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Validation of Analytical Method for Determination of 352 Pesticide Residues in Soil by LC- MS/MS

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ABSTRACT

This study is to evaluate the capabilities of LC MS/MS for pesticide residues determination in soil. It is considered a rapid and simultaneous method for identification and quantification for 352 pesticide residues in soils. This method has been developed to study a realistic pesticide residues validation and this procedure for testing soil contamination is sensitive and easy to perform. Pesticides, are the most cost-effective means of pest and weed control, allow the maintenance of current yields and so contribute to economic viability. Concern about the environmental impact of repeated pesticide use has prompted research into the environmental fate of these agents, which can emigrate from treated fields to air, other land and water bodies. How long the pesticide remains in the soil depends on how strongly it is bound by soil components and how readily it is degraded. An applicable LC with tandem mass spectrometers (LC–MS/MS) using electro spray ionization (ESI) are identified as techniques most often applied in multi-residue methods for pesticides at present. Therefore, applicability and sensitivity obtained with LC–ESI–MS/MS is individually compared for each of the selected pesticides. A liquid chromatographic (LC-MS/MS) method was found to be specified to determine the residues of certain organochlorine, organonitrogen, carbamates, and organophosphorous pesticides in several types of soil (e.g. composite, sand and mud soil).The method performance was tested on 352 pesticides representing different types of pesticides. The average recovery of these pesticides using a concentration ranged between 0.01-0.5 mg/kg (ppm) varied between 70 and 120%. The reproducibility expressed as relative standard deviation was less than 20%. The method showed to be linear at least up to 0.1 mg/kg. The limit of quantitation (LOQ) in soil samples was 0.01 mg/kg. The measurement uncertainty expressed as expanded uncertainty and in terms of relative standard deviation (at 95% confidence level) was found to be within the range of ± 30%.

Key words: Pesticide residues, validation, soil, LC- MS/MS.

Introduction

Pesticides have been widely used throughout the world since the middle of the 20th century. Based on the compilation of the British Crop Protection Council, approximately 860 active substances are formulated in pesticide products currently (Tomlin, 2003). These substances belong to more than 100 substance classes. Benzoylureas, carbamates, organophosphorous compounds, pyrethroids, sulfonylureas, or triazines are the most important groups. The chemical and physical properties of pesticides may differ considerably. There are several acidic pesticides; others are neutral or basic. Some compounds contain halogens, others phosphorous, sulfur, or nitrogen. These heteroatoms may have relevance for the detection of pesticides. A number of compounds are very volatile, but several do not evaporate at all. This diversity causes serious problems in the development of a "universal" residue analytical method, which should have the widest scope possible.

Pesticides are part of a large group of organic compounds that present extremely diverse physico-chemical properties. Pesticides are used for controlling fungi, weeds and insects etc. Chemical plant protection agents should be applied at specific concentrations according to agro technical needs. Misuse of pesticides can lead to excessive contamination of the environment, i.e. soil, water and air. Even when applied in accordance with Good Agricultural Practices (GAP), they can leave residues, which can be detrimental to food safety (Fern´andez-Alba, 2005 a). Accumulation of pesticides in the environment results in high levels of these dangerous chemicals in crops and animal feed, which ultimately leads to human hazards. Potential toxicity of pesticides is the main hazard associated with their agricultural use. However, long term environmental exposure also has a negative impact on health. This is particularly important when human populations are exposed to pesticides by consumption of contaminated food (Badach *et al.*, 2007). Multi-residue pesticide analysis in soil has traditionally been carried out by mass spectrometry (LC–MS/MS), because of its excellent efficiency in chromatographic separation and its general sensitivity and ability to identify compounds. Until today, most of the investigated pesticides in food samples have been insecticides, acaricides and fungicides, which generally could be analysed adequately by LC-MSMS (Fern´andez-Alba, 2005 b). However, a large number of well known and frequently applied pesticides have been banned from the European Union as a consequence of the Directive 91/414/EEC, which aims to ensure safe food on the market. Therefore, over recent years, new active

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ingredients have been developed through more specific reactions. These recent pesticides can be produced by the synthesis of more complex molecules, which normally can be analyzed by LC. The same holds are true transformation/degradation products or metabolites. Liquid chromatography (LC) to mass spectrometry (MS) enables the analysis of several hundreds of pesticides (Kamińska *et al.*, 2004).

Material and Methods

Reagents:

- Acetic acid 100% , Merck.
- De-ionized Water, Generated by Millipore water-purification system.
- Acetonitrile, 99.9% HPLC grade (LabScan) or similar quality.
- Methanol, 99.9% HPLC grade (Merck) or similar quality.
- Formic Acid, 98-100% (Riedel–de Haen).
- Ammonia Solution, 33% (Riedel–de Haen).
- Tetradecane, 99% HPLC grade (Aldrich).
- Ethyl Acetate, 99.8% (LabScan) or similar quality.
- n-hexane, 97% (Sigma Aldrich) or similar quality.
- Cold Water (< 4 °C).
- Magnesium Sulfate, Anhydrous, grit, (e.g. Fluka No. 63135).
- Magnesium Sulfate, Anhydrous, Fine Powder, (e.g. Fluka No. 63136), phthalates may be removed in a muffle furnace (4.19) by heating to 550 °C overnight.
- Sodium Chloride, 99% (Riedel–de Haen).
- Sodium Hydroxide, 99% (Riedel–de Haen).
- Disodium Hydrogencitrate Sesquihydrate, (e.g. Fluka No. 71635).
- Trisodium Citrate Dehydrate, (e.g Fluka No. S4641).
- Florisil, 60-100 mesh, pesticides residue analysis grade (Fluka).
- Silica Gel 60 (Fluka).
- Sodium Hydroxide Solution, c = 5 mol/l: Dissolve 2g of sodium hydroxide in approximately 5 ml of de-ionised water and complete to 10ml.
- Formic Acid Solution in Acetonitrile, σ = 5 ml formic acid/100 ml: dilute 0.5 ml of formic acid to 10ml with acetonitrile .
- Eluent Mixure A (hexane/ethyl acetate, 8/2) for silica-florisil Clean up: complete 200 ml ethyl acetate to 1000 ml with n-hexane .
- Ammonium formate buffer (pH = 4): Dilute 100 ml mobile phase stock solution with 800ml methanol-water (1:1), the pH should be 4±0.1, adjust if necessary.
- Ammonia Solution (3%): complete 10ml ammonia solution to 100 ml with water.
- Silica Gel-Florisil Cartridge: block a 10ml PE syringe with a pool of glass wool add 1g±0,02g florisil, 0.1g±0.01g silica Ge and 0.2g±0.01g magnesium sulphate .

