness from Hewlett-Packard (Palo Alto, USA) for GC-MS analysis were used.

2.2 Pesticide Standard Solution

Standard stock solutions of each pesticides were prepared by weighing a known quantity (10 mg approx.) of each HCH, γ-HCH (Lindane), p,p'-DDT, heptachlor, aldrin, endosulfan ether, endosulfan-I, endosulfan-II, endosulfan sulphate, lambda-cyhalothrin, cypermethrin, bifenthrin, deltamethrin, permethrin-I & permethrin-II, fenvalerate-I & fenvalerate-II, hexachlorobenzene, o-chlorothalonil, m-chlorothalonil, p-chlorothalonil, hexaconazole, captan and trifluralin standards into separate 10 mL volumetric flasks and the volume was made upto the mark with n-hexane (≈1 mg/mL concentration of each pesticide). A stock mixture of all pesticides was prepared by transferring 1 mL of each pesticide standard stock solutions into same volumetric flask of 100 mL capacity and the volume was made upto the mark with n-hexane. The resultant stock mixture contained 10 µg/mL (10ppm) concentration of each pesticide. The standard stock mixture was analyzed by GC-ECD after suitable dilution. All standard and stock solutions were stored in refrigerator at 4 - 6 °C.

2.3 Sample/Matrix Spiking Procedure

Various soils (red, black, sandy and clay) having different characteristics were selected (**Table 1**). A quantity of 1 kg soil sample was homogenized; slurry of representative soil sample was prepared in acetone and spiked in duplicate at 0.01 µg/g levels with standard stock mixture of pesticides. The slurry was thoroughly mixed and allowed to stand overnight at room temperature.

A volume of 1 liter homogenized groundwater sample was fortified in duplicate with standard stock mixture of pesticides at 0.005 µg/mL levels. Solution was stirred thoroughly and allowed to stand for 2 - 3 hr at room temperature.

2.4 Pesticides Residue Extraction from Soil

100 g sample of each soil was transferred separately into 250 mL flask and extracted with 150 mL acetone for 45 min using an Orbital Shaker. The contents were filtered and residual cake was re-extracted twice with 100 mL acetone for 30 min, filtered and washed with 50 mL acetone. Filtrate and washings were collected and pooled. All the four soils were similarly extracted using dichloromethane (DCM) and methanol, separately. The soil extracts were concentrated to near dryness using Rotary Vacuum Evaporator at <40 °C. The concentrated dichloromethane extract was dissolved in 5 mL n-hexane and analyzed directly by GC. The acetone and methanol extracts were transferred to 250 mL separatory funnel, 100 mL distilled water and 25 mL saturated sodium chloride solution was added and re-extracted twice with 100 mL dichloromethane. The organic layer was collected by passing through a bed of anhydrous sodium sulphate and evaporated to dryness at <40 °C. Residues were dissolved in 5 mL n-hexane and analyzed directly by gas chromatography.

2.5 Pesticides Residue Extraction from Water

500 mL water sample was transferred into a separatory funnel and 5 g anhydrous sodium chloride and 1 mL sodium lauryl sulphate (2% solution) was added and mixed thoroughly. The sample was extracted thrice with 50 mL n-hexane and the organic layer was collected after passing through a bed of anhydrous sodium sulphate. The water samples were extracted similarly with dichloromethane and ethyl acetate, separately. The n-hexane, dichloromethane and ethyl acetate extracts were evaporated to dryness using a Rotary Vacuum Evaporator at <40 °C. The residue was dissolved in 10 mL n-hexane and analyzed by gas chromatography.

2.6 Gas Chromatographic (GC-ECD) Condition

A gas chromatograph, model Varian STAR 3350, equipped with ^{63}Ni electron capture detector (ECD) was used for analysis. The injection port and detector temperatures were 260 °C and 320 °C, respectively. The oven was programmed from an initial temperature of 200 °C, held for 2 min, increased at 8 °C/min to 320 °C and held for 4 min. The ultra pure nitrogen gas was used as carrier gas at the flow rate of 1.5 mL/min in column and 30 mL/min as make-up for ECD. Injection was in the split mode with split ratio of 15:1 and injection volume was 1 µl. Chromatograms were recorded with Star Workstation computing integrator.

2.7 GC-MS Condition

A gas chromatographic system of Hewlett Packard 6890 series coupled with Hewlett Packard 5973 mass selective detector (GC/MS) was used for the identification of pesticides. The injection port and GC-MS interface temperatures were 260 °C and 280 °C, respectively. The ion source compartment and quadrupole mass analyzer were set at temperature 230 °C and 150 °C, respectively. The GC oven was programmed from a initial temperature of 110 °C, increased at 8 °C/min to 250 °C and held at 250 °C for 2.5 min, again increased at 10 °C/min to 280 °C and held for 4 min at 280 °C. Helium was used as carrier gas at the flow rate of 1 mL/min. Injection volume was 1 µl in splitless mode, purge set on, after 2 min and purge flow was 20 mL/ min. The mass spectrometer was operated in the electron impact (EI) scan ionization mode at electron energy of 70 eV. Spectra were recorded in the mass range of 50-550 amu using HP ChemStation software.

