THIN LAYER CHROMATOGRAPHY OF PESTICIDES AND THEIR RESIDUES

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Recent progress in the analysis of organo-phosphorus, organo-chlorine, carbamate, urea, uracil pesticides and their residues by thin layer chromatographic methods employing chemical and enzymatic methods is reviewed.

Amongst various analytical methods for pesticide residues thin layer chromatography (TLC) is easily adaptable in routine analysis. This review highlights the work done during the last five years on TLC methods for analysis of pesticide formulations and pesticide residues. In 1938, Izmailov & Shraiber[1] observed that division of substances into different zones on a thin layer of adsorbent placed on a glass plate, using only a drop of substance under test, enables one to obtain satisfactory results in a minimum time. In 1947, Williams[2] reported the use of thin layers of adsorbent held between two horizontal glass plates with a small hole on the top plate for application of sample and developer, and the chromatogram was made in circular manner. From then onwards extensive contributions to the development of TLC were made resulting in various adsorbents, binding agents[3] and different equipment for preparation of chromatostrips[4]. With the development of standard absorbent (e.g. silicagel, plaster of Paris) and a system involving standard size glass plates (5 cm × 20 cm and 20 cm × 20 cm) the use of TLC techniques increased after 1958. TLC has found wide recognition in a number of fields and its sensitivity of detection is of interest to analytical chemists, particularly those working in Defence on the analysis of pesticides and their residues. Most comprehensive work on the subject of separation of pesticides by TLC is that of Walker & Beroza[5]. Application of TLC in the qualitative detection and quantitative estimation of organo-chlorine, organo-phosphorus and other pesticides has already been reviewed[6-8].

Although gas liquid chromatography (GLC) is the most sensitive method for the separation and quantitative estimation of pesticide residues, TLC is simpler and more economical. Advantages of TLC over GLC have been reported earlier. TLC is far more sensitive than paper chromatography; moreover the more frequently used adsorbents (silicagel and alumina) have inherent clean-up properties as well which entails minimum pre-purification of the extract containing pesticide residues.

DDT, *DDE*, and *DDD* are poorly separated by TLC with chloroform as solvent while paper chromatography resolves them. Similarly, toxaphene which is made up of many isomers and different chlorinated camphene products, gives only one or two spots by TLC, indicating that the resolution by TLC is not too efficient. However, the speed of the method (about one hour) and high capacity of the coated plates (about 250 μg per spot) along with the simplicity of procedure and equipment make TLC as most promising method for analysing pesticide residues. A review on the application of TLC to the quantitative analysis of food additives and pesticides in foods has already been published[9].

ORGANO-PHOSPHORUS PESTICIDES AND RESIDUES

There has been an increase in use of organo-phosphorus pesticides compared to organo-chlorine pesticides. TLC is a popular method for identification and semi-quantitation of organo-phosphorus pesticides. Both chemical and enzymatic methods were used for detection of pesticide residues on thin layer plates.

Chemical Methods

A quantitative TLC method[10] was described for the separation and identification of organo-phosphorus pesticides, i.e. dichlorovos, dimethoate, malathion, methyl parathion, parathion and trichlorophon in acutely poisoned rats and chickens using silicagel *G* as adsorbent with chloroform-acetone or chloroform carbontetrachloride (1 : 1) as solvents and different coloured spots were observed when sprayed with silver nitrate, alcoholic sodium hydroxide and palladium chloride. Several organo-phosphorus insecticides in biological material[11] were identified and qualitatively analysed by thin layer and paper chromatography.

Dimefox, *bis*-dimethyl-aminofluorophosphine oxide has been detected and determined quantitatively by TLC on silicagel-kieselguhr plates using ninhydrin[12].

