

# An quantificational method for 51 pesticide residues determination in Pu'er tea by LC-MS/MS

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**Abstract:** Pesticide residues in tea is a major issue due to their widely used in tea cultivation. Thus, to protect consumers, an appropriate method for determination of their residues in tea should be done. In this study, a method for the simultaneous determination of 51 pesticides in tea was developed and validated. The tea sample was extracted by acetonitrile and purified SPE cleanet TPT column followed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) with multi-reaction monitoring (MRM) mode. The method was validated according to the linearity, limit of detection, precision, the percentage of recovery at three different spike levels. The linear concentration range used was 10-100ng/ mL, the square of Correlation coefficient  $r^2$  was more than  $>0.995$ . Recoveries were adequate being in the acceptable range of 72-89% and RSD of  $<19\%$  for all the analytes at three level of 0.01,0.05 and 0.11mg/kg, the LOD of all chemicals from 0.001 mg/kg to 0.01 mg/kg .The method was applied for the determination for 400 tea samples collected from Pu'er which contain green tea and black tea. Among the analyzed samples , 36 % samples had Imidacloprid and 25% sample contain Acetamiprid, which were at a level below the European Union maximum residue levels (EU-MRLs). The information would be beneficial for Pu'er tea exporters.

**Key words:** multi-pesticide residue determination; puer tea; LC-MS/MS

## Introduction

Nowadays ,tea has become a popular beverage throughout the world with it has pleasant flavours and antioxidant quality that is good for human health.Thus , Market demand for tea gradually improved. To ensure the high yield of tea ,different pesticides were inevitably used in tea growing.

Pesticides are commonly used in the control of weeds and crop diseases. Especially insecticides, herbicides and plant growth regulators are spread on tea plantations<sup>1-2</sup>. The presence of pesticide residues in tea is becoming a priority concern for the consumer's as its accumulation will have a risk to health<sup>3-4</sup>. In order to protect the consumer's health and also promote the development of tea industry ,the content of pesticide residues in tea should be less than the maximum residue level. Thus, establishing a reliable analysis method to monitor and detect of pesticides in tea products

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is very urgent.

So far Various determination strategies and techniques for pesticides detection in tea have been published, including GC-electron capture

detection (GC-ECD), GC-flame photometric detection (GC-FPD), GC with a flame ionization detector (GC-FID), HPLC-fluorescence detector (HPLC-FLD), GC-MS and LC-MS/MS etc<sup>5-16</sup>. Among the all the methods, Conventional liquid Chromatography high effective separation function coupled with MS a validated method to conformation compound is becoming a new routine pesticide residue determination programs, which exhibits higher sensitivity and specificity<sup>17-18</sup>.

The purpose of this article is concentrate on developing a multi-pesticide residue analytical method for the determination of fifty-one pesticides in tea using LC/MS/MS. Finally, the established method was used for the residue analysis of 400 tea samples collected from different area in Pu'er.

## 1. Reagents and Materials

Reference standards of 51 Pesticides were obtained from Agro-Environmental Protection Institute Ministry of agriculture (China). chromatography grade methanol, acetonitrile, and formic acid were from J. T. Baker . Solid phase column(SPE,) were purchased from Agela Technologies. Pesticide standard stock solutions were respectively diluted by methanol to a concentration of 10 ug/mL and stored at a temperature of -20 degrees centigrade until use . A mixed working solution of 100ng/mL in methanol containing all selected Pesticide standard was prepared. Intermediate working solutions ,Matrix matched calibration standards were prepared by diluting mixed standard solution to reach the final concentrations of 10, 20, 40 , 60, 80, and 100 ng/mL.

### 1.1 Samples

A total of 401 tea samples were purchased from the local market in Pu'er. Among the sample 200 green tea and 200 black tea were collected from Pu'er , one organic tea was obtained from ZUXIANG tea garden(an organic tea garden which has conferred on the organic food certification ).All collected samples were smashed into powder by the use of shredding machine and stored in dryer until to analysis.