Preparation of standard solutions:

Pesticides:

Pesticides reference standards were purchased from Dr. Ehrensdorfer (Augsburg, Germany), with purity >95% were used to prepare stock solution.

Stock Solutions:

Reference standard solutions of concentration 1000 µg/ml were prepared in toluene and kept at 4 ±2 ^{o}C.

Spiking mixture solution:

Mixture 20 µg/ml from all compounds was prepared in toluene and used as spiking mixture stored in refrigerator at 4 ±2 ^{o}C.

Calibration mixture solution:

Calibration mixtures of concentration levels and, 0.001, 0.002, 0.005, 0.01, 0.05 and 0.1 ug/ml for LCMS/MS were prepared in methanol and stored in refrigerator at 4 ±2 ^{o}C. The preparation of multiple standards covering a broad concentration range will allow the construction of a linear calibration curve.

Injection standard solution:

Working standard of Aldrin with concentration of 0.1 ug/ml was prepared in n-hexane/ acetone (9:1) solution used as injection standard for LCMS/MS.

Method of Analysis:

Extraction and Partitioning:

1- Transfer a representative test portion of sample into a 50 ml centrifuge Tube.
2- Weigh 10g into the centrifuge tube.
3- Add 10 ml of acetic acid 1% concentration and shake 2 min then ultrasonic for 1 minute.
4- Add 10 ml of acetonitrile.
5- Close the tube and shake vigorously for 2 min.
6- Add the prepared buffer-salt mixture (4 g magnissium sulphate + 1g sodium chloride + 0.5g sod. Hydrogencitrate sesquihydrate+ 1g sod.citrate)
7- Close the tube and immediately shake vigorously for 2 min. and centrifuge for 5 min. with 4000 min^{-1}.
8- An aliquot of 6 ml of the acetonitrile phase is transferred for LC-MS-MS injection.

Conditions of LCMS/MS:

HPLC analyses were performed on a C18 reversed-phase column (100mm × 2.1mm, 4_m from Jones Chromatography) and were operated at room temperature. The LC Mobile phase was composed of (5 mM Ammonium formate solution in Methanol/Buffer (1:9): dilute 50 ml of stock buffer with 450 ml Methanol/buffer (1:9), the PH should be 2.78 ± 0.1, adjust if necessary, stable for one week in refrigerator. The total run time was set for 5 min. The temperature of the auto sampler was maintained at 4◦C and the injection volume was 40 ul.
Electro spray ionization (ESI) MS–MS

MS detection was done on a Sciex API 4000 triple stage quadrupole mass spectrometry (Applied Biosystems, Foster City, CA, USA). Nitrogen was used for the gas nebulizer. The ions were monitored by Multiple Reaction Monitoring (MRM). The source block temperature was set at 450 ◦C and the electrospray capillary voltage to 5.5 kV.

Results and Discussion

As soil pollution by pesticides can affect many biological systems, the widespread use of potentially harmful pesticides has recently come under scrutiny in Africa (Kaminska *et al.*, 2004 and Thrupp, 1996). Once contaminated, the soil may take a long time to clear (Prenazzi and Ziglio, 1995) and there is always the danger of bioaccumulation. This method is used to detect very little amount of organochlorines, organonitrogene, carbamates and organophosphorus pesticides at the concentration of mg/kg. The recoveries of 352 pesticides are ranged between 70-120%. Typical validation characteristics {accuracy (trueness and precision) and linearity} were obtained by carrying out a simple method, to determine pesticide residues in soil using LC-MSMS.

The performance characteristics of the method were established by validation procedures employing assays with standard solutions, sample blanks and spiked samples. Linearity, matrix effect, trueness, precision, selectivity, limits of detection and of quantification were determined. The fitness for purpose of this method was assessed based on its performance characteristics

The method was validated for 352 pesticides residues in Soil. The validation was performed at three concentration levels using 6 replicates determinations. The concentration levels were 0.01, 0.05 and 0.1 mg/kg.

Thus a total of 18 samples were spiked and analyzed. A blank sample was included for soil matrix. The experiments were performed by different analysts and on different days.

The calibration curve was determined by the analysis of each of the 352- pesticides at 6 calibration levels, i.e.0.001, 0.002, 0.005, 0.01 and 0.1 μg/L. The calibration curves were best fitted to a linear curve. The majority of the correlation coefficients (R) were higher or equal to 0.9999.

Accuracy:

Accuracy is expressed in terms of two components: “Trueness” and “Precision”.

Trueness:

The trueness of the method was studied to show how close the mean of a set of results (produced by the method) is to the true value. To check trueness of the method, spiked samples are used at different levels. Bias expressed as absolute relative difference percent (RD %) was not exceeded 20 %.

Precision Repeatability and Reproducibility:

Precision was studied to show how close results are to one another. The two most common precision measures are (repeatability) and (reproducibility).

As precision often varies with analyte concentration, repeatability and reproducibility were calculated for soil matrix and all pesticides and degradations products at all 3 spiking levels. The repeatability is given as the relative standard deviation on the results from two or more analysis of identical samples, by the same operator, on the same instrument and within a short period of time. Repeatability is calculated from the double determinations.

In-house reproducibility is relative standard deviation on results obtained under reproducibility conditions, with the same method on the same sample by different operators within a larger period of time. The In-house reproducibility is a combination of the repeatability variance and the in-house reproducibility.

The repeatability experiments were performed with six replicates of spiked samples by same operator, same apparatus, same method and short intervals of time. The relative standard deviation (CV %) was ≤ 10 %. The repeatability and reproducibility has been calculated in accordance to ISO 5725-2 Ref

In this study intra-laboratory reproducibility was only considered, soil samples fortified at spiking level are analyzed by different analysts on several days and injected on different instruments. The relative standard deviation (CV %) was ≤ 15 %.

Linearity:

Method linearity was checked by making recovery tests at different levels limit of quantification (LOQ), spiking level and high concentration for 352 compounds. The method found to be linear from LOQ up to high level. The correlation coefficient was found not less than 0.9992. Data in Tables 1 illustrate that the mean recoveries for the tested pesticides in spiking level ranged between 70 and 120 % for fortified levels ≤ 1mg/kg.

Uncertainty:

Parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measured. The parameter may be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval.

In estimating the overall uncertainty, it may be necessary to take each source of uncertainty and treat it separately to obtain the contribution of each source.

Each of the separate contributions to uncertainty is referred to as an uncertainty component. When expressed as a standard deviation an uncertainty component is known as standard uncertainty. The total uncertainty combined standard uncertainty, equal to the positive square root of the sum of the squares of the individual uncertainty components. For most purposes in analytical chemistry, an expanded uncertainty should be used. The expanded uncertainty provides an interval within which the value of the measured is believed to lie a higher level of confidence. Expanded uncertainty is obtained by multiplying the combined uncertainty, by a coverage factor k, for confidence level of 95% k is 2.

