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Simultaneous determination of 102 pesticide residues in Chinese teas by gas chromatography–mass spectrometry

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Abstract

An efficient and sensitive method for simultaneous determination of 102 pesticide residues in teas has been established and validated. The multi-residue analysis of the pesticides in teas involved extraction with acetone–ethyl acetate–hexane, clean-up using gel permeation chromatography (GPC) and solid-phase extraction (SPE), and subsequent identification and quantification of the selected pesticides by gas chromatography–mass spectrometry (GC–MS) under retention time locked (RTL) conditions. For most of the target analytes, the optimized pretreatment processes led to no significant interference on analysis from sample matrix, and the determination of 102 compounds was achieved in about 120 min. Pesticide residues could be determined in low sub-ppb range, from 0.01 μg/mL for hexachlorobenzene to 2.5 μg/mL for propargite, with average recoveries ranging from 59.7 to 120.9% (mean 88%) and relative standard deviations (RSDs) in the range 3.0–20.8% (mean 13.7%) for all analytes across three fortification tea levels. The limits of detection (LODs) were much lower than the maximum residue levels established by the European Union (EU) legislations.

Keywords: Pesticides; Multi-residue analysis; Tea; GPC; SPE; GC–MS; Validation

1. Introduction

Tea is an old and popular beverage consumed worldwide and valued for its specific aroma and flavor as well health-promoting properties [1]. However, tea drinking can also represent a significant potential source of human exposure to pesticides and other hazardous chemicals, which are unavoidably or improperly used for protection against pests and putrescence during plant cultivation and product-manufacturing processes [2,3]. During recent years, there has been an increasing public concern and scientific investigation related to the presence and control of pesticide residues in herbal products of plant teas to assess the potential health hazards more thoroughly [3–8]. Because of high consumption rate and significant health risk of detrimental residues in teas, people from both producer and consumer countries pay more attention to tea safety.

Tea was cultivated in prehistoric times [9], and now China has the largest area of tea plantation and thus is the second largest tea exporter in the world [10,11]. However, for the time being, the fixed limits have not been assigned yet for many pesticide residues in teas, and importing countries are free to maintain or set their own different tentative limits or even establish more and more stringent maximum residue limits (MRLs) for the pesticide in teas from exporting countries [2]. For example, according to new MRLs set by European Union Commission Directive 42/2000/EC, up to 108 pesticides have been limited by maximum residue levels in tea since July 1, 2001 [12]. Another European Directive 91/414/EEC, implemented by the Plant Protection Products Regulations in 2003, limited more types of pesticides to detectable level residues in certain food samples tested. Therefore, trace-level and multi-residue analysis of pesticides in teas have become more important because of the increasing challenges from EU regulatory agencies and other tea-importing countries.

Generally, analysis of most pesticide residues is carried out in a sequence of several steps, e.g. target extraction from sample matrix, then clean-up and pre-concentration, followed by

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chromatographic separation and determination [13–15]. For the sample pretreatment, gel permeation chromatography (GPC) and solid-phase extraction (SPE) that serve as efficient methods have been widely applied for pesticide residue analysis. The capillary gas chromatography–mass spectrometry (GC–MS) has become very popular in pesticide residue analysis. It can quantify and confirm the results by its selected ion monitoring (SIM) spectra. With retention time locked gas chromatography–mass spectrometry (RTL-GC–MS), the detection selectivity is greatly improved by linking the locked retention time to the mass spectral data. It reduces the risk of false positives. Nowadays, these methods have been widely developed to analyze multi-residues in fresh vegetables, fruit, water and honey [16–31].

This work proposes a rapid, efficient and sensitive method for simultaneous determination of 102 pesticides residues, including organochlorine, organophosphorous and pyrethroid insecticides, triazine and acetanilide herbicides, and other miscellaneous pesticides in Chinese teas using SPE, GPC and RTL-GC–MS techniques. Validation of the method complied with the acceptability criteria by EU regulatory organizations for pesticide residue analysis in food samples [29]. The developed method was successfully applied for double-blind test of tea samples among different laboratories from China.