### 1.2 Sample Extraction and purification

2 grams of tea powder was weighted and transferred into a 50-mL centrifuge tube. Then 15 mL acetonitrile was added into the centrifuge tube. The centrifuge tube was shaken vigorously for 30 min by constant temperature vibrato (IKA,KS4000i,Germany) at 400 rpm. Afterward, the mixture was centrifuged for 5 min at 4000 rpm. All supernatant was taken into a 50 mL specimen bottle .To complete extraction of pesticides from the tea, 15mL acetonitrile was used to re-extract the residual of sample, and repeat above program, then coupled first supernatant with the later .The supernatant was concentrated by using the Rotary Evaporator(Buch, R-215,Switzerland) with 40 °C water bath reach to about 1mL. The concentrated extract was passed through activated solid phase extraction (SPE ) column, then the target analyte was eluted from the SPE column by 30 mL mixed solution of acetonitrile : methylbenzene (toluene)(3:1, v/v) under the atmospheric pressure . The eluant was dried by using the Rotary Evaporator. 1mL of the mobile phase mixture (20% mobile phase A and 80% mobile phase B) was used to re-dissolve the extracts and then transferred into 2 mL vial for analysis at LC-MS/MS after filtration with disposable nylon membrane filter (0.22 micron). The amount of the sample in the final extract was equivalent to 2 g/mL.

## 2. Instrumental Analysis

## 2.1 LC-MS/MS conditions

a liquid chromatography-mass spectrometry system was used for the identification and quantification of the selected pesticides. The system was consisted of liquid chromatography(Agilent Technologies,1260 infinity, USA) and a triple quadrupole mass spectrometer (Applied Biology Corporation, 3200, USA). Separation was performed using a Phenomenex kinetex column (2.6u ,C18 ,100×2.1 mm) with column oven temperature was 40 °C . the injection volume was 10 µL and the total run time was 27 min. The analysis was carried out in gradient mode , the program was 0–3min,70% mobile phase B; 3-9min, 60 % mobile phase B; 9-15 min, 40 % mobile phase B; 15-23 min, 1 % mobile phase B; 23-27 min,99 % mobile phase B. Mobile phase A is acetonitrile and the mobile phase B is consisted of water containing 0.1% formic acid. The mobile phase flow rate was 0.4 mL/min;

The mass spectrometry system was a triple quadrupole which was equipped with an electro spray ionization (ESI) source operated at the positive ion mode. The operating conditions were as follows: sheath gas (nitrogen) pressure was 30 arbitrary units; Auxiliary gas (nitrogen) pressure was 10 arbitrary units; spray voltage was 5500 V; capillary temperature was 425 °C. The collision gas pressure was 1.5 mTorr. The acquisition was made in the mutiple reaction monitoring (MRM) mode. The retention times and LC-MS/MS parameters for the target pesticides are presented in Table 1.

Table 1 LC-MS/MS parameters and retention times for the target pesticides

pesticides	RT (min)	Quantification ion pair(m/z)	DP (V)	CE (V)	Conformation ion pair(m/z)	DP (V)	CE (V)
Imidacloprid	5.53	256.2/209.9	41	23	256.2/175.2	41	23
Diflubenzuron	12.81	311.0/158.2	26	19	311.0/141.2	26	47
Carbendazim	4.35	192.2/160.2	36	27	192.2/132.1	36	41
Methomyl	4.56	163.1/88.1	16	13	163.1/106.0	16	13
Thiamethoxam	5.00	292.0/211.0	51	17	292.0/181.0	51	31
Hexythiazox	18.62	353.0/228.0	56	21	353.0/168.0	56	33
Phoxim	16.81	299.1/129.1	36	19	299.1/77.1	36	49
Carbofuran	7.34	222.2/123.1	26	29	222.2/165.2	26	15
Propoxur	7.23	210.1/111.0	21	19	210.1/168.1	21	11
Tricyclazole	5.96	190.0/163.0	46	31	190.0/136.0	46	37
Acetamiprid	5.75	223.2/126.1	36	29	223.2/99.1	36	47
Flufenoxuron	19.04	489.1/158.2	61	25	489.1/141.2	61	65
Propiconazole	13.77	342.1/159.1	46	43	342.1/69.1	46	33
Tebuconazole	12.47	308.0/70.0	21	39	308.0/125.0	21	47
Thiabendazole	4.68	202.1/175.1	56	35	202.1/131.2	56	43
Cartap hydrochloride	0.65	150.0/105.0	33	22	150.0/61.0	31	34
Imidaclothiz	5.64	262.1/181.1	30	21	262.1/122.1	29	50
Trichlorfon	5.10	257.1/221.1	34	18	257.1/109.2	32	27
Aldicarb	6.18	208.2/116.1	11	11	208.2/89.1	11	21
Atrazine	7.87	216.1/174.1	51	19	216.1/104.0	51	39
Benalaxyl	14.58	326.2/148.2	31	29	326.2/91.1	31	49
Difenoconazole	15.46	406.2/251.1	56	37	406.2/253.1	56	33
Diniconazole	13.47	326.0/70.0	51	45	326.0/159.0	51	39

