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Determination of the Pesticide in Waste Water in Karauli (Rajasthan) by Differential pulse polarography

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Abstract: A Voltammetric procedure was developed for the trace determination of pesticides using Differential pulse polarography in waste water samples were described. This waste water used in irrigation of crops and vegetables in area of Karauli . Using DP polarograms of digested waste water samples in Britton Robinson buffer (BR buffer) (pH-2.87) quantities of pesticides were determined. Results obtained from the Differential pulse polarographic study of pesticide in waste water of Karauli in part per million ranges are presented in table 1.1. Which indicate that among all the pesticide Endosulphan was found in maximum concentration followed by Chlorpyrifos. Cypermethrin pesticide concentration was not observed in waste water

Key Words: Endosulphan, Chlorpyrifos Cypermethrin, DP polarography.

Introduction

Insecticides are substances from the group of pesticides intended for preventing, destroying, repelling or mitigating insects1 although there are benefits to the use of insecticides, there are also drawbacks, such as potential toxicity to humans and other animals. Residues in fruit and vegetables, cereals, processed baby food and foodstuffs of animal origin are controlled through a system of statutory maximum residue limits2. The increasing use of pesticides, especially herbicides and insecticides, in agriculture,

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forestry, and domestic activities for controlling pests causes pollution of the water resources, environment, as well as of many food stuff. The leaching run-off from agricultural and forest lands; deposition from aerial applications and residue from the industrial wastewater treatment are mainly responsible for the water contamination3. The pesticides form a strong class of water and environment pollutants, as they are sometimes non biodegradable. The toxicity of pesticides and their degradation products make these chemical substances potentially hazardous contaminants of the environment4. According to the Stockholm Convention on Persistent Organic Pollutants, nine of the dozen of the most harmful and persistent organic chemicals are pesticides5.

The insecticides can be grouped by means of sorting into chemical families. Major insecticide families include organochlorines, organophosphates, carbamates, and neonicotinoids. Organochlorine hydrocarbons (e.g. DDT) could be separated into dichlorodiphenylethanes, cyclodiene compounds, and other related compounds. They operate by disrupting the sodium/potassium balance of the nerve fiber, forcing the nerve to transmit continuously. Their toxicities vary greatly, but they have been phased out because of their persistence and potential to bioaccumulate6. For instance, due to Insecticides extreme stability of highly toxic organochlorines, these formerly popular products (like the above-mentioned DDT) have largely been replaced by organophoshates and carbamates. Nevertheless, they are toxic as well, operating through inhibition of the enzyme acetylcholinesterase, allowing acetylcholine to transfer nerve impulses indefinitely and causing a variety of symptoms such as weakness or paralysis. Moreover, organophosphates are quite toxic to vertebrates, and have to be, replaced by less toxic carbamates7.

CHLORPYRIFOS

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By the activities of modern industries and agriculture many anthropogenic organic pollutants have found their way into the environment. Therefore, the distribution of insecticides in marine water samples deserves great interest8. Organophosphorous pesticides are very important from a toxicological point of view due to their bioaccumulation ability. Chlorpyrifos is an organophosphorous insecticide widely used for urban and domestic pest control, including turf maintenance, and as a termiticidal barrier in around or under buildings. Chlorpyrifos pesticide also uses in Agricultural crop plant (cotton, sugarcane, vegetables, cereals, canola, rice, pome fruit, stone fruit, citrus, tropical fruit and grapes) for pest control. Organophosphorous insecticides exert their effects by inhibiting the activity of an enzyme known as acetyl cholinesterase that is important in the transmission of nerve impulses. Chlorpyrifos can be readily absorbed by the mammalian skin, and can cause health risks9-10. Various chromatographic11-19, spectrometric20-23 and electrochemical24-30 techniques have been used for the determination of insecticides. Chlorpyrifos was determined in natural waters and soil samples by magnetic particle-based ELISA30-33, and number of spectrophotometric methods34-38. The simultaneous determination of the carbamate pesticide carbaryl and a group of organophosphate pesticides including Chlorpyrifos was developed using reversed phase HPLC39.To our knowledge there has been no study on the use of adsorptive stripping voltammetric determination of Chlorpyrifos in a commercial formulation40. Thus, the voltammetric reduction behavior of Chlorpyrifos and the DPP polarographic determination of the aforementioned pesticide in a pesticide formulation, vegetable, waste water and soil samples were investigated.