Method Recovery:

Certified reference material was not available for all pesticides in soil. In the absence of reference materials, trueness has been calculated as the recovery of the validated compounds from the soil at the three spiking levels.

The recoveries for each of the validated compounds are presented in (Table 1)

The recovery was tested for 352 compounds fortified in soil on different concentration levels. The average recovery and relative standard deviation on each level were calculated.

The results of the present study (Table 1) showed that about 86.5% of tested pesticides (352 pesticides) have accepted recovery and coefficient of variation in all three tested levels (0.01, 0.05 and 0.1 mg/kg). The rest tested pesticides have problematic sensitivity in LC-MSMS because of the limitations regarding their solubility, volatility, ionization, stability, etc.

The limit of quantification (LOQ) was 0.01 mg/kg with recovery ranged between 70 and 120% for most pesticides. The coefficient of variation (CV) at the LOQ was <10% for most pesticides.

Table (1) shows the average recoveries %, and the coefficient of variation (CV %) for the organochlorine, organonitrogen, carbamates and organophosphorus pesticides compounds residue in fortified soil.

Table 1: The average recoveries %, avarage and the coefficient of variation (CV %) for the tested pesticides in fortified soil.

No.	Soil	0.01 mg/kg		0.05 mg/kg		0.1 mg/kg		LOQ
	Pesticides –Transitions	Avarage Rec%	CV%	Avarage Rec%	CV%	Avarage Rec%	CV%	
1	Abamectin 890.5/305.3K	96%	15%	92%	21%	90%	12%	0.01
2	Acephate 184.0/125K	90%	8%	82%	13%	75%	1%	0.01
3	Acetamiprid 223.2/126K	86%	7%	90%	2%	75%	2%	0.05
4	Acrinathrin 559/181K	80%	3%	76%	10%	68%	4%	0.01
5	Aldicarb Sulfoxide207.3/132K	102%	8%	90%	3%	85%	11%	0.01
6	Aldicarb Sulphone223.1/76.2M	93%	6%	91%	3%	80%	4%	0.01
7	Aldicarb208.2/116K	87%	7%	102%	7%	76%	5%	0.01
8	Ametryn228.0/186K	78%	8%	93%	7%	70%	2%	0.01
9	Amidosulfuron-370.1-218K*	57%	4%	85%	8%	53%	5%	0.05
10	Aminocarb_209_122*	22%	5%	144%	5%	40%	12%	0.05
11	Anilofos367.9/125.1K	82%	7%	95%	2%	71%	2%	0.01
12	Atrazine216.1/104K	85%	8%	95%	2%	75%	1%	0.01
13	Azaconazol-300-159K	81%	6%	94%	3%	72%	2%	0.01
14	Azamethiphos-325-139K*	14%	4%	94%	3%	25%	5%	0.05
15	Azimsulfuron425/156K	78%	7%	92%	3%	70%	5%	0.01
16	Azinophos-Et_346_132	84%	8%	90%	3%	73%	3%	0.01
17	Azinophos-Me_318_125	91%	9%	83%	3%	77%	4%	0.01
18	Azoxystrobin404.0/344.2K	84%	7%	85%	1%	71%	3%	0.01
19	Barban_258_143*	67%	12%	68%	4%	58%	11%	0.05
20	Beflubutamid-356.1-91.1K	85%	7%	66%	5%	68%	3%	0.01
21	Benalaxyl326.3/148.1K	81%	8%	91%	3%	69%	3%	0.01
22	Bendiocarb224/109.1K	86%	7%	93%	2%	76%	4%	0.01
23	Benfuracarb_411_102	119%	17%	92%	3%	102%	48%	0.01
24	Bensulfuron-Me411.0/149K*	61%	7%	93%	2%	58%	2%	0.05
25	Benthivalicarb isopropyl-382.1-116.1K	78%	7%	95%	5%	69%	3%	0.01
26	Benzoximate-364-105K	62%	8%	98%	6%	60%	3%	0.01
27	Bifenazate-Na_301_170*	5%	3%	90%	2%	19%	33%	0.05
28	Bispyribac431/275K	80%	6%	97%	2%	70%	3%	0.01
29	Bitertanol_338_269	85%	9%	88%	4%	73%	6%	0.01
30	Boscalid343/140K	81%	6%	87%	3%	69%	6%	0.01
31	Bromacil261/188K	89%	5%	96%	4%	77%	5%	0.01
32	Bromuconazole_376_159	83%	6%	93%	5%	72%	4%	0.01
33	Bupirimate317.0/166.2K	77%	8%	90%	3%	68%	5%	0.01
34	Buprofezine306.2/116K	80%	8%	97%	4%	72%	3%	0.01
35	Butachlor312.3/162K	92%	11%	93%	2%	79%	6%	0.01
36	Butocarboxim sulfoxide-207.1-132.1K	102%	8%	94%	2%	85%	21%	0.01
37	Butocarboxim-208-116L	94%	6%	84%	7%	79%	3%	0.01
38	Butralin296.0/222.2K	101%	12%	88%	4%	88%	5%	0.01
39	Butylate-218.1-156.2K	81%	6%	94%	2%	70%	3%	0.01
40	Carbaryl202.1/127.1K	88%	6%	95%	2%	76%	5%	0.01
41	Carbendazim192.1/132.1K	93%	5%	93%	3%	80%	3%	0.01
42	Carbetamide-237.2-118.1K	90%	4%	92%	3%	76%	3%	0.01
43	Carbofuran222.1/123K	98%	5%	100%	3%	83%	3%	0.01
44	Carbofuran-3OH238.3/163.1L	74%	8%	97%	2%	68%	3%	0.01
45	Carbosulfan_381.1_118	102%	28%	93%	2%	82%	27%	0.05
46	Carboxin236.0/142.9K*	50%	8%	83%	2%	36%	3%	0.05
47	Chlorbromuron-293-182K	80%	7%	83%	2%	68%	3%	0.01
48	Chlorfenvinphos359/155K	86%	8%	81%	3%	71%	4%	0.01
49	Chlorfluazuron540.0/158K	114%	15%	90%	2%	102%	5%	0.01
50	Chloridazon-222-104K	92%	4%	92%	2%	78%	5%	0.01
51	Chloroxuron-293-182K	84%	9%	92%	3%	73%	3%	0.01
52	Chlorpyrifos349.5/115.1K	103%	15%	89%	2%	86%	6%	0.01
53	Chlorpyrifos-Me322.0/124.9K	73%	9%	83%	1%	92%	5%	0.01
54	Chlorsulfuron_358_141*	61%	7%	3%	1%	43%	3%	0.05
55	Chlorthiophose-360.9-192K	114%	18%	92%	2%	104%	4%	0.01
56	Chlrbufam-224-153.9K	78%	8%	93%	2%	69%	6%	0.01
57	Chromafenozide_395_175	73%	8%	89%	4%	65%	1%	0.01
58	Cinidon-Et-394.1-348.1K	127%	18%	95%	4%	114%	5%	0.01

Table 1: Continued.