Epoxiconazole	11.84	330.0/121.0	36	27	330.0/101.0	36	63
Fenazaquin	18.62	307.0/161.0	41	31	307.0/147.0	41	35
Fenobucarb	9.70	208.0/152.0	6	13	208.0/95.0	6	21
Hexaconazole	12.88	314.0/70.0	36	39	314.0/159.0	26	37
Isoprocarb	8.40	194.2/95.1	31	20	194.2/137.2	31	13
Isoproturon	8.20	207.2/72.1	46	29	207.2/46.1	46	31
Methamidophos	0.99	142.0/94.0	31	19	142.0/125.0	31	17
Metolcarb	6.60	166.2/109.1	16	15	166.2/94.2	16	37
Monocrotophos	4.68	224.0/127.0	46	21	224.0/98.0	46	17
Methidathion	9.80	303.0/145.1	21	15	303.0/85.2	21	29
Myclobutanil	11.30	289.0/70.0	31	33	289.0/125.0	31	41
Penconazole	12.90	284.0/159.0	41	39	284.0/70.0	41	29
Piperonyl Butoxide	17.67	356.2/177.2	21	28	356.2/119.0	21	35
Pirimicarb	5.21	239.2/72.1	33	34	239.2/182.2	33	21
Prochloraz	10.52	376.1/308.0	21	17	376.1/70.1	21	37
Propargite	19.26	368.0/231.0	6	17	368.0/175.0	6	21
Propiconazole	13.77	342.1/159.1	46	43	342.1/69.1	46	33
Triadimefon	11.59	294.0/197.0	36	21	294.0/225.0	36	19
Triadimenol	9.69	296.1/70.1	11	19	296.1/227.2	11	15
Pyriproxyfen	18.20	322.0/96.0	26	21	322.0/185.0	26	29
Quinoxifen	16.40	308.0/197.0	21	43	308.0/162.0	21	57
Rotenone	13.95	395.0/213.0	66	29	395.0/192.0	66	31
Simazine	6.60	202.1/132.1	46	25	202.1/124.3	46	25
Pymetrozine	3.12	218.0/105.0	51	27	218.0/78.0	51	47
Propanil	9.26	218.0/126.9	52	55	218.0/161.7	57	35
Furathiocarb	17.99	383.2/195.4	17	36	383.2/167.1	26	32
Chlorotoluron	7.66	213.0/72.3	55	27	213.0/140.1	38	34
Fenchlorphos	22.24	321.0/125.1	34	29	321.0/288.7	32	27
Prometryn	7.65	242.0/158.2	67	28	242.0/200.1	54	27

## 2.2 Method Validation

To ensure analysis credibility. The analytical method was validated by evaluating the linearity, accuracy, precision and limit of detection (LOD).

## 2.3 Accuracy and Precision

The method accuracy and precision was determined by recovery tests which using organic tea samples spiked with mixed standard solution at 0.01, 0.05 and 0.1 mg/kg. Recovery test was done by analyzing three replicates . Organic tea was spiked prior to the extraction procedure by the addition of a mixed pesticide standard working solution to reach the final fortification levels. After fortification, the sample was equilibrated by settling for 30 min before to extraction in order to ensure the sufficient contact of the analytes with the organic tea. Then, the samples were prepared and analysed according to the method described earlier.

Precision in case of repeatability (RSD) was determined at fortification levels of 0.01, 0.05, and 0.10 mg/kg with three

replicates. The Mean recovery rate and RSD were listed in the table 2.

Table 2 Mean recovery (%) and RSD (%) of the selected pesticides in organic tea at different fortification levels (n=3)