CHEMICAL IDENTITY

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(a) Name (CAS): O, O-Diethyl-O-(3, 5, 6-trichloro-2-pyridinyl) phosphorothioate

(b) Common name: - Chlorpyrifos

(c) CAS number: - 2921-88-2

(d) Molecular formula: - $C_9H_{11}Cl_3NO_3PS$

(e) Molecular weight: - 350.6

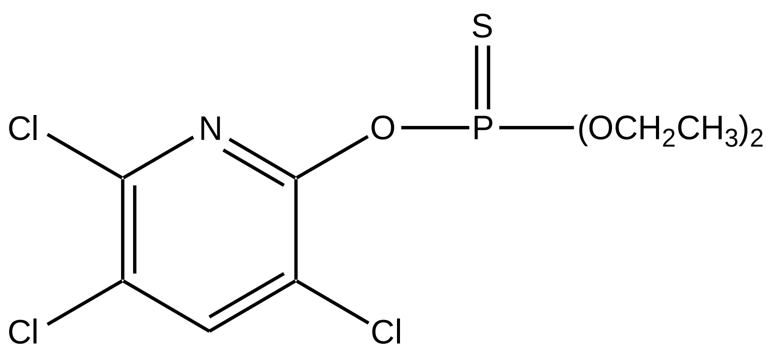

Fig. 1.1: - Structure of the pesticide Chlorpyrifos.

PHYSICO-CHEMICAL PROPERTIES

Melting Point: 42-43.5oC

Vapour Pressure: 2.7 mPa at 25oC

Water Solubility: 1.4 mg/L at 25oC

Partition Coefficient: Pow = 50 000; log P = 4.7 (*n*-octanol/water)

Dissociation constant: not readily dissociable functionality

CYPERMETHRIN

Cypermethrin is a synthetic pyrethroid used as an insecticide in large-scale commercial agricultural applications as well as in consumer products for domestic purposes. It behaves as a fast-acting neurotoxin in insects. It is easily degraded in soil and

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plants but can be effective for weeks when applied to indoor inert surfaces. Exposure to sunlight, water and oxygen will accelerate its decomposition. Cypermethrin is highly toxic to fish, bees and aquatic insects, according to the National Pesticides Telecommunications Network (NPTN). It is found in many household ant and cockroach killers, including Raid and ant chalk.

CHEMICAL IDENTITY

(a) IUPAC: (RS)-y-cyano-3-phenoxybenzyl (1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate

(b) Common name: - Cypermethrin

(c) CAS Reg. No.: 52315-07-8

(d) Molecular formula: $C_{22}H_{19}Cl_2NO_3$

(e) Molecular weight: 416.32

Structural formula:

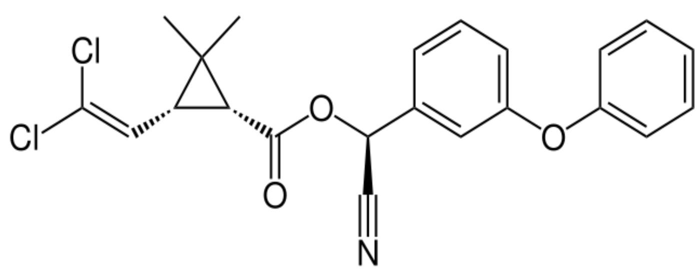

Fig.1.2:- Structure of the pesticide Cypermethrin.