3. Results and Discussion

3.1 Method Specificity and Validation

The proposed capillary gas chromatographic method was rapid, specific and efficient to detect the selected twenty pesticides within 21 minutes (**Fig. 2**) in comparision to other conventional methods, which take around 50 minutes for similar screening[6,14,15].

The method was validated before actual residue analysis. The linearity of gas chromatographic method was checked for all the analytes over a wide concentration range using both ECD and MS detectors. The correlation coefficients ranged from 0.9983 to 0.9998 for all pesticides with concentration between 0.001 µg/mL to 1.0 µg/mL for GC-ECD (**Fig. 1**). The relative standard deviations (% RSDs) varied from 0.59 to 4.96%, using six repeated injections of pesticides mixture (0.02 µg/mL concentration). Recovery experiments were performed using spiked samples of soil and water, separately, after extraction with three different solvents viz., acetone, dichloromethane and methanol for soils and n-hexane, dichloromethane and ethyl acetate for water (**Table 3, 4**).

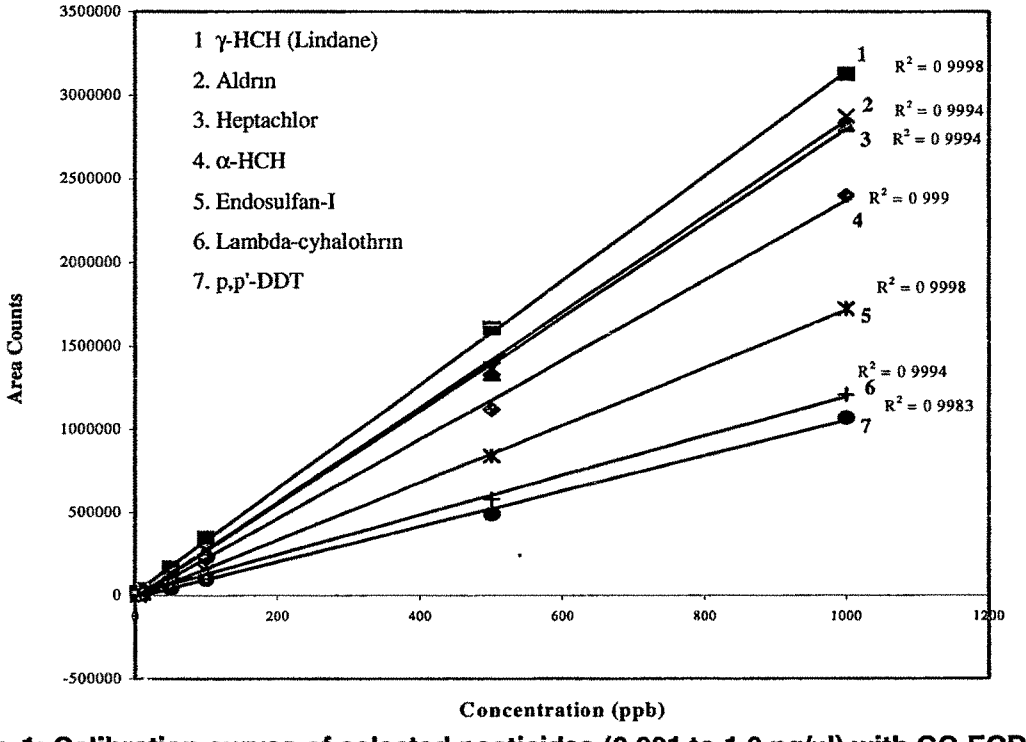

Fig. 1: Calibration curves of selected pesticides (0.001 to 1.0 ng/µl) with GC-ECD.