No.	Soil	0.01 mg/kg		0.05 mg/kg		0.1 mg/kg		LOQ
	Pesticides -Transitions	Avarage Rec%	CV%	Avarage Rec%	CV%	Avarage Rec%	CV%	
59	Cinosulfuron-414.1-157K	85%	5%	96%	3%	74%	5%	0.01
60	Clethodim360.0/164K*	44%	10%	96%	3%	48%	4%	0.05
61	Clodinafop-propargyl350.0/266K*	19%	5%	97%	2%	30%	6%	0.05
62	Clofentezine303/102K	90%	9%	100%	4%	81%	6%	0.01
63	Clomazone-240.1-125K	82%	5%	93%	3%	71%	3%	0.01
64	Cloquintocet-mexyl-336.2-192.1K	86%	9%	92%	4%	77%	4%	0.01
65	Clothianidin250.0/132K	96%	4%	99%	2%	82%	5%	0.01
66	Coumaphos-363-226.9K	88%	7%	89%	3%	75%	2%	0.01
67	Coumatetrayl293/175K	78%	7%	88%	4%	69%	2%	0.01
68	Cyazofanid_325_108*	62%	5%	87%	5%	55%	3%	0.05
69	Cycloheximide282_107*	69%	10%	90%	5%	59%	19%	0.05
70	Cyflufenamid413/203K	74%	8%	91%	4%	66%	5%	0.01
71	Cyfluthrin-NH4_451_191	115%	9%	91%	3%	97%	4%	0.05
72	Cyhalothrin-NH4_467_225	99%	8%	89%	2%	85%	5%	0.01
73	Cymoxanil_199_111	92%	5%	95%	3%	79%	3%	0.01
74	Cypermethrin-NH4_433_191	136%	16%	89%	4%	118%	3%	0.01
75	Cyproconazole_292_125	88%	6%	92%	8%	75%	4%	0.01
76	Cyprodinil226.0/118.1K	78%	8%	91%	6%	69%	5%	0.01
77	Cyromazine_167_108*	26%	5%	96%	2%	35%	7%	0.05
78	Deltamethrin-NH4_521_279*	170%	31%	93%	2%	155%	7%	0.05
79	Demeton-S-me-231-61K*	58%	12%	92%	3%	58%	5%	0.05
80	Demeton-S methylsulphon 263/ 108.9L	76%	6%	94%	3%	69%	2%	0.01
81	Desmedipham301/136K	78%	7%	92%	3%	68%	5%	0.01
82	Diafenthiuron_385_236	84%	24%	91%	3%	83%	26%	0.01
83	Diazinon305.1/169.1K	78%	8%	100%	2%	69%	3%	0.01
84	Dichlofenthion315/259K	92%	11%	101%	2%	83%	5%	0.01
85	Dichlofuanid350.1/123K*	19%	8%	109%	3%	34%	5%	0.05
86	Diclfop methyl358/120K	67%	7%	106%	3%	66%	5%	0.01
87	Diclorovs221/109L	6%	3%	95%	2%	20%	5%	0.01
88	Dicrotophos-238.1-112L	88%	5%	96%	1%	76%	4%	0.01
89	Diethofencarb268/124L	84%	7%	85%	6%	92%	4%	0.01
90	Difenoconazole406.0/251L	91%	7%	93%	8%	99%	5%	0.01
91	Diflufenican395.1/246L	80%	7%	82%	1%	69%	5%	0.01
93	Dimetaclor-256-148L	89%	6%	80%	2%	74%	3%	0.01
94	Dimethenamide-276.1-168.2L	85%	7%	90%	3%	74%	3%	0.01
95	Dimethoate230.0/171L	92%	4%	89%	3%	78%	4%	0.01
96	Dimethomorph388.0/165L	85%	6%	100%	4%	73%	17%	0.01
97	Diniconazole_326_70	94%	8%	102%	5%	84%	5%	0.05
98	Diphacinone_341_235	79%	5%	91%	24%	69%	5%	0.01
99	Disulfoton sulfone307/153L	96%	6%	88%	23%	80%	4%	0.01
100	Disulfoton sulfoxide291/185M	119%	6%	95%	3%	96%	4%	0.01
101	Disulfoton_275_61*	51%	9%	94%	3%	52%	6%	0.05
102	Diuron_233_72	86%	6%	87%	3%	73%	4%	0.01
103	Dodemorph_282_116	71%	9%	84%	5%	94%	11%	0.01
104	Dodine_228_57	118%	47%	85%	8%	101%	44%	0.01
105	Eamamectin886/158L	89%	8%	91%	9%	74%	18%	0.01
106	Edifenophos311.0/109L*	37%	9%	85%	5%	40%	3%	0.05
107	EPN-324-157L	89%	11%	89%	6%	78%	5%	0.01
108	Esfenvalerate_437_125	126%	16%	83%	3%	110%	4%	0.01
109	Ethiofencarb Sulfon-258.1-107.2L	92%	4%	87%	3%	77%	3%	0.01
110	Ethiofencarb Sulfoxid-242.1-107K	136%	6%	87%	18%	108%	2%	0.01
111	Ethiofencarb-226.1-107.1M*	46%	10%	85%	11%	46%	4%	0.05
112	Ethion385.0/143L	76%	8%	95%	4%	67%	3%	0.01
113	Ethirimol-210.1-140.1L*	44%	4%	104%	4%	47%	4%	0.05
114	Ethofumesate287/121L	85%	4%	95%	4%	74%	4%	0.01
115	Ethoprophos243.1/131L	82%	6%	88%	4%	70%	1%	0.01
116	Ethoxyquin218/160L	79%	38%	94%	16%	68%	23%	0.01
117	Etrimfos293/125L	73%	7%	92%	1%	65%	1%	0.01
118	Expoxiconazole330/101L	81%	7%	92%	1%	70%	6%	0.01
119	Famoxadone392.0/238L	73%	7%	77%	2%	61%	5%	0.01
120	Fenamidone312/236L*	49%	5%	75%	3%	45%	3%	0.05
121	Fenamiphos304.1/217L	76%	7%	82%	4%	66%	3%	0.01

Table 1: Continued.