Name of pesticide	Fortification					
	0.01mg/kg		0.05mg/kg		0.1mg/kg	
	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)
Imidacloprid	81	12	87	6	84	5
Diflubenzuron	80	7	83	11	79	9
Carbendazim	76	10	77	12	88	7
Methomyl	88	19	81	13	89	8
Thiamethoxam	79	18	84	9	83	14
Hexythiazox	74	9	82	18	77	11
Phoxim	80	14	78	9	85	7
Carbofuran	83	6	76	8	80	4
Propoxur	86	15	77	8	79	12
Tricyclazole	82	6	86	11	81	5
Acetamiprid	83	8	77	4	78	13
Flufenoxuron	84	7	80	4	84	12
Propiconazole	83	8	82	4	75	14
Tebuconazole	83	8	86	3	78	6
Thiabendazole	87	9	83	7	81	11
Cartap hydrochloride	86	7	79	8	78	12
Imidaclothiz	80	8	71	6	84	6
Trichlorfon	74	15	81	16	77	9
Aldicarb	83	6	87	8	74	2
Atrazine	73	7	75	5	87	4
Benalaxyl	76	5	80	6	78	4
Difenoconazole	80	8	87	8	86	13
Diniconazole	82	9	77	5	73	7
Epoxiconazole	79	6	83	7	81	7
Fenazaquin	80	4	87	8	76	6
Fenobucarb	79	6	87	14	89	6
Hexaconazole	89	9	84	7	79	6
Isoprocarb	83	7	78	12	80	9
Isoproturon	83	11	87	7	81	6
Methamidophos	85	12	72	6	75	5
Metolcarb	79	11	77	7	75	10
Monocrotophos	84	2	80	12	88	7
Methidathion	74	11	81	9	83	3
Myclobutanil	86	6	78	11	89	10
Penconazole	85	5	80	19	79	8

Piperonyl Butoxide	80	12	76	4	81	5
Pirimicarb	83	5	85	5	81	6
Prochloraz	81	5	87	5	83	3
Propargite	89	9	81	8	80	7
Propiconazole	85	6	79	7	81	3
Triadimefon	81	9	87	12	79	4
Triadimenol	85	16	88	5	87	5
Pyriproxyfen	82	8	75	17	78	12
Quinoxifen	80	13	77	9	83	12
Rotenone	81	11	83	6	87	8
Simazine	86	12	81	10	81	9
Pymetrozine	81	13	78	5	76	4
Propanil	79	11	88	13	84	10
Furathiocarb	74	18	87	6	89	5
Chlorotoluron	85	9	83	6	88	9
Fenclorphos	80	12	77	16	78	8
Prometryn	88	17	89	13	81	8

A satisfied accuracy and precision was found for all the analytes . The recovery percentage of  $82\pm 3.98\%$ ,  $81\pm 4.53\%$  and  $81\pm 4.38\%$  for fortification levels of 0.01, 0.05 and 0.1 mg/kg organic tea sample, respectively. The date of  $RSD \leq 19\%$  for all the chemicals.

#### 2.4 Calibration Curve and Linearity

Consideration the factor of matrix effect<sup>19</sup>, calibration curves were prepared by use of matrix-matched standards analyzed. The organic tea was treated to be blank matrix. Linearity was determined by plotting peak areas versus different known concentrations (10, 20, 40, 60, 80 and 100 ng/ mL) and so obtained linear equation and value of regression coefficient ( $R^2$ ).

The limit of detection (LOD, ng/ mL) was estimated for a response of 3 times the signal-to-noise at the lowest concentration. The calibration parameters and the limit of detection for all the selected pesticides are summarized in Table 3

Table 3 Limit of detection (LOD) and calibration parameters of the selected pesticides for tea

analyte	LOD (mg/kg)	Calibration range(mg/kg)	Calibration parameters		
			slope	intercept	$R^2$
Imidacloprid	0.001	0.01-0.1	43.67	125.92	0.995
Diflubenzuron	0.005	0.01-0.1	394.22	385.34	0.998
Carbendazim	0.001	0.01-0.1	1309.81	13726.57	0.996
Methomyl	0.001	0.01-0.1	1121.56	16269.31	0.996
Thiamethoxam	0.001	0.01-0.1	348.73	-4154.60	0.995
Hexythiazox	0.001	0.01-0.1	36.73	-131.43	0.997
Phoxim	0.003	0.01-0.1	31.22	-61.00	0.998