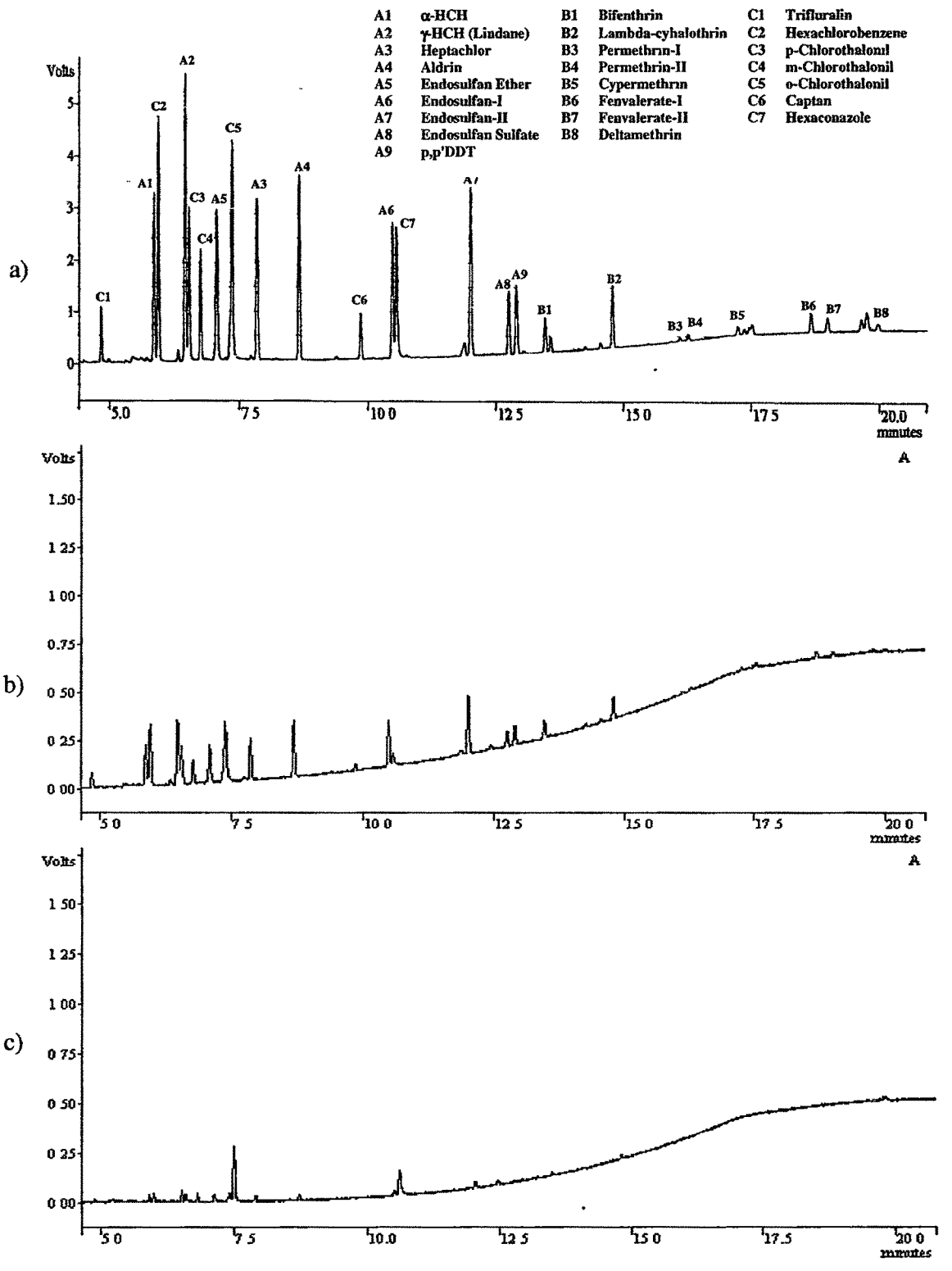

Fig. 2: GC-ECD chromatograms for standard mixture of chlorinated pesticides a) 0.1 ppm; b) 0.01 ppm; and c) 0.001 ppm.

3.2 Detector Sensitivity

The mixture of standard pesticides as well as spiked soil samples were analysed by GC-ECD and GC-MS (scan mode) to compare the sensitivity of both detectors for various pesticides. The limit of detection (LOD) was determined as the lowest concentration that produces a response, at least three times of average baseline noise (S/N=3). The detection limit of electron capture detector (ECD) for organochlorines varied from 0.0005 to 0.005 µg/mL. Among the organochlorines the maximum sensitivity was for lindane (0.0005 µg/mL) followed by aldrin, endosulfan ether, endosulfan-I and endosulfan-II (0.001 µg/mL); and HCH, heptachlor and p,p'-DDT (0.002 µg/mL). The lowest sensitivity was for endosulfan sulphate (0.005 µg/mL). ECD sensitivity for synthetic pyrethroids varied from 0.0005 to 0.01 µg/mL. The maximum sensitivity was for lambda-cyhalothrin, cypermethrin and fenvalerate-I (0.0005 to 0.005 µg/mL) followed by bifenthrin, permethrin-I, permethrin-II, fenvalerate and deltamethrin (0.002 to 0.01 µg/mL). Among herbicides/fungicides, maximum sensitivity (0.0005 µg/mL) was for o-chlorothalonil followed by p-chlorothalonil, m-chlorothalonil, trifluralin and hexaconazole (0.001 µg/mL) and then hexachlorobenzene (0.002 µg/mL). The minimum sensitivity was for captan (0.01 µg/mL). The limit of detection of method using fortified soil and water samples were also studied, which increased 2 to 5 times of instrument sensitivity due to concentration of samples after extraction (**Table 1**).

