2.1 **Methods used for the analysis of pesticides**

Pesticides have become the part and parcel of modern day agriculture. The absence of pesticides will jeopardize the health of plants, animals and humans. Pesticides are not only an agricultural commodity but find use in non-agricultural regions. But the very nature of the pesticides to kill renders them harmful for the humans and other living beings. Their extensive use has contaminated our soil, water and food, thus risking our wellbeing. Many persistent pesticides and their degradation products penetrate into the plant tissues or stay in the water and soil thus appearing in our food chain. The pesticide residues are magnified during food processing [1] thus making even the processed foods, storage house of harmful chemicals. Taking into account the rampant use of pesticides which has lead to the contamination of various strata, continuous monitoring of environmental and food samples is of utmost importance. Over the years, pesticides have been determined by many conventional as well as modern day methods like spectrophotometry [2-43], Polarography [44-50], TLC [51,52] FTIR [53], HPLC methods using different detectors [54-150], Gas chromatographic technique, using various detectors or in combination with MS [151-164], Capillary electrophoresis [165-169], Micellar electrokinetic chromatography [170, 171]. Extensive research has been carried out on the analysis of pesticide residues in foodstuffs and environmental matrices. [1,149,162,163,172-182]. The effect of pesticide exposure on the agricultural workers and children has also been the topic of research for many scientists [172-174].

2.2 **Spectrophotometric methods for pesticide analysis**

Spectrophotometry is a very valuable technique which has proven its worth in the field of pesticide analysis over the years. It is particularly popular because of its
features like ruggedness, economical, suitable for wide range of pesticides by using different reagents, detectors and techniques like flow injection, PLS (Partial least square) etc. The spectrophotometric analysis of dithiocarbamate (DTC) fungicides has been extensively carried out in literature [2-4]. Malik et al have developed several methods for the determination of DTC fungicides spectrophotometrically [10, 12, 14]. Six DTC fungicides were analyzed in a method developed by Malik et al [10], whereby the fungicides were converted into Se complex for analysis. In another method three DTC fungicides were decomposed and converted into diphenylcarbazone complexes for determination [12]. A sensitive spectrophotometric procedure is mentioned by Jhangel and Pervez [17] for the analysis of acaricide; kelthane. This method shows good sensitivity in sub parts per million levels. The alkaline hydrolysis of kelthane produces chloroform which after a series of steps forms a yellow-red complex with benzidine showing absorption maxima at 490 nm. A spectrophotometric method for determination of carbamate pesticides; carbaryl, bendiocarb, carbofuran, methiocarb, promecarb and propoxur has been proposed by Rodriguez et al [18]. After hydrolysis the pesticides are coupled with diazotized trimethylaniline (TMA) in a micellar medium. The micellar medium is used to increase the solubility and sensitivity. The method was applied for carbaryl determination in spiked tap, river and pond waters. Demibras [19] has described another method for spectrophotometric analysis of carbaryl in soil and strawberries. Carbaryl on hydrolysis gave 1-naphthol which reacted with diazotized sulphanilic acid to form a product showing absorption maximum at 475 nm. Two new methods for the determination of carbamate pesticide; carbendazim have been reported by workers [20]. The first method involves the oxidation and complex formation with 2, 2-Bipyridyl-Fe (III). The complex formed has \( \lambda_{\text{max}} \) at 512 nm. In the second method the pesticides reacts with potassium ferricyanide to form a complex absorbing at 478 nm.
Zanella et al [21] have reported a flow injection spectrophotometric method for the analysis of carbofuran in commercial preparations. The pesticide after hydrolysis with NaOH is complexed with diazotized 4-aminobenzoic acid and the resultant is spectrophotometrically determined. Jan et al [22] describe a new spectrophotometric method for carbofuran determination. The hydrolyzed product of this pesticide reacts with sodium nitroprusside to make a purple colored complex having $\lambda_{\text{max}}$ at 530 nm. 

Carbosulfan has been spectrophotometrically determined by Sao et al [23] by a sensitive and extractive method. The alkaline hydrolysis of carbosulfan is followed by its coupling with diazotized p-amino acetophenone, resulting in a red-brown dye having $\lambda_{\text{max}}$ at 465 nm. The method has been applied to carbosulfan detection in environmental samples. Rao et al [24] present a novel method for carbosulfan analysis in environmental samples. The pesticide is hydrolysed and the resultant is reacted with 2, 4-di-methoxy aniline. The formed dye is extracted into chloroform and absorbance is measured at 430 nm. Murthy and co-workers [25] have come up with a novel and sensitive method for the analysis of carbamate pesticide; carbosulfan. A yellow complex is formed in this method; the procedure has been applied to the carbosulfan detection in water and grains. Gouda et al [26] have developed three methods for the analysis of OP pesticides; malathion and dimethoate in formulations and vegetable samples. Two of the methods are based on the addition of excess Ce$^{4+}$ in sulphuric acid and determination of unreacted oxidant. The third method involves the oxidation of the two pesticides by N-bromosuccinimide (NBS) and using Amaranth dye for unreacted oxidizing agent. A highly sensitive method has been reported for cypermethrin determination [27]. The insecticide is hydrolysed and then reacted with KI and leuco crystal violet. The dye formed has very high molar absorptivity. Jan and co-workers [28] have performed analysis of OP pesticides. In this method the pesticides are first hydrolysed and then reacted with molybdate
solution to yield a blue complex. Jhangel et al [29] developed a sub ppm method for spectrophotometric analysis of dichlorvos. Hydrolysis of the insecticide is followed by its coupling with diphenyl carbazide (DPC) resulting in a wine red dye with absorption maxima 490 nm.