ENDOSULPHAN

Endosulphan is a broad spectrum Organochlorine insecticide. Endosulfan remains the major exception and is still widely applied to crops – particularly in the developing world. Due to its potential to evaporate and travel long distances in the atmosphere, endosulfan has become one of world's most widespread pollutants. Endosulfan is now found extensively in global water resources, soils, air, rainfall, snow and ice deposits and oceans. It is also found in remote ecosystems such as the Arctic, Antarctic, Great Lakes, Canadian Rockies, Costa Rican rainforests, Alps, and Himalayas. According to the European Union "endosulfan is very toxic to nearly all kinds of organisms"41 Levels in the environment are frequently high enough to impact on wildlife. According to the US EPA, "Monitoring data and incident reports confirm that endosulfan is moving through aquatic and terrestrial food chains and that its use has resulted in adverse effects on the environment adjacent to and distant from its registered use sites42 Endosulfan is detected in the tissues of animals worldwide, including polar bears, antelope, crocodiles, Minke whales, and African vultures. Endosulfan is a toxic Organochlorine pesticide. Endosulfan is widely applied on vegetables such as cauliflower, potato, spinach, etc. It reaches the body through contaminated water and food. It is highly toxic and major route for the endosulfan absorption in application tasks are dermal and respiratory43.The various disorders caused from endosulfan in humans due to toxicity are savalation, less carbohydrate and lipid content etc. Various analytical complicated methods are reported for the determination of Endosulfan. Spectrophotometric method for the determination of endosulfan is based on its liberation of sulfur dioxide by using acid reagent which is then absorbed in an absorbing medium and subsequently estimated by a suitable reagent.

CHEMICAL IDENTITY

(a) IUPAC-6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9ahexahydro-6,9-methano- 2,4,3-benzodioxathiepin-3-oxide.

(b) Common name: - Endosulphan

(c) CAS No.: 115-29-7

(d) Molecular formula: $C_9H_6Cl_6O_3S$

(e) Molar mass: 406.93

PHYSICOCHEMICAL PROPERTIES

Appearance - sold in the form of brown crystalline flakes.

Melting point 79–100 °C

Vapour pressure 1.3 × 10-3 Pa at 25 °C

Solubility in water 60–150 µg/litre; increases with decreasing pH

Structural formula:

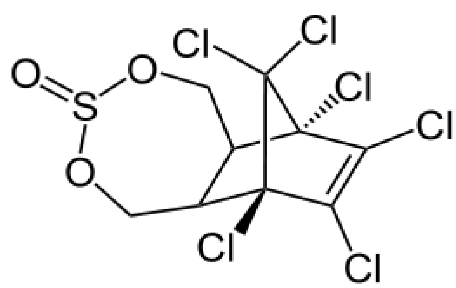

Fig.1.3:- Structure of the pesticide Endosulfan.

Experimental Section

Apparatus: An ELICO CL-362 POLAROGRAPHIC ANALYSER (Make: Elico) was used for measurement of current voltage relationship (polarograms) on electrolyzing electroactive analytes in polarographic cell. This apparatus has three electrode assembly, dropping mercury electrode as working electrode, calomel as reference electrode and platinum as counter electrode. Dropping mercury electrode had the characteristics m = 2.422 mg/sec, t = 2.5 sec and h = 60 cm. DP polarograms were recorded by the Printer Epson-LX-300+II, under the conditions of Pulse Amplitude 50 mV and 6 mV/S scan rate. Elico digital pH meter was employed to measure the pH of solution.

Reagents: All reagents used were of analytical reagent grade purity (AR). The mercury used in the dropping mercury electrode was obtained from Merck. Britton-Robinson (BR) universal buffer solutions containing a mixture of equal amounts (0.08 mol/L) of phosphoric, boric and acetic acids with sodium hydroxide (0.02 mol/L) were applied as supporting electrolyte and to provide the various pH values. Standard Stock solutions ($1x10^{-4}$ mol/L) of pesticides (technical grade, 21.5% w/w) were made up in ethanol. A series of standard solutions of pesticides were prepared by diluting the stock solution with distilled water in presence of few drops of ethanol to prevent turbidity.