The sensitivity of GC-MS (scan mode) analytical method for various pesticides was also studied (**Table 1**). The GC-MS sensitivity for organochlorines varied from 0.1 to 5.0 µg/mL, while for synthetic pyrethroids and herbicides/fungicides ranged between 0.1 to 2.0 µg/mL, which was about 100 times less than GC-ECD method. Therefore, the GC-ECD method was used for the estimation of chlorinated pesticide residues at sub-ppb level, whereas GC-MS was successfully employed for screening and identification of pesticides.

Table 1: Detection limits of various pesticides [GC-ECD and GC-MSD].

S. No.	Pesticides	Gas Chromatographic Detector					
		Electron Capture Detector				Mass Selective Detector	
		Retention Time (min)	Limit of Detection (LOD)			Retention Time (min)	LOD (µg/mL)
			Instrument (µg/mL)	Soil (mg/kg)	Water (µg/mL)		
	Organochlorine Pesticides						
A1	HCH (BHC)	5.87	0.002	0.001	0.0005	8.95	0.10
A2	γ-HCH (Lindane)	6 49	0.0005	0.0002	0.0001	9.76	0.10
A3	Heptachlor	7.87	0.002	0.001	0.0005	11.50	0.20
A4	Aldrin	8.69	0.001	0.0005	0.0002	12.32	0.10
A5	Endosulfan Ether	7.11	0.001	0.0002	0.001	10.79	0.05
A6	Endosulfan-I	10.48	0.001	0.0005	0.0002	14.11	0.10
A7	Endosulfan-II	12.01	0.001	0.0002	0.0002	15.42	0.20
A8	Endosulfan Sulfate	12.75	0.005	0.001	0.001	16.40	5.00
A9	p,p'-DDT	12.90	0 002	0.001	0.001	16.50	0.50
	Synthetic Pyrethroids						
B1	Bifenthrin	13.46	0.002	0.001	0 001	17.79	0.10
B2	Lambda-cyhalothrin	14.77	0.0005	0.0002	0.001	19.35	1.00
B3	Permethrin-I	16.03	0.01	0.005	0 002	20.54	0.50
B4	Permethrin-II	16.25	0.01	0.005	0.005	20.79	0.50
B5	Cypermethrin	17 50	0.005	0.002	0.001	22 08	0.50
B6	Fenvalerate-I	18.66	0.005	0 002	0.002	23.66	2.00
B7	Fenvalerate-II	18.88	0.01	0.005	0.002	24.11	2.00
B8	Deltamethrin	19.80	0.01	0.002	0.001	25.35	1.00
	Fungicides/ Herbicide						
C1	Trifluralin	4 86	0.001	0.0005	0.0002	8.70	0.10
C2	Hexachlorobenzene	5.96	0.002	0.001	0.0005	9.14	0.02
C3	p-Chlorothalonil	6.57	0 001	0.0002	0.0002	10.21	0.05
C4	m-Chlorothalonil	6.79	0.001	0.0005	0.0005	10.48	0.10
C5	o-Chlorothalonil	7.40	0.0005	0.0002	0.0001	10 86	0.10
C6	Captan	9.85	0 01	0.005	0.002	13.48	1.00
C7	Hexaconazole	10.57	0.001	0.0005	0.0002	14.47	1.00

3.3 Pesticides Residue Analysis in Soil Samples

Four soils collecting from various regions of India, having different physico-chemical properties (**Table 2**) were selected for residue analyses. The extraction of pesticide residues from soils were performed using different solvents, which was based on the solubility of pesticides in solvents as well as on various characteristics of soils.

Table 2: Characteristics of various soils (sandy, red, clay and black).

Soil Characters	Sandy	Red	Clay	Black
Area of collection	Undera, Baroda Gujarat, India	Pondaghat Maharastra, India	Valvada, Valsad Gujarat, India	Bardoli, Surat Gujarat, India
Clay	12.20	26.43	54.10	58.10
Silt	23.10	25.88	26.50	17.21
Sand	54.70	41.62	19.40	27.84
pH	8.30	4.81	6.76	7.19
Moisture (105 ± 5 °C)	15.50	12.49	3.41	7.58
Electrical conductivity (25 °C)	0.82 (m mhos)	0.82 (ds/m)	0.82 (ds/m)	0.73 (ds/m)
Nitrogen	0.10	0.24	0.25	0.18
Phosphorus	0.11	0.17	0.13	0.09
Potash	0.62	1.00	1.02	0.69
Calcium oxide (CaO)	0.87	1.82	1.87	1.23
Magnesium oxide (MgO)	0.85	1.22	1.27	0.92
Ferric oxide (Fe_2O_3)	2.43	0.86	4.16	0.87
Organic matter	3.11	3.20	2.22	0.98

All four types of soil samples were fortified at 0.01 µg/g (0.01 ppm) level with pesticides mixture and extracted with acetone, methanol and dichloromethane, separately. The typical GC-ECD chromatograms of pesticides mixture extracted from 0.01 µg/g spiked soil sample shown in **Fig. 3.1 & 3.2**, have good resolution of all analytes without any matrix interference.

