Voltammetric studies and Determination of pesticides in soil samples

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Abstract: With the "Green Revolution", spreading into rural areas, the demand for both fertilizers and biocidal chemicals is on increase. The biocidal agricultural chemical collectively known as pesticides are the largest group of toxic substances widely broadcast today. These pesticides have ability to destroy, prevent, repel or mitigate any pest. The use of these pesticides have resulted in higher production of food grains, oil seeds and fibre crops to take the country towards self sufficiency in these and other agricultural commodities. But all these pesticides are toxic to pests are also very harmful for vegetation and animal life.

Keywords: pesticides, fertilizers, Thiram, Methyl Parathion

1.0 Introduction: Three major problems threaten to limit the continued applications of pesticides:

1. Some pest organisms have developed resistance to these chemicals. This necessitates higher dosages or development of even more toxic chemicals to replace those to which the pests are resistant.
2. Some pesticides are not readily biodegradable and tend to persist for years in the soil.
3. Those pesticides which are not readily biodegradable move to other parts of the environment and cause detrimental effects on the organisms other than the target pests.

A number of workers have studied uptake, elimination, accumulation and fate of various kinds of pesticides. The pesticides have been reported to produce severe histopathological changes. In Rajasthan the main crops are Gram, Mustard, Wheat, Barley, Tomato, Cabbage etc. For these crops, a number of pesticides are used as listed below in table 1

Table 1: Number of pesticides

S.No.	Pesticide	Crops
1.	Malathion	Gram , Tomato, Canesugar, Groundnut, Pulses etc.
2.	Endosulfan	Pulses, Gram, Wheat , Barley, Grapes, Brinjal
3	Methyl Parathion	Mustard, Gauava, Mango, Wheat, Groundnut
4.	Aldrin	Mango, Potato, Gram
5.	Benzene hexachloride	Grains, Mustard,
6.	Thiram	Brinjal, Tomato, Chilly, Green Vegetables
7.	Phosphamidon	Wheat, Barley

Moreover they also cause dizziness, paresthesia of tongues, headache, nausea, and hyperirritability, urticaria in some cases, cyanosis, leukocytosis, tremors, convulsions, hypertension, vomiting, diarrhea and many other fatal diseases.

Out of these, two pesticides Methyl Parathion and Thiram which are much used in the agricultural fields around Jaipur were chosen for their analysis in soils and plants.

2.0 Voltammetric Study of Methyl Parathion: Reduction of Methyl parathion was studied in various supporting electrolytes viz. 0.1 M sodium –acetate- acidic acid buffer (pH4.2), lithium chloride-lithium hydroxide buffer (pH12.57), 0.1 M phosphate buffer (pH 6.1), borate buffer (pH 9.3), B.R. buffer (pH 2.89), ammonia- ammonium chloride buffer(pH 9.27) and ammonium tartarate buffer(pH 9.54) at parts per million level using differential pulse Polarography.1000 ppm stock solution of methyl parathion was prepared by dissolving accurately weighed 100 mg of the compound in 20% ethanol in 100ml of the solution 1 ml of supporting electrolyte and 10 ul of 1000 ppm methyl parathion solution were diluted to 10ml to prepare the sample solution. The solution was deaerated for the fifteen minutes by passing purified nitrogen gas.Differential pulse polarogram were then recorded using polarographic analyzer. Well defined differential pulse polarogram were obtained in all these supporting electrolytes as shown in fig1.