A flame atomic absorption spectrometric method for indirect determination of dithiocarbamate fungicides; zineb and ferbam has been reported [30]. The fungicides were decomposed and the metal content was analyzed and hence amounts of zineb and ferbam were calculated from their stoichiometric composition. Sensitive analytical methods have been reported for highly hazardous containing pesticide; Endosulfan [31, 32]. Venugopal and Sumalatha describe a method for endosulfan determination, whereby the SO$_2$ liberated on its hydrolysis forms a violet dye with diphenylbenzidine. The method was applied for endosulfan detection in water soil and vegetable samples. Raju and Gupta describe an endosulfan analysis method whereby, a pink dye is formed by using the reagents; malonyldihydrazide, p-aminobenzene and formaldehyde. Tunceli et al [33] discuss a new method for preconcentration and analysis of pesticides in river water samples. Column sorption technique was employed for the preconcentration of the analytes. Skoworn et al [34] have performed the spectrophotometric analysis of thiophanate-methyl has been carried out on the basis of iodine-azide reaction. Jan et al [35] discuss a spectrophotometric method for the determination of methyl-parathion by complexing it with different metal ions. Its complex with Co$^{+2}$ yielded lowest detection limit of 1.1 ppb and its absorbance was measured at 345 nm. A sensitive catalytic kinetic spectrophotometric method has been described for analysis of OP pesticides [36]. OP compounds act as catalysts in the oxidation reaction of LCV with iodate in presence of HCl and a violet dye is produced with $\lambda_{max}$ at 592 nm. A flow injection (FI) method has been studied for the analysis of phenols and carbamate pesticides [37]. The analytes were detected when a dye was
formed on their coupling with diazotized 2,4,6-trimethyl aniline. The method was applied for pesticides detection in pesticide formulations and water samples. Derivative spectrophotometry (DS) is a very useful technique for the analysis of pesticide residues in various matrices. DS increases the sensitivity of the simple spectrophotometric method, enhances the resolution of zero order spectra and eliminates the background noise in spectra. Baranowiska and Pieszko [38] discuss a very useful method for the determination of phenylurea herbicides. Sharma et al [39] discuss a fourth derivative spectrophotometric method for the analysis of fungicide thiram. Sodium molybdate reagent has been used to form coloured complex with thiram. The method has been applied for analysis of thiram in various food stuffs. A pesticide Azinphos-methyl has been determined using first derivative spectrophotometric technique [40]. A mixture of acetophenone and blue dye erioglaucine was used for analysis of the pesticide in commercial formulations. A simple first order derivative spectrophotometric method has been reported for the analysis of insecticide imidaclorpid [41]. The procedure was used for the determination of the insecticide in commercial formulations and it yielded good results.

2.3 **HPLC methods for pesticide analysis**

Chromatographic analysis is the most sought after technique for pesticide residue analysis whether GC, LC or in combination with LC and applying from the wide range of detectors available like UV, DAD, chemiluminescence, ECD, NPD, FD etc. [184]. HPLC is a creditable method for the analysis of wide variety of pesticides. Several heat unstable and polar pesticides show better detection with this technique. A wide range of reviews are available [185-206] on HPLC methods and sample
preparation techniques used for pesticide residue analysis from different environmental and food matrices.

2.3.1 HPLC-UV Methods

HPLC-UV is one of the most popular, efficient and cost effective methods of detection for microanalysis and separation of pesticides in different environmental matrices. The hyphenation of HPLC with UV is useful for a large number of pesticides as most of these are amenable to UV detection. Basheer et al [90] analyzed the carbamate pesticides by making use of an HPLC-UV method. Five pesticides; simazine, fenulfothion, etridiazole, mepronil and bensulide were detected by He and co-workers [91]. A multiresidue analysis of carbamate pesticides was carried out by Sánchez-Brunete et al [97]. Work has also been done on the separation of N-methyl carbamate [102] and carbamate pesticides [103]. A method was developed by Gou et al [111] for the determination of six carbamate pesticides in water with HPLC. HPLC with UV detection was used to study the extraction of organochlorine pesticides from spiked seaweed samples [93]. Chen et al [98] employed the HPLC-UV technique for analysis of organochlorine pesticides. Moreno et al describe procedures for analysis of organochlorine pesticides [104, 112]. Moreno et al [112] determined organochlorine pesticides in agricultural soils. HPLC-UV has been used for the determination of 4 pesticides in tap water and well water [114]. A paper [99] describes the use of an LC-LC method for the determination of acidic pesticides in soil. Liu et al [100] describe a method for the separation of 12 pesticides using a C18 capillary column. Linuron and diuron have been determined in human urine on a poly (methyloctylsiloxane) column [101]. In another work 11 phenylurea herbicides have been determined with HPLC [115]. Four Organophosphorous pesticides (OP) were analyzed in water by Salleh et al [105]. Another method [106] explains the
determination of 8 OP pesticides in soil using Methanol/Water mobile phase. Lourencetti [108] used HPLC-UV for the analysis of three pesticides. A method was developed to analyze cypermethrin from leaves of gingko biloba [117]. Mauldin et al [118] developed a new method for chlorpyrifos analysis. OP pesticides were quantified in water, fruit juices and fruits by Farajzadeh and associates [119]. Khan and co-workers [121] developed a new method for the analysis of two pesticides. Five pesticides were analyzed from river water by external standard method by Brondi et al [122]. Sanagi and associates [124] describe a new method for pesticides determination in water samples. He et al [125] have discussed a new HPLC-UV method for the detection of four pesticides. One of the methods elaborates the method for pesticides residue analysis from parts of eggplant [126], while in another method 18 herbicides are determined in tap water whereby they undergo a photochemical reaction followed by HPLC-UV separation [127]. HPLC-UV analysis of pesticide residues has been carried out in different vegetables by several workers [129,132,133]. Brito et al [131] developed a procedure for the determination of pesticide residues in coconut water. A method explains the quantification of ten pesticides in egg samples with HPLC-UV detection [134].