Carbofuran	0.001	0.01-0.1	1043.35	22359.14	0.997
Propoxur	0.001	0.01-0.1	1224.50	-5575.00	0.997
Tricyclazole	0.001	0.01-0.1	1610.36	11464.43	0.996
Acetamiprid	0.001	0.01-0.1	718.79	-7423.29	0.995
Flufenoxuron	0.001	0.01-0.1	305.01	1453.23	0.999
Propiconazole	0.001	0.01-0.1	707.02	1160.97	0.998
Tebuconazole	0.001	0.01-0.1	3944.20	17443.29	0.995
Thiabendazole	0.001	0.01-0.1	1129.20	11593.29	0.998
Cartap hydrochloride	0.001	0.01-0.1	26.80	596.00	0.995
Imidaclothiz	0.001	0.01-0.1	147.76	1047.98	0.995
Trichlorfon	0.001	0.01-0.1	13.44	1145.31	0.998
Aldicarb	0.001	0.01-0.1	30.03	190.50	0.997
Atrazine	0.001	0.01-0.1	1115.79	7056.70	0.996
Benalaxyl	0.001	0.01-0.1	3455.30	-1762.80	0.997
Difenoconazole	0.001	0.01-0.1	11446.34	70853.65	0.995
Diniconazole	0.01	0.01-0.1	1999.69	512.80	0.995
Epoxiconazole	0.001	0.01-0.1	1858.04	1721.95	0.997
Fenazaquin	0.001	0.01-0.1	2960.42	13857.92	0.996
Fenobucarb	0.007	0.01-0.1	412.17	814.57	0.995
Hexaconazole	0.001	0.01-0.1	2590.12	754.87	0.996
Isoprocarb	0.001	0.01-0.1	601.74	3925.76	0.999
Isoproturon	0.001	0.01-0.1	8693.72	9528.81	0.998
Methamidophos	0.005	0.01-0.1	356.89	472.53	0.997
Metolcarb	0.001	0.01-0.1	753.24	4149.61	0.997
Monocrotophos	0.001	0.01-0.1	5414.28	-52628.57	0.996
Methidathion	0.001	0.01-0.1	3303.41	24236.58	0.996
Myclobutanil	0.001	0.01-0.1	2362.62	-2870.12	0.998
Penconazole	0.001	0.01-0.1	759.40	-1768.90	0.998
Piperonyl Butoxide	0.001	0.01-0.1	2504.14	7365.85	0.998
Pirimicarb	0.001	0.01-0.1	6848.78	126951.21	0.998
Prochloraz	0.001	0.01-0.1	379.56	1040.99	0.996
Propargite	0.001	0.01-0.1	580.19	-1012.19	0.997
Propiconazole	0.001	0.01-0.1	707.02	1160.97	0.998
Triadimefon	0.001	0.01-0.1	410.90	-116.15	0.997
Triadimenol	0.001	0.01-0.1	517.41	-1433.41	0.995
Pyriproxyfen	0.001	0.01-0.1	10416.79	9786.25	0.997
Quinoxifen	0.001	0.01-0.1	862.35	-540.85	0.996
Rotenone	0.002	0.01-0.1	487.72	661.67	0.999
Simazine	0.001	0.01-0.1	1214.26	-2979.26	0.998
Pymetrozine	0.001	0.01-0.1	469.58	-2014.34	0.996
Propanil	0.001	0.01-0.1	22.01	381.00	0.997

Furathiocarb	0.003	0.01-0.1	787.79	12996.61	0.996
Chlorotoluron	0.001	0.01-0.1	915.25	22354.23	0.996
Fenchlorphos	0.001	0.01-0.1	837.12	8722.05	0.995
Prometryn	0.001	0.01-0.1	2165.64	-24.93	0.996

The limit of detection a found to be from 0.001 to 0.01 mg /kg. Linearity was very good and coefficients of determination were better than 0.995 for all the selected pesticides with matrix-matched calibration standards.

### 3. Application of the Method for Real Sample

The established method was used for the residue analysis of 400 tea samples collected from different area in puer which contain 200 green tea and 200 black tea. The concentrations of pesticide residual in samples were calculated with the help of matrix-matched calibration curve. The results showed that Imidacloprid(36 % of the total no. of samples) and Acetamiprid (25 % of the total no. of samples)frequently appeared in the tea samples, The concentration ranges of residues were 0.005-0.05mg/kg (acetamiprid), 0.01–0.05 mg/kg (imidacloprid). The contents were unexceed the EU-MRLs value: imidacloprid(0.05 mg/kg)and acetamiprid(0.1 mg/kg) .

### Conclusions

In this study , a LC-MS/MS multi-residue method for the analysis of 51 pesticide residue was developed. Satisfactory accuracy (average recoveries ranged from 72 to 89 %) and precision (RSDr  $\leq$ 19 %) was found for all the analytes. For the 51 analytes linear calibrations with coefficients  $R^2 \geq 0.995$  were obtained. The limits of detection of the total pesticides were  $<0.005$  mg /kg. Thus, the proposed method can be used successfully to monitor multiple pesticide residues in tea. Finally, the analytical method was applied successfully for pesticide residue analysis of 400 tea samples collected from different region in puer. The results revealed that puer tea carry few kinds of pesticide,if the contents were unexceed the maximum residue limit. The information could be useful for policy makers, tea exporters and the public at large.

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