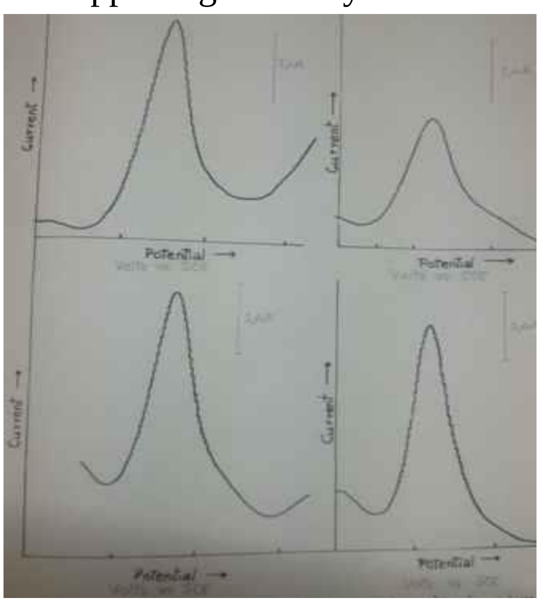

Fig1: differential pulse polarogram of methyl parathion in various supporting electrolytes.

Calibration curves in all the supporting electrolytes are linear as shown in fig 2.

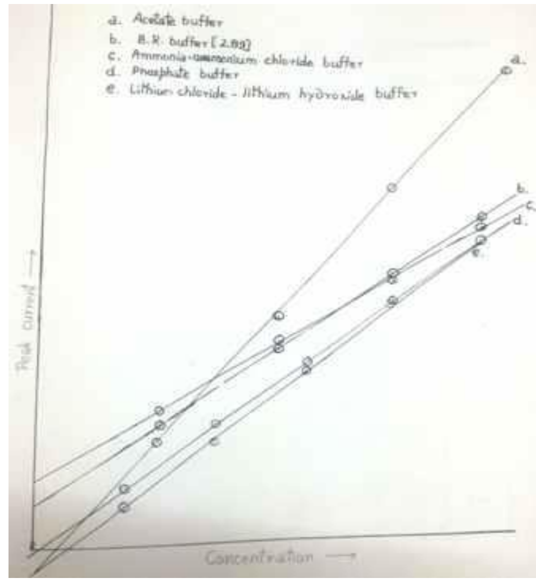

Fig2: Calibration curve of methyl parathion in various supportive electrolytes at microgram levels

2.1 Determination of Methyl Parathion in Soil Samples: Methyl Parathion was determined in soil samples taken from agricultural fields around Jaipur Mustard, Spinach, Coriander, potato etc were grown. Samples were collected separately from surface and two, six and ten inches depths using a post hole augur. The samples were mixed thoroughly and then grab samples were taken. Laboratory preparation of soil sample solutions collected from five different agricultural fields was done. These soil samples were oven dried and mashed thoroughly in a mortar. Further the samples were filtered through a 0.2 mm sieve. Extraction of Methyl Parathion from these soil samples was carried out using acetone.

One ml of soil sample solution plus one ml of the lithium chloride- lithium hydroxide buffer was diluted to ten ml and the resulting solutions were analyzed by differential pulse adsorptive stripping voltammetry using the method of standard additions. Well defined Voltammograms were obtained in all cases, out of which voltammograms and calibration curve of sample number three are given below in table 2 and fig 3.

Table2: Estimation of Methyl Parathion

Sample No.	Concentration(ppb)		Conc. Per gm of soil(ppm)	Percentage Standard Deviation
	Found	Average		
1.	255.65 316.06 273.01	281.57	1.13	9.02
2.	490.14 490.47 489.17	492.26	1.97	0.75
3.	836.89 836.48 819.29	830.89	3.32	0.99
4.	357.86 355.24 360.17	357.76	1.43	0.56
5.	430.27 425.36 432.52	429.38	1.72	0.70