2.3.2 HPLC-DAD Methods

HPLC analysis using a Diode Array Detector (DAD) is a very sensitive technique which has been widely used for pesticide determination. Jeannot et al [66] used diode array detector in conjunction with HPLC for the analysis of phenylurea herbicides. In a method developed by Thompson et al [76], Azadirachtin (Az), the natural pesticide derived from Neem has been determined by HPLC-DAD. Ferrer and co-workers [81] analyzed phenylurea herbicides by HPLC technique using diode array detection. HPLC-DAD of OP pesticides in bovine tissue was done by Valencia [92] et al. Five
OP pesticides (chlorpyrifos, chlorfenvinphos, diazinon, fenitrothion, parathion-methyl) were analyzed in bovine liver muscle by Llasera et al [107]. HPLC-DAD has been an important tool in detecting pesticide residues in various fruit and vegetable samples. Melo et al [94] determined ten commonly used pesticides on lettuce with LC-DAD. Kaihara et al [116] developed a new method for the analysis of 27 pesticides in various fruit and vegetable samples with photodiode array detection. Liang et al [123] have determined phoxim in water. A new method was applied to the pesticide determination in strawberries [130]. HPLC-DAD is instrumental in detecting pesticides in water matrices also. HPLC-DAD of 16 pesticides in groundwater samples was carried out by D’Archivio et al [95]. Salleh et al [109] detected 5 pesticides from water by using this technique. HPLC-DAD has been used to determine pesticides in surface waters [113, 120].

2.3.3 HPLC-MS Methods

Mass spectrometry (MS) in conjunction with LC (Liquid Chromatography) provides one of the most sensitive and selective methods for pesticide analysis. Ingelse et al [78] determined polar OP pesticides in aqueous samples using liquid chromatography tandem mass spectrometry. Lacorte et al [79] analyzed the OP pesticides with a very sensitive method using LC-APCI-MS. (Liquid chromatography-Atmospheric pressure chemical ionization- Mass Spectrometry). In one of the methods, pesticide residues of 17 pesticides were detected in agricultural products by LC/MS [80]. Ferrer et al [81] analyzed pesticides with the help of an LC-APCI-MS method. Mattina et al [82] developed a particle beam MS method for the analysis of phenylurea herbicides in water matrices. Schaaf et al [83] performed analysis of Az and tetranortriterpenoids from Neem parts. The method was based on the Reversed Phase HPLC and Atomic Pressure Chemical Ionization (APCI) mass spectrometry. Barrek et al [84] analyzed
the content of Azadirachtin A (Az A) in Neem Oil by LC-MS/MS and studied the chemical decomposition of Az A. Sarais et al [85] analyzed Az and azadirachtoid substances; salanin and nimbin. Sannino [86] detected three natural origin pesticides namely, abamectin, spinosad and azadirachtin in fruit and vegetable samples with LC and tandem mass spectrometry. Ambrosino et al [87] determined Az A extracts from neem seed kernels and Pozo et al [89] analyzed Az residues in oranges.

2.3.4 Other HPLC Methods

The feature of HPLC technique can be enhanced to suit the different type of analytes by using various modes of detection. Post column derivatization and chemiluminescence detection are the viable options which can be put into use for different pesticides. Nakazawa et al [57] analyzed the dithiocarbamate fungicides in vegetable samples by using reversed phase ion pair liquid chromatography with chemiluminescence detection. N-Methyl carbamates were analysed by post column photolysis and chemiluminescence detection in water, apple and pears [110]. Patsias et al [71] developed a photo diode array/post column derivatization with fluorescence detection method for the analysis of pesticides. De la Pêna [77] analysed five herbicides in river water with photochemically induced fluorescence detection. Koc and associates [128] have come up with a novel method to analyze aldicarb, propoxur, carbofuran, crabaryl and methiocarb in honey samples involving post column derivatization and fluorescence detection.

2.4 Sample Preparation techniques

Sample preparation is an important and often the limiting step in the sensitive analysis of pesticides from myriad range of matrices. A wide range of techniques are available for sample preparation and pre-concentration of pesticides from complex matrices.
prior to their detection. Sample preparation is often a multistep process involving sampling, cleanup, elution etc.