No.	Soil	0.01 mg/kg		0.05 mg/kg		0.1 mg/kg		LOQ
	Pesticides -Transitions	Avarage Rec%	CV%	Avarage Rec%	CV%	Avarage Rec%	CV%	
122	Fenamiphos-Sulfone_336_108	79%	7%	79%	3%	68%	3%	0.01
123	Fenamiphos-Sulfoxide_320_171	93%	6%	84%	7%	78%	1%	0.01
124	Fenarimol331.1/189L	73%	9%	88%	7%	63%	6%	0.01
125	Fenbuconazole337/125L	83%	9%	98%	2%	71%	4%	0.01
126	Fenfuram-202-109L	72%	7%	97%	2%	66%	2%	0.01
127	Fenhexamid302.0/55L*	49%	12%	86%	5%	50%	7%	0.05
128	Fenitrothion_278_125	109%	22%	90%	3%	94%	10%	0.01
129	Fenoxap-p-ethyl362.0/121L*	55%	8%	99%	4%	55%	4%	0.05
130	Fenoxycarb302/116L	84%	8%	96%	4%	71%	5%	0.01
131	Fenpropathrin_350_125	118%	11%	96%	3%	101%	4%	0.01
132	Fenpropidin-274.2-117.1L*	56%	4%	96%	4%	53%	4%	0.05
133	Fenpropimorph_304_116	93%	18%	97%	5%	80%	22%	0.01
134	Fenpyroximate422.0/215.1L	127%	18%	95%	4%	115%	6%	0.01
135	Fenthion sulfoxid295/109N	93%	4%	93%	4%	78%	4%	0.01
136	Fenthion_279_169	81%	7%	79%	5%	69%	3%	0.01
137	Fenthion-Oxon-Sulfone_295_104	110%	5%	99%	13%	92%	4%	0.01
138	Fenthion-Oxon-Sulfoxide_301_104	79%	10%	93%	4%	70%	4%	0.01
139	Fenthion-Sulfone_311_109*	37%	9%	93%	2%	41%	3%	0.05
140	Fenvalerate-NH4_437_125	126%	16%	94%	2%	112%	4%	0.01
141	Fipronil_437_368	80%	9%	92%	12%	67%	4%	0.01
142	Flamprop321.9/105.1L	88%	6%	92%	9%	77%	6%	0.01
143	Flonicamid-274.2-117.1L*	55%	5%	93%	6%	52%	3%	0.05
144	Florasulam_360_129	88%	7%	96%	5%	76%	2%	0.01
145	Fluazifop-p-butyl384.1/282.1L*	56%	7%	90%	2%	53%	3%	0.05
146	Flubendiamide683/274L	101%	13%	91%	2%	84%	12%	0.01
147	Flucythrinate-NH4_469.1_157	115%	13%	94%	15%	97%	6%	0.01
148	Flufenacet-364.1-152L	86%	10%	94%	14%	75%	1%	0.01
149	Flufenoxuron489.1/141.1L	99%	12%	95%	3%	90%	4%	0.01
150	Flumetesulam326.2/109.2L	90%	6%	96%	3%	77%	4%	0.01
151	Flumeturon233/160L	92%	14%	85%	3%	74%	4%	0.01
152	Fluopicolide383/145L	80%	8%	85%	3%	68%	2%	0.01
153	Fluquinconazole376/307L*	90%	8%	28%	1%	65%	2%	0.1
154	Fluroxpyr_254.9_181	89%	13%	76%	2%	71%	6%	0.01
155	Fluroxypyr-meptyl-367-209K	107%	11%	91%	19%	92%	3%	0.01
156	Flusilazole316.1/165.1L	81%	6%	93%	19%	69%	5%	0.01
157	Flutolanil324.0/242L	88%	7%	81%	1%	73%	5%	0.01
158	Flutriafol_302_109	86%	7%	86%	1%	73%	3%	0.01
159	Fluvalinate-tau503.3/181.1N	117%	15%	93%	3%	126%	4%	0.01
160	Foramsulfuron_452.9_182	69%	6%	94%	3%	63%	3%	0.01
161	Formetanate-222.1-165L	74%	7%	91%	4%	67%	3%	0.01
162	Formothion_258_125	83%	6%	91%	5%	72%	2%	0.01
163	Fosthiazate284/104L	82%	6%	89%	6%	70%	3%	0.01
164	Fuberidazole-185.1-157.2L	70%	4%	89%	4%	62%	3%	0.01
165	Furathiocarb-383.1-195.1L	74%	7%	96%	3%	65%	3%	0.01
166	Halosulfuron_434.9_182*	64%	5%	95%	2%	59%	4%	0.05
167	Haloxyfop-Et-434-288L*	43%	8%	84%	7%	44%	4%	0.05
168	Heptenophos251/109L*	11%	3%	89%	8%	24%	2%	0.05
169	Hexaconazole314.0/159L	83%	8%	85%	4%	67%	4%	0.01
170	Hexazinone-253.1-171.2L	88%	4%	84%	4%	69%	3%	0.01
171	Hexythiazox353.1/167.9L	123%	14%	88%	7%	106%	4%	0.01
172	Imazalil_296.9_159	84%	5%	87%	6%	91%	5%	0.01
173	Imazamethabenz-Me289.0/144.2L	88%	4%	73%	3%	71%	4%	0.01
174	Imidacloprid256.2/175.1L	91%	7%	75%	3%	75%	4%	0.01
175	Indoxacarb528.0/203.1L	83%	8%	95%	4%	71%	2%	0.01
176	Iprobenfos -289-205.2L	81%	8%	93%	4%	71%	2%	0.05
177	Iprodione 330.1/56.2L	107%	13%	94%	6%	92%	3%	0.01
178	Iprovalicarb321/119L	84%	6%	96%	5%	72%	2%	0.01
179	Isofenphos346/217K	83%	8%	90%	6%	72%	3%	0.01
180	Isofenphose-oxon-330.1-200.9L	82%	6%	86%	9%	70%	2%	0.01
181	Isofenphos-Me-332-231.1L	79%	7%	93%	4%	68%	3%	0.01
182	Isoprothiolane291.0/189M	82%	7%	92%	5%	71%	3%	0.01
183	Isoproturon207.3/165.1M	87%	7%	99%	4%	77%	2%	0.01
184	Karbutlte280/181M	87%	8%	99%	3%	76%	3%	0.01
185	Kresoxin_Me314/116M	82%	6%	97%	2%	72%	3%	0.01
186	Lenacil-235.1-153.1M	92%	6%	99%	2%	80%	2%	0.01
187	Linuron249.1/160M	79%	6%	97%	4%	70%	4%	0.01

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Table 1: Continued.