A TLC procedure for 42 organo-phosphorus insecticides using five ternary solvent systems and three selective chromatogenic sprays were reported for separation and identification of migrated spots[13]. Six organo-phosphorus pesticides (azinophos-methyl, carbophenothion, diazinon ethion, malathion and mevinphos) were resolved and identified by TLC in the presence of plant extracts without elaborate clean-up[14]. Organo-phosphorus insecticide degradation products[15] especially *O*-methyl-*O*-(4-bromo-2, 5 dichlorophenyl) phosphorothionate (dimethyl bromophos) have been separated by TLC on silicagel *G* using methyl cyanide and water (88 : 12) as developing solvent and 2, 6-dibromobenzoquinone-4 chloromide with acetic acid as spray reagent; same reagent in *n*-hexane or petroleum alongwith others like bromophenol blue and *N*-bromosuccinimide followed by fluoroscein were used for separation and identification of insecticides (malathion dimethoate and ethion) in traces on thin layer silicagel *G* plates exposed to bromine vapour[15]. Blue spots of organo-phosphorus pesticides and some of their break down products appeared on developed chromatoplates when sprayed with a new general chromogenic reagent, 4-picoline[17] followed first by *O*-nitrobenzene and then alkali.

Nineteen organo-phosphorus pesticides were resolved by TLC on polyamide layer[18]. Detection of pesticides on polyamide layer was superior to that of silicagel layers. Polyamide TLC[19,20] was extended to the detection of organo-phosphorus pesticide residues in foods and pesticide preparations. *DDVP* (*o*, *o*-dimethyl, 2, 2-dichlorovinyl phosphate) in plants, soil, and water was determined by TLC on silicic acid or silicagel grade *KSK* plates[21]. A comprehensive scheme for organo-phosphate insecticides from river waters and sewage effluent[22] has been suggested using TLC, gel chromatography (sephadex LH 20) and gas chromatography. TLC was used to identify a wide variety of organo-phosphate insecticides from biological materials[23]. Semi-quantitative analysis of dimethoate (Rogor) residues in foods has been accomplished by TLC[24]. Various organo-phosphorus pesticides were separated by rapid reversed phase TLC; the method was satisfactorily applied to extract of treated vegetables and to commercial pesticide preparations[25] and for detection of pesticide residues in and on seven different vegetables[26]. TLC methods for organo-phosphorus pesticides in fruits and vegetables have been studied[27]; fenthion (baytex) residues in apples and plums[28] after charcoal clean-up have been separated and estimated by TLC. Thimet and parathion from green tobacco leaves[29] and dipterex (dylox) in milk[30], have been separated and estimated by TLC. Dylox (trichlorophon), *DDVP* and malathion in water samples[31] were separated and identified by TLC; and 23 organo-phosphate insecticides in river waters have been studied[32] by TLC on layers of alumina *G*.

Diazinon, *O*, *O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothiate, and its metabolites or degradation products were resolved and identified by two dimensional TLC on silicagel plates using ten spray reagents showing sensitivities ranging from 0·05 to 1 μg. of compound[33]. Two dimensional TLC on silicagel *G* was also used for separation and identification of parathion, malathion, fenthion, dimethoate and demeton-methyl from liver using palladium chloride as spraying reagent[34]. Parathion and suspected metabolites have been separated[35-37] and analysed by TLC. Malathion, it's metabolites and isomers of malathion monocarboxylic acid have been isolated and determined[38] by TLC. Separation and identification of malathion, sumithion and parathion were effected[39] by TLC on magnesium hydroxide, which has been found to be a satisfactory substitute for commonly used adsorbents like silicagel, alumina and kieselguhr.

A rapid method was developed for separation and determination of organo-phosphorus pesticides by TLC on kieselgel *H* plates using benzene-acetone (9 : 1) mixture as solvent system and ethanolic iodine as chromogenic reagent[40]. Three chromogenic reagents [3, 5-dibromo-*p*-benzoquinone chlorimine solution in cyclohexane, *N*-ethanolic potassium hydroxide followed by *p*-nitrobenzene diazonium fluoroborate in diethylene glycol-ethanol (1 : 9) and bromine vapour exposure followed by 4-methyl unbelliferone solution in water-aqueous ammonia-ethanol (10 : 1 : 10)] were used for detection and determination of 11 organo-phosphorus insecticides by TLC [41]. Various chromogenic spray reagents for TLC of pesticides have been studied and reviewed[42]. Use of methyl yellow as a single chromogenic reagent for TLC detection of organo-phosphorus pesticides and their breakdown products was described[43]. Developed TLC plate exposed to bromine vapour and pesticides were made visible by subsequent spraying with methyl yellow.