The literature is replete with the examples of different kind of sample preparation techniques used for the pesticide residue analysis from various matrices. A number of useful reviews are available to study the different detection and sample preparation techniques used in the pesticide determination [185-205]. Liquid liquid extraction (LLE) is one of the earliest and most commonly used extraction techniques employed for pesticide residue analysis in complex media. Lacorte et al [79] carried out liquid-solid extraction of pesticides prior to their analysis. Sannino [86] extracted the pesticides from fruit and vegetable matrices using acetone followed by liquid-liquid partitioning. LLE was used by workers [117,118,128] for extraction of pesticide residues from plant parts. Khan et al [121] employed ethylacetate and hexane for the LLE of pentachloronitrobenzene and hexachlorobenzene and its metabolites prior to

![Figure 2.1: Steps in the pesticide residue analysis](image)

**Figure 2.1: Steps in the pesticide residue analysis**
their HPLC determination. Baig and co-workers [133] used this technique for extraction of three pesticides from vegetable samples.

Sonication assisted extraction has been used by Sánchez-Brunete [97] for carbamate pesticides. Koc et al [128] have successfully made use of florisil column and subsequent elution with hexane/dichloromethane for pesticide extraction.

Solid Phase extraction is one of the most commonly used and preferred technique for literature using SPE technique to extract pesticide residues of 5 herbicides from river water [77]. Ingelse and co-workers [78] used SPE for the pre-concentration of polar OP pesticides. Porous polypropylene membrane protected Micro-SPE technique was used by Basheer et al [90] for carbamate pesticides detection from soil samples. SPE cartridges with different sorbent materials were used for pre-concentration of pesticides of which Oasis HLB and Strata-X were found to give better results [95].

Chen et al [98] presented an online SPE method subsequent to dynamic MAE for the analysis of organochlorine pesticides. Quantitative determination of pesticides was achieved with a 250 fold enrichment through SPE method developed by Liu et al [100]. SPE was used as an extraction and sample preparation technique for the analysis of pesticides in human urine [101]. Sugarcane herbicides were analysed by Lourencetti and co-workers [108] using C18 SPE discs. Another paper discusses the determination of N-methyl carbamate pesticides through the use of automated SPE [110]. Bondelut PPL cartridges were used in the SPE procedure developed to detect pesticides in the Macedonian lake waters [113]. Multivariate C-nanotubes were employed for the SPE of highly leachable pesticide residues in water samples [114].

In another method phenylurea herbicides were determined in drinking water by using C18 cartridges [115]. Another paper presents comparison between LLE, SPE and SFE modes for pesticide residue determination [122]. Lee et al [127] used an online SPE method for the pre-concentration and extraction of herbicides in water. Brito and co-
workers [131] used SPE with C_{18} cartridges to analyze pesticide residues in coconut water. A useful review is resented by Picó et al [139] on the advances made in the SPE technique for analysis of quaternary ammonium herbicides determination. Sanchiz-Mallos et al [141] developed an SPE-HPLC method for analysis of phenoxy acid herbicides from drinking water. Vitali et al [143] used SPE for the HPLC-UV analysis of triazines and dinitroanilines from real water samples. Many papers in literature present SPE as a suitable enrichment technique for the Neem derived pesticide; Azadirachtin [144-146]. Microwave assisted extraction (MAE) is an effective technique for extraction of pesticide residues from several environmental and food samples. Chen et al [98] made use of MAE for the followed by on-line SPE of organochlorine pesticides. The conventional extraction methods are popular but they suffer from many drawbacks like use of large volume of solvents, agitation or heating with the solvent for long time thus increasing the risk of thermal degradation of many pesticides. But the new innovations in the field of extraction address these concerns. The novel methods of extraction like MAE, Pressurized fluid extraction, Supercritical fluid extraction (SFE), Solid phase microextraction (SPME) etc. overcome these problems as these are fast, use solvent economically, thus are environment friendly [206,207]. Moreno et al [93] performed Microwave assisted microextraction (MAME)-SPE and MAME-SPME (solid phase microextraction) with organochlorine pesticides. SPME with four different coatings of fibre like PDMS (poly dimethyl siloxane), PDMS/divinylbenzene, Carbowax/Templateated resin and polyacrylate was made use of to determine 10 pesticides [94]. MAME-SPME was also used by researchers to analyze organochlorine pesticides [104]. Salleh et al [105] used SPME and online SFCO_2 for OP pesticide analysis. Automated intube SPME analysis of carbamate pesticides was performed by Gou et al [111]. Focused microwave assistance followed
by SPME was used by some researchers for pesticide residue analysis from strawberries [130]. In another paper, authors focus on the optimization of conditions for Headspace-SPME for the determination of seven OP pesticides in natural waters [183].

Microwave assisted solvent extraction (MWASE) has been employed by Hogendoorn et al [99] for multiresidue analysis of pesticides in soil. In one of the methods, MAME and soxhlet extraction were used for the determination of OP pesticides from soil [106]. Moreno and associates [112] employed MAE with surfactants for pesticide residue analysis in soils. Singh, Foster and Khan [129] used MAE to determine pesticide residues in cooked and raw vegetables.

Continuous flow microextraction (CFME) was used by He et al [91] whereby a single drop of solvent is immersed in a continuous flowing sample solution in a 0.5 ml glass chamber. Matrix Solid Phase Dispersion (MSPD) coupled with SPE has been used as sample preparation technique by Valencia et al [92]. An MSPD method was validated for the pesticide analysis from the bovine tissues, involving C18 extraction and silica-gel cleanup [107].

A green extraction technique Supercritical fluid extraction (SFE) has also been used for pesticide residue extraction from varied matrices. Ambrosino et al [87] used SF CO2 and liquid CO2 as extracting agents. Carbamates were determined by Sun et al [103] using MAE and their subsequent extraction with SFE. Kaihara and associates [116] used SFE for multiresidue analysis in food stuffs.