The extraction efficiencies of various polar solvents viz., acetone, methanol and dichloromethane were compared for extraction of various pesticides from different types of soils. The extraction efficiency of dichloromethane was better for Sandy and Red soils for extraction of almost all groups of selected pesticides (**Fig. 3.1**). The recoveries with dichloromethane from Sandy and Red soils varied between 82.88 to 102.99% and 78.15 to 108.92%, respectively (**Table 3.1**). The acetone had good extraction efficiency for all selected pesticides from Clay and Black soils (**Fig. 3.2**). The recoveries of pesticides with acetone from Clay soil ranged from 71.62 to 103.42% and Black soil 74.91 to 101.52%, respectively (**Table 3.2**). The recovery of pesticides with methanol from all soils was not satisfactory.

Good extraction efficiency of dichloromethane from sandy and red soils was due to intermediate polarity of dichloromethane, which helped in extraction of the non-polar and slightly polar pesticides from soils having bigger particles with high sand and low clay contents. The acetone having sufficiently high polarity, extracted the pesticides from Clay and Black soils, which have smaller particles with lower sand and higher clay contents. Methanol due to its highly polar nature was inefficient for pesticides and co-extractive partitioning. Therefore, dichloromethane was most suitable solvent for extraction from Sandy and Red soils, whereas acetone was suitable for the Clay and Black soils.

Table 3.1: Pesticides recoveries from sandy and red soils [GC-ECD].

S. N°	Pesticides	Sandy			Red		
		Solvent Recovery (%)			Solvent Recovery (%)		
		Acetone	DCM	MeOH	Acetone	DCM	MeOH
Organochlorine Pesticides							
A1	α-HCH	68.19	101.16	61.71	80.58	102.53	64.75
A2	γ-HCH (Lindane)	65.93	102.24	61.49	77.00	103.05	65.74
A3	Heptachlor	70.76	94.33	62.79	66.39	108.46	65.84
A4	Aldrin	71.11	102.14	62.72	61.23	101.66	66.87
A5	Endosulfan Ether	72.93	82.88	70.20	84.25	107.74	72.12
A6	Endosulfan-I	72.67	97.90	62.00	75.72	86.34	56.25
A7	Endosulfan-II	74.35	98.85	65.40	84.43	95.30	65.41
A8	Endosulfan Sulfate	85.60	98.60	82.93	95.93	106.65	73.20
A9	p,p'-DDT	73.32	98.16	85.69	90.88	95.27	51.34
Synthetic Pyrethroids							
B1	Bifenthrin	80.21	87.37	78.20	78.63	105.96	80.64
B2	Lambda-cyhalothrin	66.09	102.75	48.49	95.47	88.39	43.89
B5	Cypermethrin	89.73	94.10	37.92	79.93	103.80	48.45
B6	Fenvalerate-I	73.28	102.99	20.51	95.95	99.21	60.64
B7	Fenvalerate-II	71.43	98.44	12.63	95.35	97.58	60.71
B8	Deltamethrin	100.68	102.77	25.31	106.82	96.60	59.93
Fungicides/ Herbicide							
C1	Trifluralin	79.57	98.81	8.56	48.78	108.92	75.50
C2	Hexachlorobenzene	62.46	88.55	50.46	41.10	90.79	59.17
C3	p-Chlorothalonil	65.93	102.24	61.49	83.80	104.03	70.64
C4	m-Chlorothalonil	72.43	86.29	12.05	41.74	78.15	44.76
C5	o-Chlorothalonil	72.93	82.88	70.20	73.13	108.58	69.59
C7	Hexaconazole	68.24	84.66	66.68	87.10	96.80	67.00