The C-V data for test solution were recorded after passing pure nitrogen gas in the test solution and 0.001% triton-X-100 was used as maxima suppressor.

Glassware: All glassware were soaked in 2.0 M nitric acid for at least 7 days, washed three times with distilled deionized water, soaked in 0.1 M hydrochloric acid until ready for use. In distilled deionized water and finally soaked.

Procedure

Sampling and digestion: Waste water samples were collected from the area of Karauli (Rajasthan India), at first dried in an oven at about 105 $^{\circ}$C until constant weight. Then it's digested by dry ash method.

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Electro analytical determination: A total of 10 ml. electrolyte was de-aerated by a stream of nitrogen gas (99.999 %) for about 15 min. Polarograms were taken by scanning the potential in the negative direction from 0.0 to –1.5 V, depending on pH, at a scan rate of 5 mV/s. to the sample solution taken in Pyrex polarographic cell including 2.0 ml. of suitable buffer solution, we add 0.1 ml. of 0.001% triton-X-100 and remaining required volume of distilled water. After that the polarographic cell was de-aerated by a stream of nitrogen gas for about 15 minutes. To ascertain the presence of the pesticide in the sample, a known quantity of stock standard solution of pesticide was added to the analyte and polarograms were recorded. An increase in the wave height of the ion signal was observed without any change in its $E^{1/2}$ values confirming the presence of pesticides in waste water samples solution.