No.	Soil	0.01 mg/kg		0.05 mg/kg		0.1 mg/kg		LOQ
	Pesticides -Transitions	Avarage Rec%	CV%	Avarage Rec%	CV%	Avarage Rec%	CV%	
188	Lufenuron511.0/141M	111%	7%	98%	3%	94%	2%	0.01
189	Malaoxon315.1/127N*	57%	7%	92%	3%	55%	4%	0.05
190	Malathion331.0/127M	70%	10%	91%	3%	78%	5%	0.01
191	Mandipropanid412/328M	80%	8%	92%	4%	70%	3%	0.01
192	Mecarbam330/227M	87%	7%	89%	2%	72%	3%	0.01
193	Mefenacet299/120M	78%	8%	95%	6%	68%	3%	0.01
194	Mefenpyr-diethyl-373-160M	72%	9%	91%	5%	73%	3%	0.01
195	Mepanipyrim224/106M	77%	7%	95%	3%	68%	6%	0.01
196	Mepronil270/119M	83%	7%	90%	4%	71%	2%	0.01
197	Metaflumizone_507_116	85%	7%	102%	5%	73%	6%	0.01
198	Metalaxyl280.2/160.1M	82%	6%	102%	4%	73%	2%	0.01
199	Metamitron203.1/104M	96%	6%	83%	2%	81%	4%	0.01
200	Metazachlor278/134M	82%	6%	81%	4%	70%	3%	0.01
201	Metconazole-320-125M	98%	9%	72%	5%	75%	3%	0.01
202	Methabenzthiazuron-222-150M	76%	6%	89%	4%	67%	4%	0.01
203	Methacrifos-241-209M*	54%	5%	72%	13%	50%	2%	0.05
204	Methamidophos142.2/94M	78%	6%	79%	12%	67%	4%	0.01
205	Methidathion303/145M	78%	7%	72%	27%	63%	3%	0.01
206	Methiocarb Sulfoxid242/185L	100%	5%	95%	2%	85%	3%	0.01
207	Methiocarb Sulphon275.1/122N	86%	6%	108%	8%	77%	2%	0.01
208	Methiocarb243.0/121.1M	86%	7%	109%	7%	77%	2%	0.01
209	Methomyl163.2/106M	102%	3%	95%	3%	85%	4%	0.01
210	Methoxyfenozide369.0/133M	74%	8%	97%	2%	65%	4%	0.01
211	Metobromuron259/148M	84%	4%	87%	3%	71%	5%	0.01
212	Metosulam418.0/175M	82%	8%	90%	11%	70%	6%	0.01
213	Metoxuron229/156M	84%	7%	89%	17%	74%	3%	0.01
214	Metribuzin215.2/187.1M	89%	5%	99%	16%	77%	2%	0.01
215	Metsulforon-Me_381.9_167	78%	6%	98%	2%	70%	3%	0.01
216	Mevenphos225/127M*	20%	5%	97%	3%	30%	4%	0.05
217	Monocrotophos224.0/127M	90%	5%	109%	2%	80%	3%	0.01
218	Monolinuron215/126M	85%	6%	102%	3%	75%	3%	0.01
219	Monuron-199-126M	90%	9%	77%	4%	77%	3%	0.05
220	Myclobutanil289.0/125M	81%	8%	77%	3%	67%	4%	0.01
221	Napropamide-272.1-129.1M	79%	8%	95%	5%	69%	4%	0.01
222	Neburon-275-114M	82%	10%	91%	4%	71%	3%	0.01
223	Nicosulfuron411/106M*	59%	5%	62%	3%	50%	5%	0.05
224	Nitenpyram-271-126M*	66%	3%	60%	3%	55%	4%	0.05
225	Novoluron493/141M	90%	6%	94%	3%	76%	6%	0.01
226	Nuarimol315.0/252M	81%	5%	100%	4%	70%	4%	0.01
227	O,S,TEPP_306.5_250.8*	6%	3%	98%	2%	21%	3%	0.5
228	Ofurace-282-160.1M	82%	6%	99%	2%	73%	3%	0.01
229	Omethoate214.0/143M	78%	14%	82%	3%	87%	4%	0.01
230	Oxadiargyl340.8/151M	83%	9%	85%	3%	90%	3%	0.01
231	Oxadiazon345.3/220M	85%	9%	89%	6%	75%	4%	0.01
232	Oxamyl237.0/72M	90%	6%	90%	5%	78%	3%	0.01
233	Oxasulfuron-407-107M	63%	5%	94%	2%	60%	3%	0.01
234	Oxycarboxin268.0/147M	95%	5%	95%	2%	81%	5%	0.05
235	Oxydemeton methyl247/108.9M	110%	2%	92%	3%	90%	2%	0.01
236	Paclobutrazol_294.1_70	79%	7%	94%	2%	69%	4%	0.01
237	Paraoxon methyl248/202.2N*	70%	3%	94%	3%	73%	4%	0.05
238	Paraoxon-Et276.2/219.9N	22%	6%	95%	2%	32%	3%	0.01
239	Parathion-Et_291.9_235.9	78%	11%	93%	4%	71%	7%	0.01
240	Parathion-Me_263.9_125	103%	14%	95%	4%	94%	9%	0.01
241	Penconazole284.0/159M	88%	8%	95%	2%	74%	4%	0.01
242	Pencycuron_329_124.6	79%	9%	93%	2%	71%	4%	0.01
243	Pendimethalin_282_194	106%	13%	89%	2%	94%	5%	0.01
244	Permethrin-NH4_408_183	117%	19%	93%	2%	108%	8%	0.01
245	Phenmedipham301.3/136M	76%	8%	96%	2%	68%	6%	0.01
246	Phenthoate321.0/163M	68%	8%	96%	3%	72%	6%	0.01
247	Phorate sulfone293/180N	87%	7%	88%	4%	74%	4%	0.01
248	Phorate sulfoxide277/199L	104%	5%	91%	3%	86%	3%	0.05
249	Phorate261/199M	74%	11%	96%	5%	68%	4%	0.01
250	Phosalone368.0/111M	67%	8%	95%	5%	63%	7%	0.01
251	Phosmet318/133M	76%	8%	90%	2%	73%	8%	0.01
252	Phosphamidon300.1/127.1M	72%	9%	88%	3%	66%	2%	0.01
253	Phoxim-299-129M	74%	8%	81%	5%	64%	4%	0.01
254	Picolinafen-377-145M	89%	33%	90%	3%	67%	9%	0.01

Table 1: Continued.