Liquid phase microextraction (LPME) was employed by Liang et al [123] for phoxim determination. Cunha et al [184] have discussed at length the current trends in the liquid liquid microextraction (LLME) for the pesticide residue analysis in food and water. Dispersive liquid liquid microextraction (DLLME) uses an extraction solvent mixture made of a highly non-polar and a water soluble polar solvent. This method
fetches high pre-concentration in a short time [208]. In recent times DLLME is gaining popularity as extraction technique for pesticide residue analysis in water samples [119,120]. He et al [125] have employed DLLME with ionic liquid extraction of pesticides from water samples. Liquid membrane microextraction is a relatively new concept in pesticide extraction which leads to high enrichment factor. Hylton et al [102] used barrier film protected, mixed solvent optimized micro-scale membrane extraction for pesticide analysis. Double phase liquid liquid microextraction (DPLMME) has been used for pesticide extraction by Sanagi et al [124] whereby, polypropylene tubular membrane has been used. Soxhlet extraction followed by membrane separation has also been used for high lipid containing matrices [134].

A new concept, molecularly imprinted polymers (MIPS) are being used up for pesticide detection. The MIPS are inexpensive, easy to synthesize, highly selective and very sensitive, these qualities make them very desirable for extracting various pesticides from varied matrices. Linuron and isoproturon were used as templates for MIPS in the analysis of phenyl urea herbicides from plant extracts [132].

Microextraction by packed sorbent (MEPS) is an innovative technique which is miniaturization of SPE. This technique is quite advantageous as it is fast, uses less solvent, requires small sample size and can be automated. Bagheri et al [209] mention the use of reinforced MEPS syringe for the analysis of triazine, OP, organochlorine and aryloxy phenoxy propionic acid pesticides in aquatic environment. MEPS procedure for the analysis carbamate pesticide; aldicarb has also been described [210].
Table 2.1 Sample Preparation Methods used in the Analysis of Pesticides