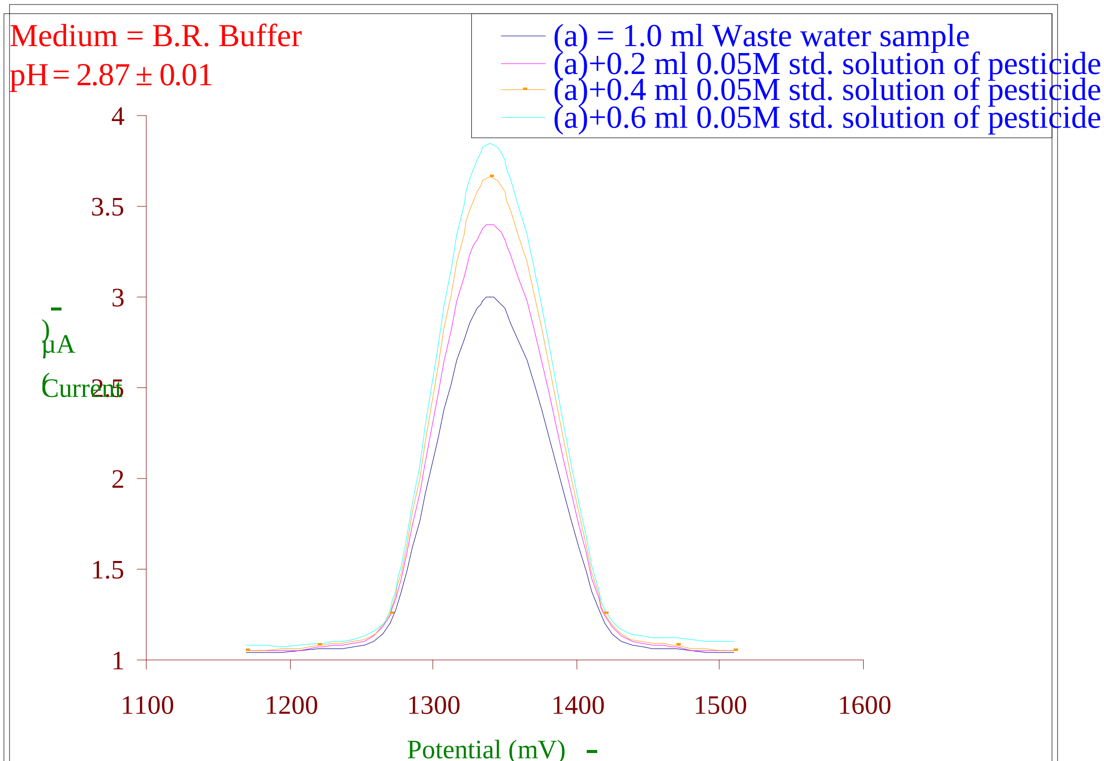

Fig. 1.1(A) :- Differential pulse polarogram of Chlorpyrifos in Waste water

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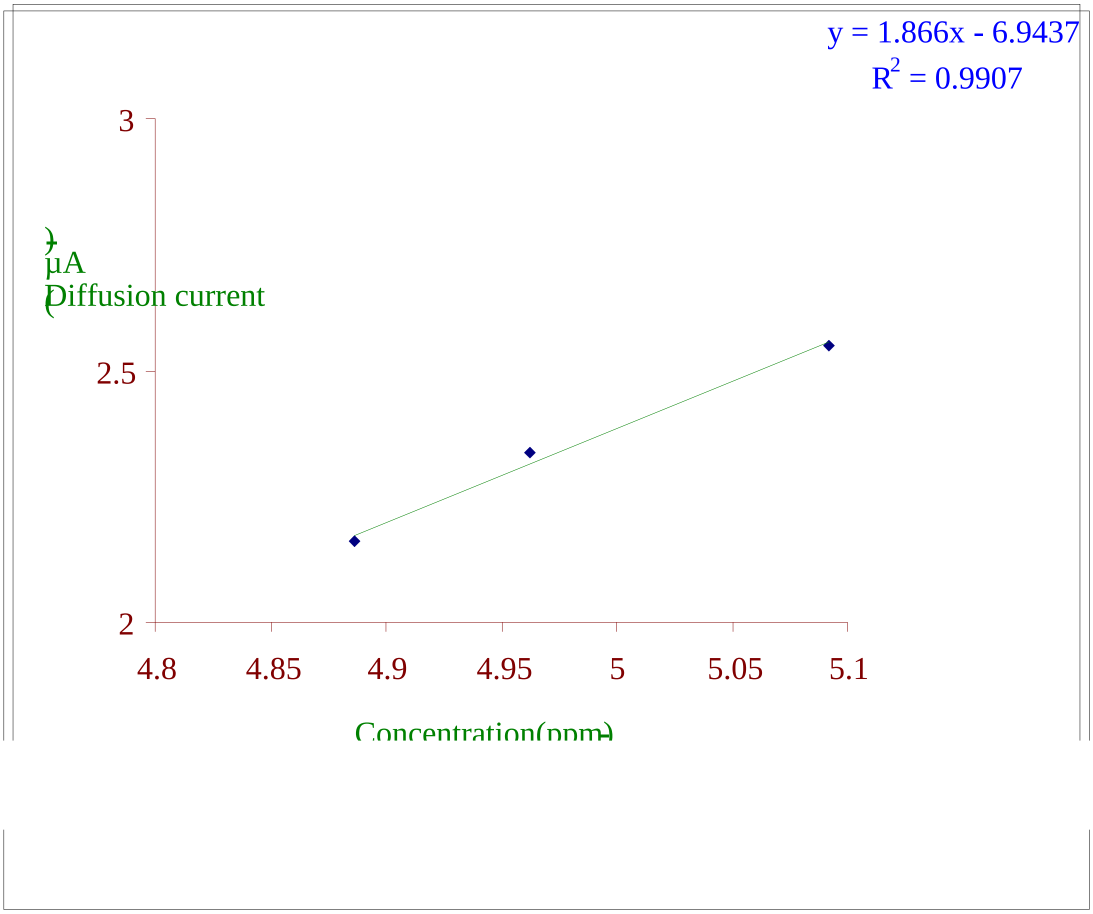