A new two dimensional TLC technique was developed for detection of organo-phosphorus pesticide residues in nanogram level. The pesticides were oxidised with bromine vapour on TLC plate after one dimensional development before development in the second direction[44].

Enzymatic Methods

Organo-phosphorus pesticides were resolved in nanogram amounts by TLC-enzymatic procedure by spraying plates with indoxyl or substituted indoxyl acetates as substrate for liver esterase[45]. A new TLC procedure has been described for detecting 17 cholinesterase inhibiting pesticides at the subnanogram level on silicagel and alumina. Detection of anticholinesterase activity is based on hydrolysis of indophenyl acetate by Bee brain cholinesterase. The inhibiting pesticides show up on the chromatoplate as white spots against blue back ground[46]. A combination of carbon-column TLC-enzyme inhibition technique for the semi-quantitative confirmation of several organo-phosphorus pesticides in plant extracts[47] and also a TLC-enzyme inhibition procedure to screen for organo-phosphorus pesticides without elaborate clean-up have been reported[48]. The TLC-enzymic identification of organo-phosphorus insecticides was studied and *Rf* values for 20 insecticides (esterase inhibitors) on silicagel *G* plates, developed in benzene or in benzene-acetone (19 : 1, 9 : 1 or 2 : 1) given[49].

Esterase-inhibition technique was also used for detection of organo-phosphorus pesticides isolated from food sample on TLC when exposed to bromine vapour and sprayed with aqueous solution of freeze-dried human or horse serum with substrate solution containing 2-naphthyl acetate and fast blue salt; the pesticide areas appeared as white or yellowish-white spots on reddish-violet background[50]. Screening method for organo-phosphorus pesticide residues in vegetables or fruits was reported utilising TLC on silicagel *G* and the pesticides were detected by cholinesterase-inhibition method[51] and estimated by comparing spot areas with those of standards. A cholinesterase-inhibition method was modified for detection of organo-phosphorus insecticides on TLC using Bee brain enzymes[52] and animal liver esterases[53].

ORGANO-CHLORINE PESTICIDES

Of late, there has been a tendency to replace chlorinated hydrocarbon pesticides which accumulate in the system. Consequently the use of some chlorinated pesticides such as *DDT* and its derivatives has considerably decreased. However, residues of these pesticides still persist in the environment and a number of publications have appeared on their detection and analysis utilising mostly chemicals methods and occasionally enzymatic techniques. A review has been published on application of TLC to analysis of chlorinated hydrocarbon and phosphorus pesticides[54].