Key: DCM : Dichloromethane
MeOH : Methanol

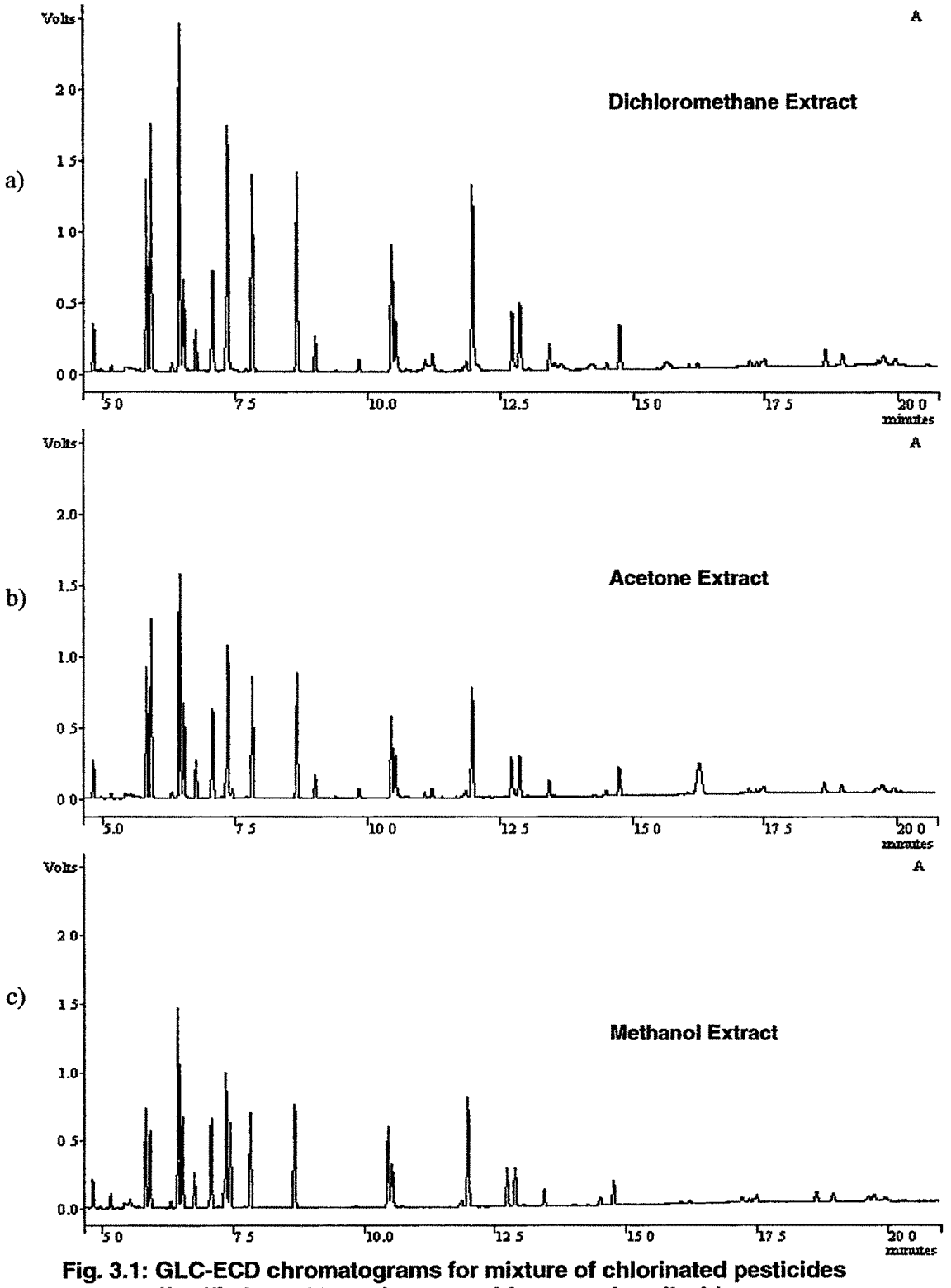

Fig. 3.1: GLC-ECD chromatograms for mixture of chlorinated pesticides (fortified at 0.01 ppm) extracted from sandy soil with a) dichloromethane (DCM), b) acetone, and c) methanol.
[Refer Fig. 2a, page124 for peaks identification]

Table 3.2: Pesticides recoveries from clay and black soils [GC-ECD].