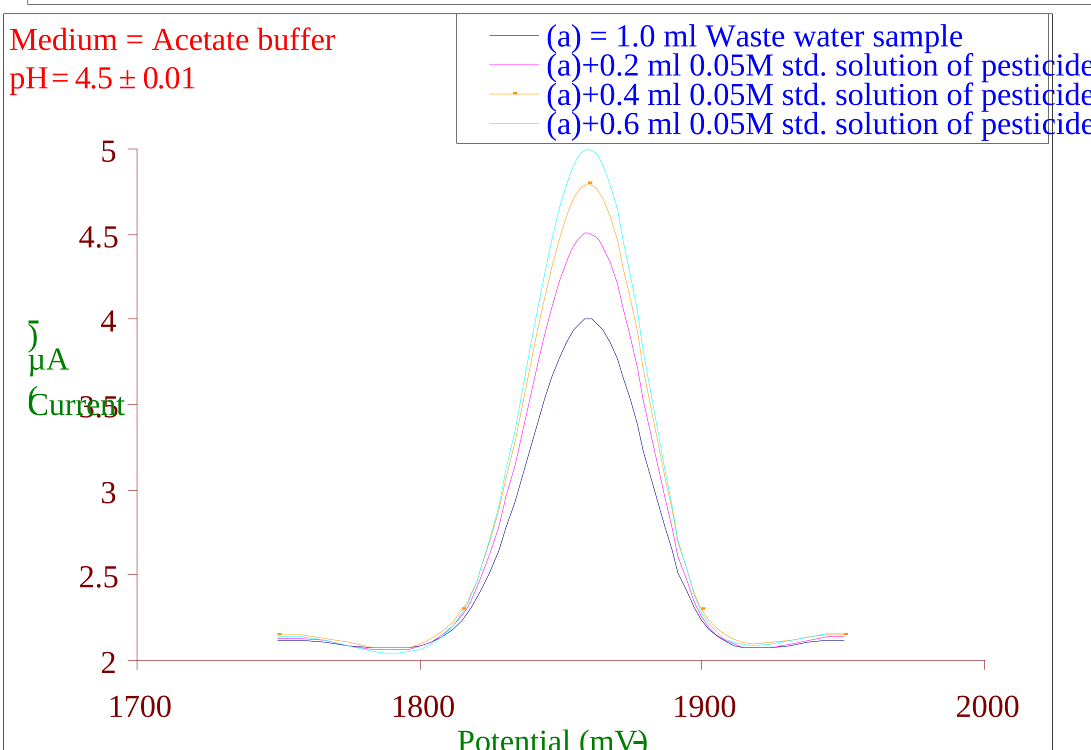

Fig. 1.2(A) :- Differential pulse polarogram of Endosulphan in Waste water

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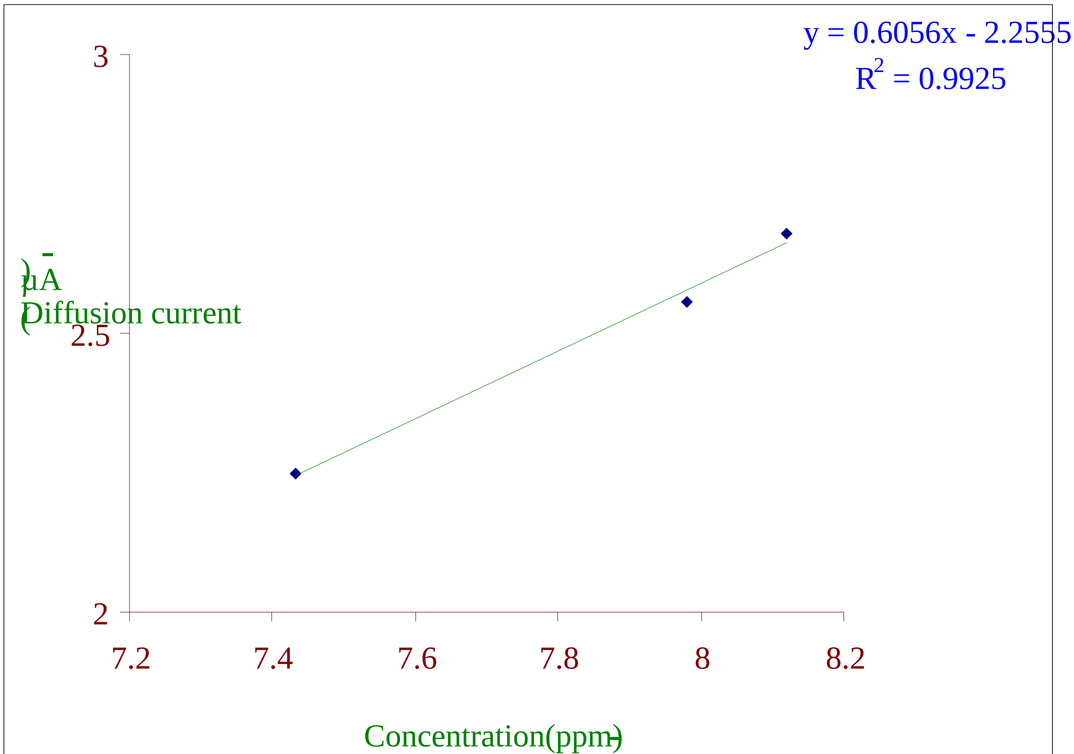

Fig. 1.2(B) :- Calibration curve of Endosulphan in Waste water

Table – 1.1

Trace analysis of Pesticides in Waste water sample

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Sample	Supporting electrolyte/Buffer	Half wave potential as E1/2 (volts)	Conc. in ppm			% Error	Mean deviation	Standard deviation
			Taken	Observed	Mean			
Chlorpyrifos	Britton-Robinson (BR) (pH-2.87)	-1.36 V	5	4.886 4.962 5.092	4.910	0.003	0.074	0.104
Endosulphan	Acetate buffer pH-4.5±0.01	-1.86 V	8	7.433 7.980 8.121	7.844	0.019	0.274	0.363

Representative Polarograms for different pesticide (Chlorpyrifos, and Endosulphan) in waste water determined are shown in Fig. 1.1(A) to Fig. 1.2. (A) Calibration curve of standard addition of pesticide are given in Fig. 1.1(B) to 1.2(B). Linearity of calibration curves was obtained in all cases with the value of correlation factor (r) near to one. Linear relationship between concentration and diffusion current (Id) has been proved statistically by applying straight line equation to all calibration curves.

The results obtained from the Differential pulse polarographic study of pesticide in waste water of Karauli in part per million ranges are presented in table 1.1. Which indicate that among all the pesticide Endosulphan was found in maximum concentration followed by Chlorpyrifos. Cypermethrin pesticide concentration was not observed in waste water

Recently **Industrial Toxicology Research Center (ITRC), Lucknow** has established a central facility for safety evaluations of pesticides with the following objectives.

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- To generate toxicological data on different pesticides synthesized, manufactured or formulated by national laboratories and private sector industries within the country.
- To conduct carcinogenic, teratogenic and multigeneration studies on selected strains of experimental animals, invivo tests using bacterial mutants, human cell links and lymphocytes to map mutagenic and carcinogenic effects and interference immune mechanism.
- To study cytogenic effects of pesticides using bone marrow cells of intact animals.
- To develop new techniques for monitoring and predicting harmful effects of pesticides on target and non-target organisms and their diffusion in the environment.
- To provide expertise for diagnosing toxic hazard’s symptoms and developing methods of their prevention and control.

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