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Matrix</th>
<th>Pesticide</th>
<th>Cleanup technique</th>
<th>Method</th>
<th>Analysis</th>
<th>Recovery (RSD%)</th>
<th>Detection Limits</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Soil</td>
<td>Carbamates (carbaryl, propham, methiocarb, promecarb, chlorprophan, barban)</td>
<td>Micro spe, Oasis HLB cartridge</td>
<td>C$_{18}$ disc in polypropylene membrane</td>
<td>HPLC-UV, ACN/water 40/60, 225 nm</td>
<td>93-110(4-11%)</td>
<td>LOD 0.01-0.4 ng g$^{-1}$</td>
<td>90</td>
</tr>
<tr>
<td>2.</td>
<td>Natural water sample</td>
<td>Simazine, fensulfoxthion, etidiazole, mepronil, bensulide</td>
<td>CFME</td>
<td>Single drop of sample collected in microsyringe, injected to HPLC</td>
<td>HPLC-UV, ACN/water 50/50, 220 nm</td>
<td>86.9-106</td>
<td>LOD 0.6-3ng mL$^{-1}$</td>
<td>91</td>
</tr>
<tr>
<td>3.</td>
<td>Bovine tissue</td>
<td>Parathion-methyl, fenitrothion, parathion, chlorfenvinphos, diazinon, ethion, fenchlophos, chlorpyrifos, carbofenthion</td>
<td>MSPD coupled with SPE</td>
<td>C$_{18}$, silica</td>
<td>HPLC-DAD</td>
<td>89.7-99.9(0.7-4.7)</td>
<td>0.04-.25 µg g$^{-1}$</td>
<td>92</td>
</tr>
<tr>
<td>4.</td>
<td>Seaweed sample</td>
<td>4,4´DDD, dieldrin, 4,4´DDT, 2,4´DDT, 4,4´DDE, aldrin</td>
<td>MAME-SPME</td>
<td>PDMS-DVB</td>
<td>HPLC-UV, MeOH/Water 84/16</td>
<td>87.4-101(7.9-10.3)</td>
<td>138-348 ng g$^{-1}$</td>
<td>93</td>
</tr>
<tr>
<td>5.</td>
<td>Lettuce</td>
<td>10 pesticides (acetamiprid, azoxystrobin, cyprodinil, fenhexamid, fludioxonil, folpet, iprodione, metalaxyl, primicarb, tolyfluanid)</td>
<td>SPME</td>
<td>PDMS, PDMS/DVB, CW/TPR, PA</td>
<td>HPLC-DAD, MeOH/Water (0.1% trifluoroacetic acid), 224 nm</td>
<td>N. R.</td>
<td>0.28-1.54 mg Kg$^{-1}$</td>
<td>94</td>
</tr>
<tr>
<td>6.</td>
<td>Ground water</td>
<td>16 pesticides (aldicarb, atrazine, desethylatrazine,</td>
<td>SPE</td>
<td>C$_{18}$, graphitised carbon black,</td>
<td>HPLC-UV, ACN/water(0.1%)</td>
<td>71-111(1-10%)</td>
<td>0.003-0.014 µg L$^{-1}$</td>
<td>95</td>
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<tr>
<td>7.</td>
<td>Tomatoes</td>
<td>Benomyl, tebuthiuron, simazine, atrazine, diuron, anetryn</td>
<td>SPE</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;, aminopropyl</td>
<td>HPLC-UV, ACN/0.01% aqueous NH&lt;sub&gt;4&lt;/sub&gt;OH (35/65), 235 nm</td>
<td>Commercial NH&lt;sub&gt;2&lt;/sub&gt; 81-106(0.7-41) Commercial C&lt;sub&gt;18&lt;/sub&gt; 29-57(9.2-55%)</td>
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<td></td>
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<td>desysopropylatrazine, carbofuran, 2,4-D, dicloran, fenitrothion, iprodione, linuron, metalaxyl, metazachlor, phenmedipham, procymidone, simazine, vinclozolin)</td>
<td>Oasis HLB, Lichrolut EN, Strata-X</td>
<td>phosphoric acid) 50/50, 200-400 nm</td>
<td>Stata X 71-113(1-10%)</td>
<td></td>
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<tr>
<td>8</td>
<td>Soil</td>
<td>Oxamyl, methomyl, Propoxur, carbofuran, carbaryl, methiocarb</td>
<td>SAESC</td>
<td>Ultrasonication, MeOH extraction</td>
<td>HPLC-FI, 82.9-99.8 (0.4-10%)</td>
<td>1.6-3.7 µg Kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Wheat, rice, corn, bean</td>
<td>Pentachloronitrobenzene, p,p&lt;sup&gt;′&lt;/sup&gt;DDE, p,p′DDT, o,p&lt;sup&gt;′&lt;/sup&gt;DDE, o,p&lt;sup&gt;′&lt;/sup&gt;DDT, o,p&lt;sup&gt;′&lt;/sup&gt;DDD</td>
<td>DMAE-SPE</td>
<td>Online spe C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>HPLC-UV, ACN/water, 238 nm</td>
<td>89-101(0.8-6.5%)</td>
<td>Wheat 19-37 (ng g&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Soil</td>
<td>10 pesticides (bentazone, bromoxynil, metsulfuron-methyl, 2,4-D, MCPA, MCPP, 2,4-DP, 2,4,5-T, 2,4-DB, MCPB)</td>
<td>MASE</td>
<td>--</td>
<td>LC-LC</td>
<td>60-90(5-25%)</td>
<td>5-50 µg Kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Tap water and apples</td>
<td>Simazine, fensulfothion, isopropcarb, fenobucarb, chlorothalonil, etridiazole, mepronil, pronamide, mecoprop, bensulide, isofenphos, terbutol</td>
<td>SPE</td>
<td>Octyl bonded silica</td>
<td>Capillary HPLC</td>
<td>85-107 (4.1-10.7% apples, 4.1-8.4 water)</td>
<td>0.15-0.8 µg mL&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>Urine</td>
<td>Diuron, linuron</td>
<td>SPE</td>
<td>Microwaved PMOS on silica</td>
<td>HPLC-UV ACN/water (40/60) 254 nm</td>
<td>85-103(0.37-1.8%)</td>
<td>14 µg L(^{-1}) (diuron)</td>
<td>2.8 µg L(^{-1}) (linuron)</td>
</tr>
<tr>
<td>13.</td>
<td>Methanol</td>
<td>Carbamate pesticides (Aldicarb, propoxur, carbofuran, carbaryl, methiocarb)</td>
<td>Barrier film membrane extraction</td>
<td>Octanol barrier film used</td>
<td>HPLC-UV, ACN/water/MeOH 214 nm</td>