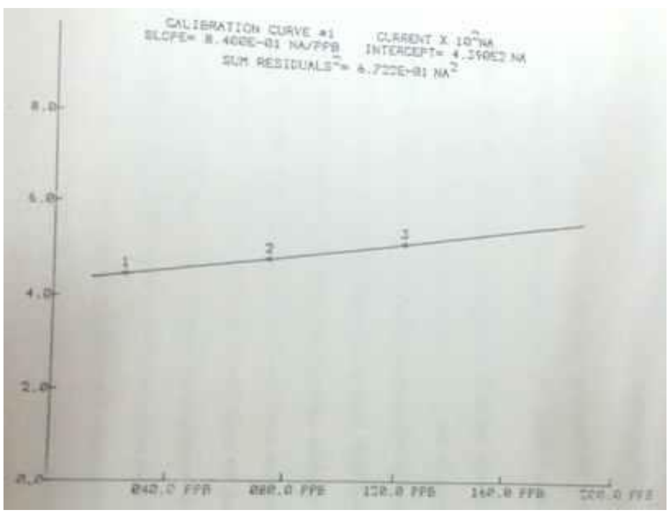

Fig 3: Calibration curve for estimation of methyl parathion in soil sample

3.0 Voltammetric study of Thiram: Adsorptive stripping Voltammetric study of Thiram was carried out in sodium acetate-acetic acid buffer, 0.1 M phosphate buffer, borate buffer, lithium chloride- lithium hydroxide buffer, B.R. buffer of differing pH, ammonia-ammonium chloride buffer at parts per billion levels. 100 ppm stock solution of Thiram was prepared by dissolving accurately weighed 10 mg of the compound in 50% DMSO solution. Sample solutions of known concentrations of thiram were prepared by adding requisite amounts of thiram solution to 1 ml of supporting electrolyte and diluting it to 10 ml. Deaeration with purified nitrogen gas of A.R grade was done for 15 mins prior to the analysis. Well developed peak voltammograms were recorded using polarographic analyzer model 384 A. It is shown in fig 4 given below. Effects of parameters initial potential, accumulation time and modulation amplitude were studied and their optimum values were chosen for these analyses.

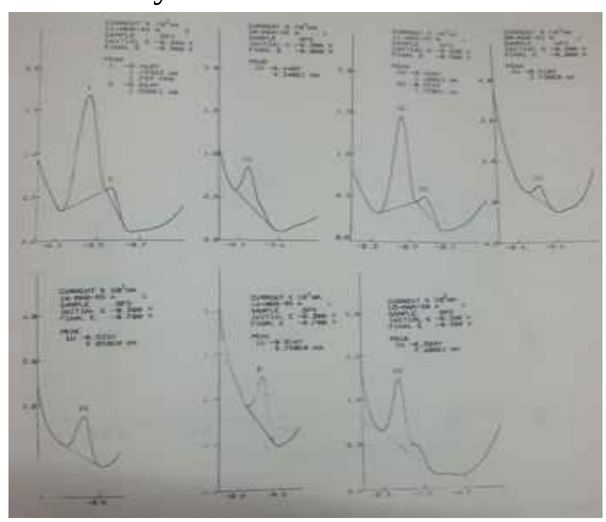

Fig 4: Differential pulse adsorptive stripping voltammograms of thiram in different supporting electrolytes

3.1Determination of Thiram in Soil Samples: Soil samples are collected from different agricultural fields near Jaipur. Procedure for sample collection was same as that for methyl Parathion. The compound was extracted from these soils using dimethyl glyoxime. 5 gms of soil samples was accurately weighed in a beaker and 10 ml of DMSO was added to it. The contents were shaken well and then filtered for complete extraction. The process was repeated twice each time with 10 ml of DMSO. The Solution was then made up of 50 ml. in volumetric flask. These samples were analyzed for Thiram in lithium Chloride – lithium hydroxide buffer using differential pulse adsorptive stripping voltammetry. Representative peak voltammograms of thiram in soil sample number 3 and its calibration curve is shown in fig 5. Table 3 gives thiram concentration in five agricultural fields near Jaipur. All these results are very reproducible with standard deviation varying from 0.7 to 3.5 %.