Chemical Methods

Two dimensional TLC to identify organo-chlorine pesticide in blood and tissues was reported[55]. Blood sample was extracted with methanol and chloroform, water was added and the chloroform separated by centrifuging. The extract was spotted on silicagel *G*, TLC plates, developed in hexane, dried and again developed in cyclo-hexane. Plates were sprayed with silver nitrate and compared with standards which were analysed on separate plates. A simple and rapid method was employed for resolving[56] 11 different organo-chlorine pesticides by two dimensional TLC on silicagel *G*, and on alumina-coated plates[57]. Separation and identification of *DDT* analogs by two dimensional TLC was done in the presence of polychlorinated biphenyl compounds[58]. Chlorinated insecticides were separated by unidimensional TLC on silufol plates when sprayed with acetone solution containing silver nitrate, water, 2-phenoxyethanol and drops of hydrogen-peroxide[59]. A system combining gas and thin layer chromatography and infrared spectrophotometry for the separation, quantitation and identification of *DDT* and 12 of its reactive products was developed[60]. Infrared spectroscopy in combination with TLC has been applied for the identification of *DDT* and related compounds[61]. Some organo-chlorine pesticides (1, 1-*bis* (*p*-chlorophenyl)-2, 2; 2-trichlorcethane, γ-hexachlorocyclohexane, aldrin etc.) in straw-berries, cherries, citrus fruits, milk, fish, cotton-oil, wine, water, air and blood were separated and determined by TLC utilising alumina on silicagel *KSK*-2 in mixtures with plaster as adsorbent[62]. Pesticides such as aldrin and dieldrin were detected by TLC on silicagel *G* plate using solvent system consisting of petroleum ether and carbon tetrachloride (1 : 1); the spraying reagent used was rhodamine *B*[63]. α-and γ-*BHC* were separated and identified by TLC on alumina and on silicagel with hexane or petroleum ether containing 20% vaseline as the solvents. Intensity of straining was much more for the spots on alumina than for silicagel. Similar effect was observed with *DDT* but not with heptachlor[64].

Aldrin, *DDT*, dieldrin, endosulfan, endrin, lindane and dichlorofluoride were resolved and identified by TLC on silicagel *G* with ligroine (b.p. 40-60°)-carbon tetrachloride (1 : 1) mixture as developer and diphenylamine-zinc chloride in acetone as spraying reagent[65]. Seventeen commonly used chlorinated pesticide residues have been isolated by TLC on four types of adsorbents[66] while chlorinated pesticide residues in

fruits and vegetables have been determined by TLC on plates washed with water and treated with silver-nitrate[67]. *DDT*, lindane and related chlorinated insecticides have also been identified by same TLC procedure[68-72] as used for milk, meat and eggs. Separation of chlorine containing pesticides like α-hexachlorocyclo hexane, δ-heptachloro cyclo hexane, *DDT* etc. was performed by TLC on kieselgel *G* utilising *n*-hexane, cyclo hexane or its mixture as mobile phase and indophenol blue as a chromogenic reagent[73]. Chlorinated insecticides separated by TLC has been analysed directly with densitometer, using *o*-toluidine as spraying reagent and UV irradiation[74]. A series of chlorinated insecticides was submitted to TLC on silicagel *G* in the system cyclo hexane-chloroform methanol (10 : 3 : 2). The developed plates were sprayed with phosphate buffer (pH 8) and trypsin solution[75]. *DDT* and analogs were separated from interfering polychlorinated biphenyls (*PCBS*) by TLC[76]; also *PCBS* were determined by TLC after solvent-partitioning and florisil clean-up[77,78]. Organo-chlorine pesticides and polychlorinated biphenyls (*PCBS*) in animal food were separated into two groups by TLC after solvent extraction clean-up and determined directly by GLC[79].

Chlorinated pesticides like aldrin, *DDT*, endrin, lindane, chlordane and heptachlor were detected and determined in market-vegetables by TLC using a multiband layers consisting of a band of activated charcoal-silicagel between two bands of silicagel on a glass applicator[80]. Organo-chlorine pesticide residue in fruits and vegetables were detected by utilising TLC on silver-nitrate-impregnated alumina[42]. A simple and rapid clean-up procedure for isolation and determination of chlorinated pesticides in milk, fats and oils has been described using TLC with silicagel as adsorbent[81]. *DDT* and related compounds were analysed by TLC on aluminium oxide chromatoplates[82]. Some chlorinated pesticides (*DDT*, lindane, endrin and heptachlor) were also separated and identified by TLC procedure on magnesium hydroxide using *N*-*N*′-dimethyl *p*-phenylene diamine hydrochloride as a chromogenic reagent[83]. A collecting device for removing organo-chlorine insecticide zone from thin layer plates was developed[84], and pesticides analysed subsequently by GLC. Removal of interfering substances from vegetables extracts prior to TLC determination of organo-chlorine pesticide residues by mixing aqueous silver-nitrate solution containing acetone with alumina for clean-up was reported[85]. Effects of humidity on TLC of organo-chlorine insecticides on thin layer of aluminium oxide *G* were studied[86]. Activity of adsorbent decreased with increasing humidity. Methoxy-chlor, dieldrin and heptachlor were poorly separated at 14% relative humidity but completely resolved at 60%. The influence of humidity for the most common TLC adsorbents (i.e. aluminium oxide, silicagel, kieselguhr, polyamide, cellulose, carbon, magnesium hydroxide and magnesium silicate) was studied[87].