No.	Soil	0.01 mg/kg		0.05 mg/kg		0.1 mg/kg		LOQ
	Pesticides -Transitions	Avarage Rec%	CV%	Avarage Rec%	CV%	Avarage Rec%	CV%	
255	Picoxystrobin-368-145M	79%	7%	100%	20%	69%	3%	0.01
256	Piperonyl butoxid356.0/119M	88%	7%	98%	3%	77%	3%	0.01
257	Pirimicarb desmethyl225/168N	62%	5%	87%	4%	57%	2%	0.01
258	Pirimicarb239.2/182.3M	71%	6%	84%	3%	62%	3%	0.01
259	Pirimiphos-Et334.1/182.3M	89%	8%	95%	4%	77%	3%	0.01
260	Pirimiphos-Me306.2/108M	82%	8%	93%	3%	71%	3%	0.01
261	Prochloraz376.0/308M	86%	7%	94%	9%	76%	6%	0.01
262	Profenofos373.0/144.1M	75%	10%	90%	9%	85%	6%	0.01
263	Profluralin348/276M	98%	16%	76%	3%	81%	8%	0.05
264	Promecarb208.0/109.1M	93%	6%	79%	2%	76%	3%	0.01
265	Prometon-226-142M	79%	7%	77%	23%	67%	3%	0.01
266	Prometryn242.0/158M	79%	7%	103%	14%	70%	2%	0.01
267	Propachlor-212.1-169.9M	71%	8%	84%	16%	64%	2%	0.01
268	Propamocarb HCl189.0/102N	75%	5%	83%	16%	71%	8%	0.01
269	Propanil218/127N	83%	10%	96%	3%	74%	4%	0.01
270	Propaquizafop-444.1-100.1N	79%	11%	99%	5%	74%	3%	0.01
271	Propargite368.0/175N	108%	9%	85%	6%	92%	3%	0.01
272	Propazine-230-146N	88%	10%	93%	3%	76%	2%	0.01
273	Propazine-2OH-212-128M	64%	5%	72%	9%	81%	6%	0.01
274	Propetamphos-282-138N	78%	8%	80%	5%	98%	2%	0.01
275	Propiconazole342.1/159N	84%	8%	103%	3%	75%	3%	0.01
276	Propoxur210.1/111.1N	94%	5%	92%	5%	79%	3%	0.01
277	Propyzamide256/173N	82%	8%	95%	3%	72%	2%	0.05
278	Proquinazid373/331N	102%	17%	94%	1%	95%	3%	0.01
279	Prosulfocarb-252.1-128N	90%	8%	89%	17%	77%	2%	0.01
280	Prothioconazole_344_125	76%	14%	99%	16%	72%	7%	0.01
281	Prothioconazole-Desthio_312_125	77%	24%	92%	5%	92%	16%	0.01
282	Pymetrozine218.2/105.1N	90%	2%	98%	5%	82%	12%	0.01
283	Pyraclostrbin338/163N	83%	7%	97%	5%	71%	3%	0.01
284	Pyraflufen Et413/253N	64%	7%	96%	4%	60%	5%	0.01
285	Pyrazophos374.0/222N	86%	7%	95%	3%	75%	3%	0.01
286	Pyrazosulfuron-Et_415_182	69%	6%	96%	3%	63%	1%	0.01
287	Pyrethrins329.1/161.1N	80%	8%	95%	1%	72%	3%	0.01
288	Pyridaben365/147N	99%	17%	95%	2%	93%	3%	0.01
289	Pyridalyl_489.9_109	85%	11%	92%	3%	79%	7%	0.01
290	Pyridaphenthion341/0189N	81%	7%	91%	3%	70%	3%	0.01
291	Pyridate-379-207.1N*	38%	13%	114%	6%	51%	6%	0.05
292	Pyrifenox295.0/263N	101%	6%	120%	6%	89%	4%	0.01
293	Pyrimethanil_200_107	75%	8%	85%	6%	67%	3%	0.01
294	Pyriproxyfen322.2/227.3N	98%	15%	99%	6%	91%	3%	0.01
295	Pyroxsulam_435_166	88%	3%	92%	3%	75%	3%	0.01
296	Quinalphos299/163N	80%	7%	95%	3%	71%	4%	0.01
297	Quinmerac-222-140.9N	79%	6%	83%	12%	70%	2%	0.01
298	Quinoxyfen308/162N	121%	24%	84%	13%	113%	4%	0.01
299	Quizalofop-Et373.0/255N	70%	11%	94%	2%	68%	4%	0.01
300	Rimsulfuron_432_182*	47%	7%	90%	1%	49%	5%	0.01
301	Rotenone395/192N	78%	8%	103%	23%	71%	2%	0.01
302	Sebuthylazine_230_104	85%	7%	82%	5%	67%	3%	0.01
303	Sebuthylazine-desethyl-202.1-146.1M	91%	7%	92%	2%	79%	3%	0.01
304	Simazine202/132N	93%	5%	91%	2%	79%	6%	0.01
305	Simetryn-214.1-124.1N	82%	7%	95%	5%	73%	2%	0.01
306	Spinosad-A_732.2_142	74%	10%	96%	4%	69%	9%	0.05
307	Spinosad-D_746.2_142	73%	24%	92%	8%	66%	8%	0.01
308	Spirodiclofen411/313N	79%	10%	87%	9%	71%	4%	0.01
309	Spiroxamin298/100N*	56%	10%	92%	9%	53%	8%	0.05
310	Sulfotep-323-171N	76%	10%	92%	9%	69%	3%	0.01
311	Tebuconazole308.0/125N	90%	9%	100%	4%	78%	6%	0.01
312	Tebufenozide353.0/133N	78%	9%	93%	9%	67%	4%	0.01
313	Tebufenpyrad334/145N	98%	8%	101%	4%	84%	4%	0.01
314	Tebutam-234.2-199.2N	109%	9%	103%	4%	88%	10%	0.01
315	Tebuthiuron229/116N	89%	5%	92%	4%	76%	4%	0.01
316	Tepraloxydim342/166N	90%	7%	96%	4%	79%	3%	0.01
317	Terbufos289/103N	74%	10%	95%	15%	67%	6%	0.01
318	Terbumeton-226.2-170.1N	79%	6%	93%	15%	70%	2%	0.01
319	Terbuthialzine230.0/104N	86%	7%	88%	3%	74%	3%	0.01

Table 1: Continued.