<td>(1.9-9.5%)</td>
<td>0.001-5.5 µg L(^{-1})</td>
<td>102</td>
</tr>
<tr>
<td>14.</td>
<td>Soil</td>
<td>Carbamate pesticides (propoxur, chlorpropham, propham, methiocarb)</td>
<td>MAE SFE</td>
<td>OAD Methanol CO(_2) + Methanol</td>
<td>HPLC-UV, ACN /water (40/60) 225 nm</td>
<td>81.8-102(4.9%)</td>
<td>66-98(5.5%)</td>
<td>N. R.</td>
</tr>
<tr>
<td>15.</td>
<td>Agricultural soil</td>
<td>Organochlorine pesticides (4,4’-DDD, dieldrin, 4,4’-DDT, 2,4’-DDT, 4,4’-DDE)</td>
<td>MAME SPME</td>
<td>POLE PDMS/DVB</td>
<td>HPLC-UV, MeOH/Water (85/15)</td>
<td>(5.5-8.4%)</td>
<td>56-96 ng g(^{-1})</td>
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<tr>
<td>16.</td>
<td>Water</td>
<td>Organophosphorous pesticides (bensulide, diazinon, EPN, chlorpyrifos)</td>
<td>SPME-SFCO(_2)</td>
<td>PA(spme)</td>
<td>HPLC-UV, MeOH/Water (80/20)</td>
<td>(8.6-13.5%)</td>
<td>40-600 µg L(^{-1})</td>
<td></td>
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<tr>
<td>17.</td>
<td>Soil</td>
<td>8 OP pesticides (dimethoate, methidathion, parathion-methyl, malathion, ethoprophos, parathion-ethyl, diazinon, chlorpyrifos)</td>
<td>MAME Soxhlet extraction</td>
<td>POLE, Genapol X-080 Hexane/Acetone</td>
<td>HPLC/UV, MeOH/Water(35/65)</td>
<td>20.5-82 (0.8-2.1%) with Genapole-X080</td>
<td>0.2-11.3 ng mL(^{-1}) (Genapol-X080)</td>
<td></td>
</tr>
<tr>
<td>18.</td>
<td>Bovine muscle, liver</td>
<td>5 OPPs (chlorpyrifos, chlorfenvinphos, diazinon, fenithrothion, parathion-methyl)</td>
<td>MSPD</td>
<td>C(_{18}) extraction, silica gel clean-up</td>
<td>HPLC-DAD, MeOH/Water, gradient flow, 244-287 nm</td>
<td>55-100 (1.9-5.2%) in liver samples</td>
<td>50-100 ng g(^{-1}) (liver), 25-50 ng g(^{-1}) (muscle)</td>
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<td>19.</td>
<td>Soil, soil-vinasse</td>
<td>Diuron, hexazinone, tebuthiuron</td>
<td>SPE</td>
<td>C$_{18}$</td>
<td>HPLC-UV, MeOH/water (45/55), 247 nm</td>
<td>78-120 (&gt;10%)</td>
<td>0.025-0.05 mg Kg$^{-1}$</td>
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</tr>
<tr>
<td>20.</td>
<td>Water</td>
<td>Simazine, chlorothalonil, bensulide, thiobencarb, EPN</td>
<td>SPME/SFE</td>
<td>PA/SFCO$_{2}$</td>
<td>HPLC-PDA, ACN/water(60/40)</td>
<td>(7.4-12%)</td>
<td>0.07-0.219 mg L$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>21.</td>
<td>Water, Apple, pear</td>
<td>N-methyl carbamate pesticides (Propoxur, bendiocarb, carbaryl, promecarb)</td>
<td>SPE</td>
<td>C$_{18}$</td>
<td>HPLC-CL</td>
<td>99-96 (0.49-0.81%, water)</td>
<td>3.9-36.7 ng L$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>Water</td>
<td>Carbamate pesticides (carbaryl, propham, methiocarb, promecarb, chlorpropham, barban</td>
<td>SPME</td>
<td>In-tube spme</td>
<td>HPLC-UV, ACN/water (50/50) 220 nm</td>
<td>97.3-100 (1.7-5.3%)</td>
<td>1-15 µg L$^{-1}$</td>
<td></td>
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<tr>
<td>23.</td>
<td>Agricultural Soil</td>
<td>Organochlorine pesticides (4,4’-DDD, Dieldrin, 4,4’-DDT, 2,4’-DDT, 4,4’-DDE, Aldrin)</td>
<td>MAE</td>
<td>(POLE+Polyoxyethylene10 Cetyl ether), (POLE+Polyoxyethylene10 Stearyl ether), surfactant mixtures used</td>
<td>HPLC-UV, MeOH/Water (85/15) at 220 and 238 nm</td>
<td>44.7-99.1 (Cetyl mixture) 44.8-103.6 (Stearyl mixture) (0.275-0.655%)</td>
<td>86.4-806.4 ng g$^{-1}$ (cetyl mixture) 150.8-734 ng g$^{-1}$ (stearyl mixture)</td>
<td></td>
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<tr>
<td>24.</td>
<td>Surface waters</td>
<td>Dimethoate, 2,4-D, linuron and MCPP</td>
<td>SPE</td>
<td>Bond Elut PPL cartridges</td>
<td>HPLC-UV-DAD, ACN/Water/Acetic acid (39/59/2) 229,249 nm</td>
<td>64-92% (2.6-8.3%)</td>
<td>0.01-0.31 µgL$^{-1}$</td>
<td></td>
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<tr>
<td></td>
<td>Sample Type</td>
<td>Components</td>
<td>Extraction Method</td>
<td>Clean-up Method</td>
<td>Detection Method</td>
<td>Detection Limits</td>
<td></td>
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<tr>
<td>25</td>
<td>Tap Water Well water</td>
<td>Atrazine, dicloran, metazachlor, simazine</td>
<td>SPE</td>
<td>Multi-walled carbon nano tubes</td>
<td>HPLC-UV, ACN/Water 230 nm</td>
<td>92.7-95.3 (tap water) (2.5-4.6)</td>
<td>5-15 ng L⁻¹</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Drinking Water</td>
<td>Phenylurea herbicides (11 pesticides)</td>
<td>SPE</td>
<td>C₁₈</td>
<td>HPLC-UV, ACN/Phosphate buffer (35/65)</td>
<td>32.6-150 (1.1-6.7%)</td>
<td>3.8-43.6 µg L⁻¹</td>
<td></td>
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<tr>
<td>27</td>
<td>Fruits and vegetables</td>
<td>27 pesticides</td>
<td>SFE</td>
<td>Extrelut NT + Bond Elut C₁₈, Elution with CAN</td>
<td>HPLC-PDA, 230 nm</td>
<td>49.3-103.6 (30.5-0.4%) for cucumber</td>