2. Experimental

2.1. Materials

Pesticide standards were purchased from Sigma (Poole, UK) and Merck (Taiwan), and were of purity >90% (w/w). Stock solution containing 102 pesticides each at a concentration of 100 μg/mL was prepared in ethyl acetate and stored at −20 °C. The working solutions were obtained daily by appropriate dilutions with *n*-hexane and stored in a refrigerator (4 °C). All the solvents (acetone, ethyl acetate, *n*-hexane and cyclohexane) were of HPLC grade. Sodium chloride and anhydrous sodium sulfate (dried at 650 °C for 4 h and stored in a desiccator) were both of analytical grade. Analytical regent grade chemicals and redistilled water were used unless otherwise specified. The tea samples used for this study were products from Hunan, Zhejiang, Jiangxi, Fujian and Guangdong provinces in China, and blank tea for preparing calibration standard and quality control (QC) samples was provided by Hunan Entry–Exit Inspection and Quarantine Bureau Technique Center, China.

2.2. RTL-capillary GC–MS

Gas chromatographic analyses were performed on a HP 6890 gas chromatograph (Agilent, Palo Alto, CA, USA) equipped with a HP 5973 mass-selective detector and retention time locking software. A HP-5 MS fused silica capillary column of 30 m × 0.20 mm I.D. and 0.25 μm film thickness from Agilent was used. Helium (purity ≥ 99.999%) was used as a carrier gas at a flow rate of 0.6 mL/min. A volume of 2 μL extract was injected in splitless mode. The injection temperature was 220 °C. The oven temperature was programmed from initial temperature 50 °C (held for 1 min) to 250 °C at 2 °C/min, and finally at 8 °C/min to 280 °C (held for 45 min). The mass spectrometer was operated with an EI source in the scan mode. The electron energy was 70 eV, and the interface temperature was maintained at 220 °C. The solvent delay was set to 10 min. Mass spectrometric confirmation was carried out in the SIM mode using the characteristic fragment ions for each pesticide. The analysis was carried out by using the SIM mode under RTL conditions. Peak location and screening of the target pesticides was performed by matching GC–MS retention times, using the RTL screener software [19].

2.3. GC–MS identification

The GC conditions were optimized to the greatest extent to separate the 102 pesticides with a single GC column. Different temperature programs, flow rates and column identity were tested and verified in order to resolve the analytes of the standard mixture during an acceptable run time. For the MS detection, the analytical parameters of the mass spectrometer detector were optimized to maximize generation of the molecular ion peak of analytes and their characteristic fragment ions. The ions were selected based on the follow principles: (1) first priority for the molecular ions; (2) fragment ions with higher molecular weight and stronger abundance; (3) characteristic ions with selectivity in distinguishing impurity, for example, 109 and 194 *m/z* for caffeine, from tea matrix; and (4) non-common peak ions for analytes with close retention times.

In GC, retention index techniques including relative retention time are routinely used with specially formulated retention index standards and in-house libraries or dedicated software database [19,32]. In our study, the RTL method has proved to offer superior precision not only within a single-instrument method, but also between inter-laboratory chromatograms reproduced from one GC to another during a long period of analysis.

Three qualifier ions were used for identification and qualitative purposes. The qualifier ions chosen for identification along with their relative abundances and the typical retention time are summarized in Table 1.

2.4. Sample preparation and clean-up

2.4.1. Sample preparation

Tea sample was chopped and homogenized. Then, 1000 g of homogenized sample was weighed into a 20 mL centrifuge tube and mixed with 5.0 mL water and 1.0 g sodium chloride. The mixture was vortexed for 30 s and allowed to stand for 30 min. After triple extraction each with 4.0 mL of acetone–ethyl acetate–*n*-hexane (1:2:1 v/v/v) for 3 min followed by centrifugation at 2500 rpm for 2 min, the organic phase was combined and dried with 1.0 g of anhydrous sodium sulfate, then filtrated and reduced to about 5 mL with nitrogen stream at 45 °C. The residual extract was diluted to 10 mL with ethyl acetate for subsequent purification in GPC.