No.	Soil	0.01 mg/kg		0.05 mg/kg		0.1 mg/kg		LOQ
	Pesticides -Transitions	Avarage Rec%	CV%	Avarage Rec%	CV%	Avarage Rec%	CV%	
320	Terbutryn-242.2-186N	79%	7%	87%	5%	68%	1%	0.01
321	Tetrachlorvinphos-367-127N*	50%	9%	93%	4%	51%	4%	0.05
322	Tetraconazole372.0/159N	83%	8%	90%	4%	71%	4%	0.01
323	Tetramethrin_332.2_135	78%	8%	94%	2%	71%	7%	0.01
324	Thiabendazole202.1/131N	79%	3%	97%	21%	66%	3%	0.01
325	Thiacloprid253.2/126N	82%	8%	95%	4%	72%	4%	0.01
326	Thiamethoxam292.0/181.2N	91%	3%	93%	4%	77%	3%	0.01
327	Thifensulfuron-Me_387.9_167	76%	4%	79%	1%	64%	4%	0.01
328	Thiobencarb258.3/125N	83%	7%	78%	2%	70%	2%	0.01
329	Thiocyclam-OH_181.9_136.9*	32%	4%	91%	3%	38%	7%	0.05
330	Thiodicarb355.1/108N	75%	7%	90%	2%	65%	6%	0.01
331	Thiofanox_219_61	70%	23%	84%	2%	73%	16%	0.01
332	Thiophanate-Me343.0/151N	9%	2%	88%	2%	91%	7%	0.01
333	Tolclophos-Me_301_125	83%	8%	87%	3%	72%	4%	0.01
334	Tolylfluanid364.0/137N	80%	7%	86%	4%	85%	3%	0.01
335	Tralkoxydim330/138N	92%	10%	93%	2%	83%	2%	0.01
336	Triadimifon294.1/197N	90%	6%	90%	2%	76%	3%	0.01
337	Triadiminol_296_70	87%	7%	94%	3%	74%	15%	0.01
338	Triasulfuron-402-141N	78%	7%	91%	2%	70%	3%	0.01
339	Triazophos314.2/119N	82%	9%	93%	2%	72%	2%	0.01
340	Triazoxide_248_124*	53%	6%	91%	1%	51%	7%	0.05
341	Triclopyr butatyl356.2/237.7N	60%	9%	92%	83%	59%	6%	0.01
342	Triclorfon257/109N	89%	4%	92%	12%	75%	4%	0.01
343	Tricyclazole190/136N	81%	5%	72%	4%	68%	5%	0.01
344	Trietazine-230-132N	88%	11%	69%	3%	69%	1%	0.01
345	Trifloxystrobin409.0/186N	77%	8%	97%	4%	69%	3%	0.01
346	Triflumizole346.3/278N	80%	8%	99%	3%	71%	4%	0.01
347	Triflumuron_358.9_156	80%	7%	88%	2%	69%	5%	0.01
348	Triforine_433_388	81%	5%	89%	3%	69%	4%	0.01
349	Triticonazole_318_70	94%	11%	90%	3%	75%	8%	0.01
350	Vamidothion-288.1-118N	81%	5%	85%	3%	69%	3%	0.01
351	Xylylcarb (Meobal)180/108N	108%	12%	93%	3%	95%	27%	0.01
352	Zoxamide-336-159.1N	81%	10%	97%	2%	71%	2%	0.01

The calculation of the detection limit (LOD) has been based on the results of the lowest spiking level for which the results met the acceptance criteria, as three times the standard deviation of the absolute recoveries. The limits of determination for the pesticides included in the validation are presented in Table(1). The ions used for quantification are presented in Table (1).

All above mentioned criteria have been met, the detection limits have been calculated and accepted results (repeatability, reproducibility and recovery).

Conclusion:

A simple procedure using LC-MSMS was found to be very efficient in determination of different pesticide residues in soil. The method gives distinct advantages over the typical techniques of multi-residue analysis in soil by extraction with simple extraction method despite ensuring satisfactory precision and accuracy at residue level as low as 0.01 mg/kg. LC–MS/MS could analyze the entire 352 tested pesticides. Satisfactory recoveries (70–120%) were obtained below the level of 0.1 mg/kg. The method offers low level of measurement uncertainty (<30%), indicating suitability to the requirements of the international standards as per the ISO/IEC 17025 for laboratory accreditation.

This method was validated for 352 pesticides, isomers or degradation products. The detection limits ranged from 0.01 to 0.1 mg/kg. Work on the method will continue, particularly detection the pesticide on quadruple instrument and MS/MS.

References

AOAC Official Methods of Analysis, 2003. 991.07.

Badach, H., T. Nazimek and I.A. Kamińska, 2007. Pesticide content in drinking water samples collected from orchard areas in central Poland. Ann. Agric. Environ. Med., 14: 109-114.

Directive 91/414/EEC, 1991. Concerning the placing of plant protection products on the market, Off. J. Eur. Commun., No. L230/1.

European Union, Pesticide EU-MRLs Database, Regulation (EC) No. 396, (2005), http://ec.europa.eu/sanco pesticides/public/index.cfm.
Fern´andez-Alba, A.R., 2005a. Chromatographic-Mass Spectrometry Food Analysis for Trace Determination of Pesticide Residues, vol. XLIII, Elsevier,Amsterdam, The Netherlands, p. 113.
Fern´andez-Alba, A.R., 2005 b. Chromatographic-Mass Spectrometry Food Analysis for Trace Determination of Pesticide Residues, vol. XLIII, Elsevier, Amsterdam, The Netherlands, p. 403.
ISO 5725-2:1994, Accuracy (trueness and precision) of measurement methods and results -- Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.
ISO/IEC 17025, 2005. General Requirements for the Competence of Testing and Calibration Laboratories.
Kamińska, I.A., A. Oldak and W.A. Turski, 2004. Geographical Information System (GIS) as a tool for monitoring and analyzing pesticide pollution and its impact on public health. Ann. Agric. Environ. Med., 11: 181-184.
Kaushik, B., D.P. Oulkar; S. Dasgupta; S.B. Patil, S.H. Patil, R. Savant and P.G. Adsule, 2007. Validation and uncertainty analysis of a multi-residue method for pesticides in grapes using ethyl acetate extraction and liquid chromatography–tandem mass spectrometry. Journal of Chromatography A, 1173: 98-109.
Pesticide Analytical Manual, 1994. Third Edition, Vol.1, Section 302, US, FDA.
Prenazzi, G. and G. Ziglio, 1995. Regulations and Management. *In:* Pesticide Risk in Ground water. M Vighi, E Funari., editor. Chapter 10. Boca Raton, CRC Lewis Publishers, pp: 203-240.
Thrupp, L.A., 1996. New partnerships for sustainable agriculture. Washington DC, World Resources Institute.
Tomlin C.D.S., 2003. The pesticide manual-A world compendium, 13th edition. Hampshire: British Crop Protection Council (BCPC).