<td>0.005-0.1 ppm</td>
<td></td>
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<tr>
<td>28</td>
<td>Ginkgo biloba leaves</td>
<td>Cypermethrin</td>
<td>LLE</td>
<td>Hexane/Ocatne(99:1)</td>
<td>HPLC-UV, Hexane/THF (99/1) 254 nm</td>
<td>81 (3.2%)</td>
<td>0.1 mg Kg⁻¹</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>Black oil sunflower seeds</td>
<td>Chlorpyrifos</td>
<td>LLE</td>
<td>Acetonitrile/Phosphate buffer (90:10)</td>
<td>HPLC-UV, ACN/Phosphate buffer (75/25) 230 nm</td>
<td>&gt;95(0.81-4.1%)</td>
<td>0.221 µg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Water samples, fruit juice and fruits</td>
<td>Organophosphorous pesticides (fenitrothion, diazinon, ethion)</td>
<td>DLLME</td>
<td>Chloroform, methanol</td>
<td>HPLC-UV, Methanol, 210 nm</td>
<td>54.9-69.4 (2.2-4.1)</td>
<td>2-3 ng mL⁻¹</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>Surface water sample</td>
<td>Carbamate pesticides (metolcarb, carbofuran, carbaryl, isoprocard, diethofencard)</td>
<td>DLLME</td>
<td>Water/ACN/Trichloromethane</td>
<td>HPLC-DAD, MeOH/Water (60/40)</td>
<td>86-97.2 (3.5-8.7%)</td>
<td>0.1-0.5 ng mL⁻¹</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Soil</td>
<td>PCNB and HCB</td>
<td>LLE</td>
<td>Ethyl acetate and hexane</td>
<td>HPLC-UV, MeOH/Water (96/4), 300 nm</td>
<td>97.8-99.2 (1.4-2.9%)</td>
<td>0.0001-0.0003 µg mL⁻¹</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Type</td>
<td>Herbicides</td>
<td>Extraction Method</td>
<td>External Standard Method</td>
<td>Detection Method</td>
<td>Recovery (%</td>
<td>Limit of Detection</td>
<td></td>
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<tr>
<td>33</td>
<td>River Water</td>
<td>Tebuthiuron, hexazinone, diuron, 2,4-D, ametrine</td>
<td>LLE SPE SFE</td>
<td>HPLC-UV, ACN/Water (28/72) 238 and 254nm</td>
<td>94%(LLE) 98%(SPE) 28-58%(SFE)</td>
<td>10-30 μg L⁻¹</td>
<td>122</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Water</td>
<td>Phoxim</td>
<td>LPME</td>
<td>HPLC-DAD</td>
<td>(8.4%)</td>
<td>10 ng mL⁻¹</td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>Water</td>
<td>Parathion, phoxim, phorate, chlorpyrifos</td>
<td>DLLME</td>
<td>HPLC</td>
<td>101.8-113.7 at 200 μg L⁻¹ (&gt;4.7%)</td>
<td>0.1-5 μg L⁻¹</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Eggplant</td>
<td>Diazinon, malathion, sumithion</td>
<td>LLE Ethylacetate</td>
<td>HPLC-UV ACN/Water (70/30) 254 nm</td>
<td>88.53-119.59 (11.2-12.8%)</td>
<td>0.02 mg kg⁻¹</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>Tap water</td>
<td>18 herbicides</td>
<td>SPE Photochemical</td>
<td>HPLC-UV detection after photochemical reaction, phosphate buffer/ CAN</td>
<td>77-103 (0.8-2.6%)</td>
<td>0.1-2.3x10⁻¹⁰ M</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>Honey</td>
<td>Aldicarb, propoxur, carbofuran, carbaryl, methiocarb</td>
<td>Florisil column</td>
<td>HPLC-PCD, FD, water/ACN (90/10)</td>
<td>77.3-85.1 (1.7-2.3%)</td>
<td>4, 5 ng g⁻¹</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Strawberries</td>
<td>Carbendazim, diethofencarb, azoxystrobine, napropamide, bupirimate</td>
<td>Focussed microwave assisted extraction</td>
<td>SPME HPLC-DAD</td>
<td>(3-7.3%)</td>
<td>0.05-1 mg Kg⁻¹</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Coconut water</td>
<td>Captan, chlorothalonil, carbendazim, lufenuron, diafenthiuron</td>
<td>SPE C₁₈ methanol elution</td>
<td>HPLC-UV, 254 nm</td>
<td>75-104 (1.4-11.5%)</td>
<td>≥2 mg Kg⁻¹</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sample Type</td>
<td>Analytes</td>
<td>Extraction Method</td>
<td>Solvent</td>
<td>Detection Method</td>
<td>Recovery</td>
<td>LOQ</td>
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<tr>
<td>41.</td>
<td>Vegetables</td>
<td>Triazophos, profenofos and chlorpyrifos</td>
<td>LLE</td>
<td>Ethylacetate</td>
<td>HPLC-UV</td>
<td>(&gt;20%)</td>
<td>N. R.</td>
<td></td>
</tr>
<tr>
<td>42.</td>
<td>Egg samples</td>
<td>10 pesticides</td>
<td>Soxhlet extraction, membrane separation</td>
<td>---</td>
<td>HPLC-UV</td>
<td>60-98%</td>
<td>0.002-0.018 mg/kg</td>
<td></td>
</tr>
<tr>
<td>43.</td>
<td>Citrus samples</td>
<td>diflubenzuron, flufenoxuron hexaflumuron and hexythiazox</td>
<td>MSPD</td>
<td>C-8, silica sorbent, Dichloromethane eluent</td>
<td>HPLC-UV, 200 nm</td>
<td>74-84%</td>
<td>0.15-0.25 µg/g (LOQ)</td>
<td></td>
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<tr>
<td>44.</td>
<td>Water</td>
<td>8 Organophosphorous pesticides</td>
<td>CPE</td>
<td>Polyoxyethylene 10 lauryl ether and GenapolX-080</td>
<td>HPLC-UV</td>
<td>27-105%</td>
<td>&gt;30 µg L⁻¹</td>
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</tbody>
</table>
References


Chromatography.