S. N°	Pesticides	Clay			Black		
		Solvent Recovery (%)			Solvent Recovery (%)		
		Acetone	DCM	MeOH	Acetone	DCM	MeOH
Organochlorine Pesticides							
A1	α-HCH	84.73	83.95	81.62	88.66	84.67	78.26
A2	γ-HCH (Lindane)	84.20	78.91	75.78	94.95	85.83	79.16
A3	Heptachlor	91.08	84.10	83.35	79.38	71.09	68.94
A4	Aldrin	83.70	69.82	77.18	92.02	83.32	74.89
A5	Endosulfan Ether	84.98	69.36	75.15	92.78	56.23	66.74
A6	Endosulfan-I	82.13	69.01	73.58	81.75	76.45	68.32
A7	Endosulfan-II	84.84	74.01	78.15	87.73	83.67	71.65
A8	Endosulfan Sulfate	93.31	90.41	91.91	87.83	59.11	57.27
A9	p,p'-DDT	99.77	91.77	93.76	99.04	69.62	76.35
Synthetic Pyrethroids							
B1	Bifenthrin	90.20	68.96	94.00	92.75	78.39	59.18
B2	Lambda-cyhalothrin	82.52	104.57	100.19	93.09	44.90	35.45
B5	Cypermethrin	78.59	61.20	105.33	89.62	83.80	118.69
B6	Fenvalerate-I	85.92	106.65	107.06	86.62	27.38	59.34
B7	Fenvalerate-II	88.49	101.12	102.20	97.54	30.13	70.88
B8	Deltamethrin	77.66	71.54	95.92	80.58	25.69	111.03
Fungicides/ Herbicide							
C1	Trifluralin	87.07	83.16	76.31	77.68	66.16	72.39
C2	Hexachlorobenzene	71.62	67.03	42.79	74.91	81.50	45.21
C3	p-Chlorothalonil	83.69	64.66	76.56	101.52	61.10	73.46
C4	m-Chlorothalonil	74.69	57.26	57.90	77.01	36.45	32.00
C5	o-Chlorothalonil	89.18	80.00	78.27	97.68	96.63	94.51
C7	Hexaconazole	103.42	62.38	81.46	86.41	65.60	89.35