Table 3: Determination of Thiram in Soil Samples

Sample No.	Concentration (ppb) Found	Average	Conc. Per gm of soil(ppm)	Percentage Standard deviation
1.	371.04 357.06 360.14	362.75	3.63	1.65
2.	437.86 392.58 416.72	415.72	4.16	4.45
3.	109.07 112.73 111.22	111.01	1.11	1.01
4.	164.28 168.36 167.47	166.70	1.67	1.05
5.	579.38 583.52 585.30	582.73	5.83	1.06

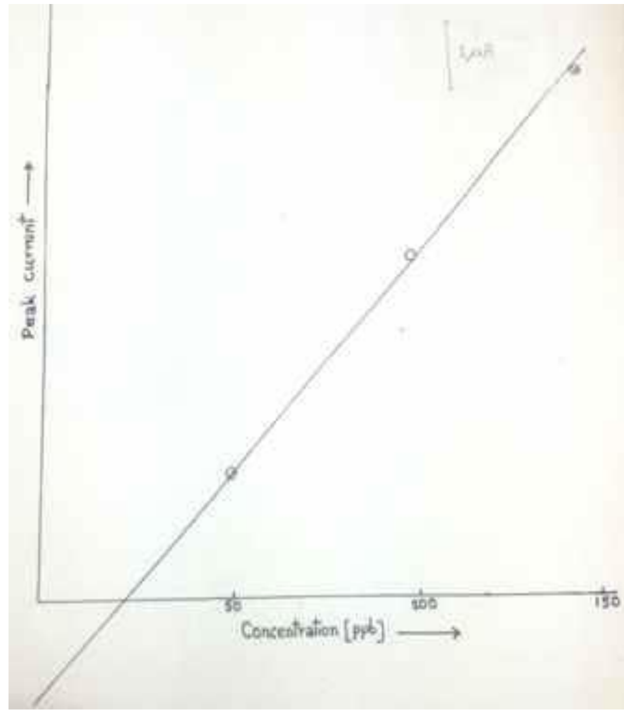

Fig5: Calibration curve of thiram analysis in soil sample

4.0 Conclusion: Voltammetric methods namely differential Polarography and differential pulse adsorptive stripping voltammetry were used to determine pesticides in soil samples of different agricultural fields. Results obtained for the pesticides methyl parathion and Thiram are given in this paper, which shows that these pesticides can be determined in soil samples with great accuracy with relative standard deviations.

References:

1. Rupp, Elinore, B:Zuman, Peter, sestakova, Ivana, Horak, Vaclav.J Agric. Food Chem., 40(10), 2016-21(1992).

2. Frankenberger WT, Tabatabai MA, Jr, Tabatabai MA. Factors affecting L-asparaginase activity in soils. Biol. Fert. Soils. 1991;11:1, 5.

3. Frumkin H. Agent Orange and Cancer: An Overview for Clinicians. CA Cancer J Clin. 2003;53:245. [PubMed].

4. Garbarino JR, Snyder-Conn E, Leiker TJ, Hoffman GL. Contaminants in Arctic snow collected over northwest Alaskan sea ice. Water,Air and Soil Pollution. 2002;139:183–214.

5. Geluso KN, Altenbach JS, Wilson DE. Bat mortality: pesticide poisoning and migratory stress. Science. 1976;194:184–186. [PubMed]

6. Glotfelty J, Schomburg J. Volatilization of pesticides from soil in Reactions and Movements of organic chemicals in soil. In: Sawhney BL, Brown K, editors. Madison, WI: Soil Science Society of America Special Pub; 1989.

7. Dissipation and Residues of Thiram in Potato and Soil,Shaowen Liu, Aijuan Bai, LiZhou, ChuanshanYu, Yanjie Li,Sufang Fan, and Canping Pan, Journal of Chemistry, Volume 2015, Article ID 623847, 6 pageshttp://dx.doi.org/10.1155/2015/623847.

7. Proposed method for Modern Voltammetric studies, Dr.Bhawana Mathur, JETIR , vol.5, Issue 12, Page 21-24, Dec 2018.