2.4.2. GPC procedure

The diluted extract was reconstituted and further purified using a Gilson GPC system (Gilson, Villiers Le Bel, France)

Table 1
GC–MS conditions for identification and quantitation of 102 pesticides

Peak no.	Pesticide selected	Retention time (min)	Monitor ions, *m/z* (intensity %)			Peak no.	Pesticide selected	Retention time (min)	Monitor ions, m/z (intensity)		
			Quantitation	Conformation **1**	Conformation **2**				Quantitation	Conformation **1**	Conformation **2**
1	DCIP	15.20	121 (100)	77 (75)	107 (21)	52	Mecarbam	72.81	131 (100)	159 (54)	329 (17)
2	Dichlorvos	27.76	109 (100)	185 (35)	220 (6.5)	53	Procymidone	73.7	96 (100)	255 (6.8)	283 (40.6)
3	Dichlobenil	33.09	171 (100)	136 (21)	173 (63)	54	Endosulfan	73.84	339 (100)	263 (86.8)	277 (92)
4	Chlormephos	39.01	121 (100)	188 (8.6)	154 (70)	55	Triflumizole	73.92	278 (100)	179 (41)	206 (65)
5	Heptenophos	47.46	124 (100)	21 (17)	250 (14.6)	56	Butachlor	75.24	160 (72.1)	176 (100)	188 (44)
6	Tecnazene	48.29	203 (100)	215 (78.7)	261 (65.5)	57	Dieldrin	76.15	263 (100)	220 (5.5)	293 (2.7)
7	Diphenylamine	49.06	169 (100)	141 (10.6)	154 (2.4)	58	Fenamophos	76.21	303 (100)	260 (24)	288 (34)
8	Fenobucarb	49.29	121(100)	150 (28)	207 (0.5)	59	Profenofos	76.57	139 (100)	337 (88.5)	208 (90)
9	Baygon	49.60	110 (100)	137 (2.4)	152 (37.7)	60	DDT	76.72	210 (100)	105 (53)	281 (80)
10	Hexaflumuron	50.32	176 (100)	277 (38.5)	279 (23.4)	61	Myclobutanil	78.89	179 (100)	206 (23.5)	245 (17)
11	4-t-pebylphenol	52.96	205 (100)	219 (3.8)	234 (11)	62	Buprofezin	78.77	105 (100)	172 (46)	305 (8.6)
12	Bendiocarb	53.14	151 (100)	166 (43)	223 (11.6)	63	Perthane	79.24	223 (100)	165 (8.1)	178 (7.6)
13	HCH	53.4	181 (100)	109 (28.4)	219 (89)	64	Binapacryl	79.42	55 (17)	83 (100)	117 (1.1)
14	Phorate	53.50	121 (100)	97 (50)	260 (72.7)	65	Chlorobenzilate	79.84	139 (57)	111 (22.6)	251 (100)
15	Trifluralin	53.63	306 (100)	264 (69)	290 (13.5)	66	Ethion	81.37	231 (100)	153 (60)	384 (14.8)
16	Hexachloroenzene	53.88	284 (100)	142 (19.4)	249 (25.8)	67	Sulprophos	82.38	156 (81)	280 (12)	322 (100)
17	Thiometon	54.41	127(100)	192 (29)	223 (10)	68	Mepromil	82.49	119 (100)	227 (4.7)	269 (24)
18	Dimethoate	55.75	125 (57)	87 (100)	229 (18.5)	69	Triazophos	82.84	161 (100)	172 (42)	313 (10)
19	Lindane	56.81	183 (100)	111 (56)	219 (96)	70	Edifenphos	83.38	173 (100)	218 (18.6)	310 (58)
20	Carbofuran	56.66	164 (100)	149 (60)	221 (25)	71	Propiconazole	84.83	173 (100)	191 (28)	259 (70)
21	Atrazine	57.01	200 (100)	183 (0.7)	215 (53)	72	Hexazinone	85.91	171 (100)	128 (12.3)	252 (4.1)
22	Chlorbufam	57.11	127 (100)	153 (17)	223 (92)	73	Propargite	87.21	135 (100)	215 (1.8)	350 (27)
23	Fonfos	57.92	137 (100)	174 (11.8)	246 (78.7)	74	Phosmet	90.52	160 (100)	192 (2)	317 (5)
24	Terbumeton	57.66	231 (100)	153 (17.6)	186 (12)	75	Acarol;Bromopropylate	91.26	341 (71.6)	157 (100)	185 (42)