Key: DCM : Dichloromethane
MeOH : Methanol

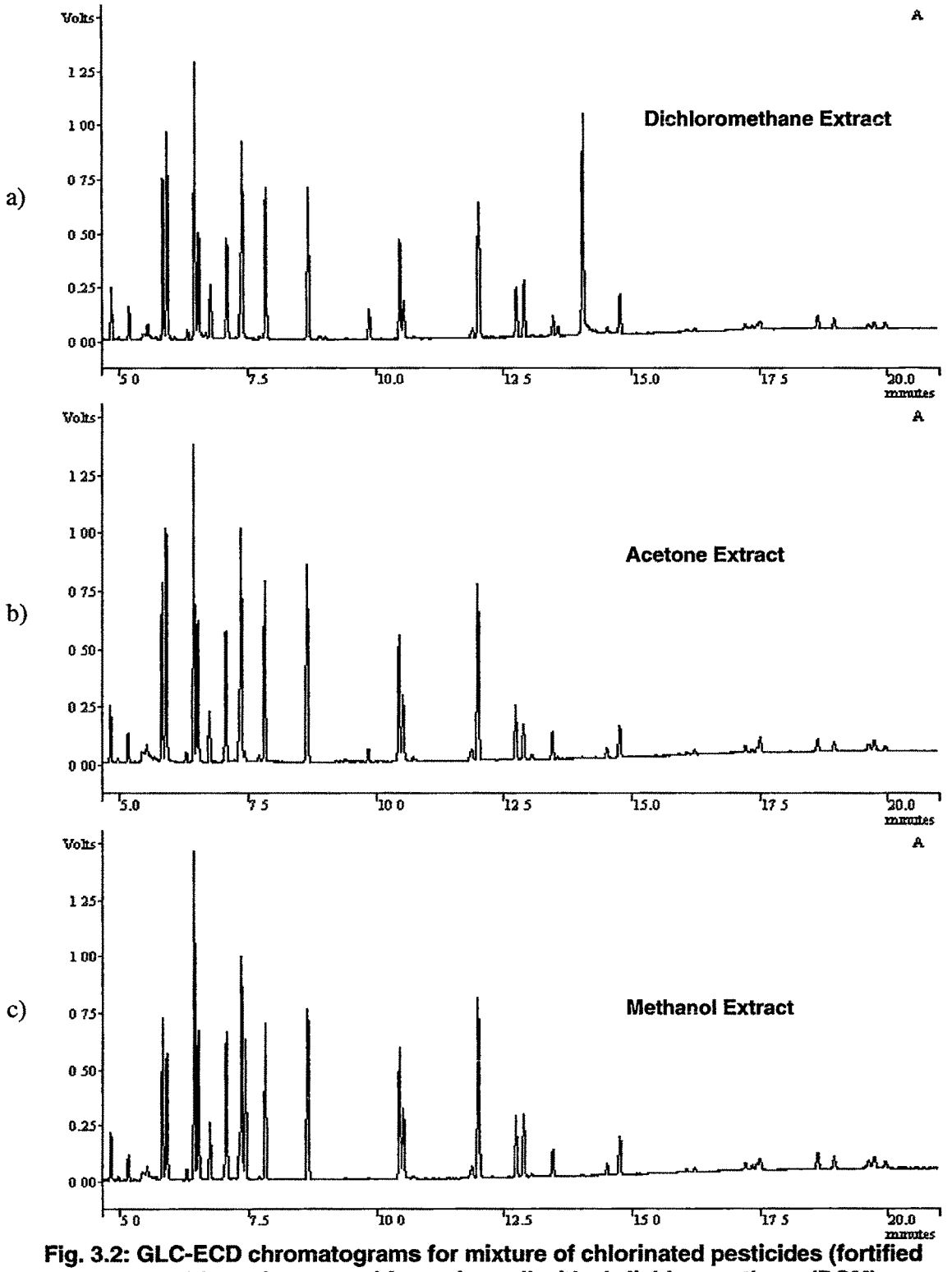

Fig. 3.2: GLC-ECD chromatograms for mixture of chlorinated pesticides (fortified at 0.01 ppm) extracted from clay soil with a) dichloromethane (DCM), b) acetone and c) methanol. [Refer Fig. 2a, page 124 for peaks identification]

3.4 Pesticides Residue Analysis in Ground Water Samples

The spiked ground water samples with pesticide mixture (0.005 µg/mL) were also extracted with various solvents viz., n-hexane, dichloromethane (DCM) and ethyl acetate, separately to evaluate the extraction efficiencies of solvents. The extraction efficiency of dichloromethane was highest (recovery 76.21 to 119.20%) followed by n-hexane (recovery 63.82 to 111.39%) and least with ethyl acetate (recovery 13.89 to 76.29%) for all groups of selected pesticides viz., organochlorine, synthetic pyrethroids and fungicides/herbicide (**Table 4**).

Table 4: Pesticides Recoveries from Ground Water by GC-ECD.

S. No.	Pesticides	R.T. (min)	Solvent Recovery (%)		
			n-hexane	DCM	Ethyl Acetate
Organochlorine Pesticides					
A1	α-HCH	5.87	94.36	101.72	52.69
A2	γ-HCH (Lindane)	6.49	95.30	95.63	45.14
A3	Heptachlor	7.87	79.12	101.28	40.32
A4	Aldrin	8.69	78.96	102.19	45.98
A5	Endosulfan Ether	7.11	85.99	102.95	49.09
A6	Endosulfan-I	10.48	79.05	100.05	45.00
A7	Endosulfan-II	12.01	85.24	90.24	38.23
A8	Endosulfan Sulfate	12.75	81.20	100.21	18.21
A9	p,p'-DDT	12.90	81.57	97.55	16.54
Synthetic Pyrethroids					
B1	Bifenthrin	13.46	63.82	76.21	13.89
B2	Lambda-cyhalothrin	14.77	100.27	99.62	40.59
B5	Cypermethrin	17.50	80.37	89.82	56.04
B6	Fenvalerate-I	18.66	108.21	118.94	58.06
B7	Fenvalerate-II	18.88	111.39	119.20	60.54
B8	Deltamethrin	19.80	104.52	111.61	50.47
Fungicides/ Herbicide					
C1	Trifluralin	4.86	93.63	115.74	70.55
C2	Hexachlorobenzene	5.96	94.28	96.13	52.46
C3	p-Chlorothalonil	6.57	74.98	78.51	42.75
C4	m-Chlorothalonil	6.79	94.91	92.90	35.29
C5	o-Chlorothalonil	7.40	96.96	117.47	58.12
C7	Hexaconazole	10.57	79.12	101.28	76.29

Key: DCM : Dichloromethane

Higher recovery with dichloromethane may be due to its semi-polar nature, which helped to break hydrogen bonding between pesticides and water molecules more efficiently. Therefore dichloromethane was most suitable solvent for the extraction of organochlorines, synthetic pyrethroids and fungicides/herbicide from water samples.

4. Conclusion

The extraction efficiencies of different organic solvents were studied for the most .suitable solvent for extraction of selected pesticides of different groups from various soil (red, black, sandy and clay) and water samples. The dichloromethane was found as ideal extraction solvent to extract all the selected pesticides from sandy and red soil samples as well as ground water samples with recovery between 76 to 120%, while acetone was suitable for clay and black soils having recovery ranged from 71 to 104%.

A simple, efficient and economic extraction technique was developed for extraction of pesticides from various soil and water samples, which does not require any clean-up or derivatisation procedure prior to analysis. A rapid and sensitive gas chromatographic method with electron capture detector was developed for simultaneous quantitation of twenty selected pesticides within 21 min. The limit of detection of method was between 0.0002 to 0.005 mg/kg for soil and 0.0001 to 0.005 µg/mL for water samples. The correlation coefficients were in the range of 0.9983 to 0.9998, with concentration ranged from 0.001 to 1.0 µg/mL, and the relative standard deviation (% RSD) was between 0.59 to 4.96% for selected pesticides. The proposed method can be used for routine residue analysis of chlorinated pesticides in various soil and water samples, due to its simplicity, short analysis time and better sensitivity.

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