TLC-enzymatic identification and mode of action of chlorinated hydrocarbon insecticides was studied[88].

CARBAMATE, UREA AND URACIL PESTICIDES

Carbamate, urea and uracil pesticides are of continuing importance and are being used to replace the existing chlorinated insecticides. A number of methods have been suggested to detect and determine the above type of pesticides by TLC utilising chemical as well as enzymatic techniques.

Chemical Methods

Carbamate, thiocarbamate and uracil pesticides were detected on TLC plates using hydroiodic acid as spraying reagent[89]. A simple, rapid and sensitive TLC procedure was developed for identification and determination of carbamate insecticides using three reagents for detection[41]. A rapid clean-up for carbaryl using channel-layer chromatography prior to semiquantitative determination by TLC was described[90]. Carbamate and phenyl urea pesticide residues in natural waters were detected by TLC on acidic silicagel plates with 6 solvent systems utilising 4-dimethyl amino benzaldehyde or diazotisation and coupling with 1-naphthol as chromogenic agents for location[91]. Carbamate pesticide residues on tobacco were identified and determined by extracting the sample with dichloromethane in presence of sodium sulphate, reducing the extract to a small volume, subjecting to TLC on alumina, developing with hexane acetone (9 : 1) and subsequently spraying with fast blue *B* and 3, 5-dichloro-*p*-benzoquinone chlorimine[92]. Separation of uracil by two dimensional TLC procedure was carried out[93].

Urinary metabolites of carbaryl in chicken were separated and determined[94] by TLC and GLC. Sevin (carbaryl) residues in plant tissues[95], apples[96] and food products[97] were also identified by TLC. Methyl-carbamate insecticides as the corresponding 4-nitrobenzeneazo derivatives, found in rice grain, were estimated by TLC[98]; phenyl carbamate and phenyl urea herbicides and their metabolites were separated by two dimensional TLC using the same solvent in both directions[99]. *O*-sec-butylphenyl *N*-methylcarbamate was

separated from phenolic impurities by TLC on silicagel plates[100]. 1-naphthyl-*N*-hydroxy, *N*-methylcarbamate, a metabolite of carbaryl was identified by TLC procedure[101]. 22 carbamates and related compounds were identified on polyamide layers[102] employing suitable solvent systems. *N*-methylcarbamate insecticides were determined quantitatively *in situ* on TLC reporting fluorigenic labelling of carbamates with dansyl chloride[103] and also reporting the fluorigenic labelling of *N*-methyl and *N*, *N'*-dimethyl carbamates with 4-chloro-7-nitrobenzo-2, 1, 3-oxadiazole on TLC plates [104]. The carbamates were treated with dansyl chloride a fluorigenic labelling reagent prior to TLC analysis to form fluorescent[105] derivatives and TLC properties of these derivatives were also investigated[106]. A simple method was reported in which sevin was hydrolysed and the 1-naphthol liberated isolated by TLC on silicagel *G* adsorbent, sprayed with diazotized benzidine and estimated colorimeterically[107].

Enzymatic Methods

Sevin (carbaryl) was detected[108] on TLC with bee brain enzymes at a sensitivity of 0·01 ng. Sensitivity of pig and beef-liver estereases for detecting carbamate pesticides like aldicarb, carbaryl and carbofuran was studied on TLC and it was found that the pig-liver was more sensitive than the beef-liver and that picogram amount of carbamates could readily be detected[109] on silicagel *G*.

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