25	Propyzamid	58.66	173 (100)	145 (32)	240 (9.2)	76	EPN	91.36	157 (100)	169 (47.5)	323 (8.1)
26	Disulfoton	59.54	88 (100)	125 (15.8)	274 (23)	77	Tertramethrin	91.64	123 (28)	135 (4.4)	164 (100)
27	Diaznion	59.89	199 (41.5)	179 (100)	304 (78)	78	Methoxychlor	92.75	227 (100)	152 (7.3)	212 (5.4)
28	Chlorothalnil	60.29	266 (100)	194 (8.0)	229 (11.5)	79	Bifenthrin	93.33	181 (100)	166 (30)	197 (0.8)
29	Etrimofos	61.88	125 (100)	170 (29)	224 (17)	80	Fenpropathrin	93.95	181 (100)	152 (17.3)	208 (26.3)
30	Pirimicarb	62.31	166 (100)	138 (8.0)	238 (24)	81	Phenothrin	96.34	123 (100)	183 (64)	350 (4.7)
31	Metribuzin	63.25	198 (100)	144 (13.7)	171 (8.8)	82	Phosalone	96.93	182 (100)	154 (20)	367 (30)
32	Heptachlor	63.52	272 (100)	135 (16)	237 (16)	83	Furathiocarb	97.15	163 (100)	194 (24)	325 (11.7)
33	Acetochlor	63.58	146 (100)	162 (87)	223 (65)	84	Mefenacet	98.19	192 (100)	148 (20)	298 (6.4)
34	Methyl-chlorpyrifos	63.60	286 (100)	125 (53)	167 (0.2)	85	Fenarimol	99.13	139 (100)	219 (69)	295 (21)
35	Methyl-parathion	63.69	263 (100)	125 (60)	170 (1.8)	86	Lambda-cyhalothrin	99.80	181 (100)	197 (79)	208 (49)
36	Vinclozolin	63.82	285(100)	198 (48.9)	212 (66.4)	87	Tebufenzid e	100.35	133 (100)	105 (19)	296 (16)
37	Fenchlorphos	64.95	285 (100)	125 (9.5)	167 (3.3)	88	Pyraclofos	100.63	360 (100)	138 (50)	194 (57.7)
38	Ametryn	64.91	185 (35.5)	212 (79.3)	227 (100)	89	Bitertanol	101.40	170 (100)	212 (1)	337 (0.6)
39	Metalaxyl	65.17	206 (100)	220 (38.5)	249 (25.6)	90	Pyridaben	101.85	364 (6.2)	147 (100)	309 (5.5)
40	Prometrye	65.34	184 (100)	199 (28.5)	226 (74.5)	91	Permethrin	101.63	183 (100)	163 (24.8)	390 (0.094)
41	Fenitrothion	66.46	277 (100)	125 (39)	260 (55.7)	92	Baythroid	103.27	163 (100)	127 (22)	206 (70)
42	Aidrin	66.67	263 (100)	293 (41)	265 (10.8)	93	Cypermethrin	103.90	163 (100)	127 (23)	181 (80)
43	Methyl-pirimiphos	66.93	290 (100)	276 (81)	305 (76.6)	94	Flucythrinate	104.44	199 (100)	181 (46)	451 (28)
44	Malathion	67.87	173 (100)	125 (89)	158 (43.7)	95	Etofenprox	104.48	163 (100)	107 (45.6)	376 (25)
45	Chlorpyrifos	68.43	314 (100)	197 (64.7)	258 (39.5)	96	Silnfluofen	104.87	286 (100)	207 (18.6)	393 (3.2)
46	Parathion	68.54	291 (100)	139 (39.5)	235 (17.7)	97	Fenvalerate	105.98	181 (100)	207 (63)	225 (45)
47	Bromophos	69.74	331 (100)	125 (76)	213 (11)	98	S-fenvalerate	106.61	181 (100)	207 (63)	225 (40)
48	Chlorfenvimphos	72.37	267 (100)	295 (23.9)	323 (51.5)	99	Mavrik	106.80	250 (100)	181 (18.5)	502 (2.8)
49	Pyrifenox	71.48	262 (100)	187 (41)	294 (18.6)	100	Difenoconazole	107.09	323 (100)	230 (2.6)	265 (75)
50	Quinalphos	72.44	146 (100)	157 (61)	173 (240)	101	Deltamethrin	108.03	181 (100)	208 (28.6)	253 (61.5)
51	Methidathion	73.84	373 (100)	237 (40)	272 (33)	102	Azoxystrobin	109.21	344 (100)	388 (33)	403 (14)

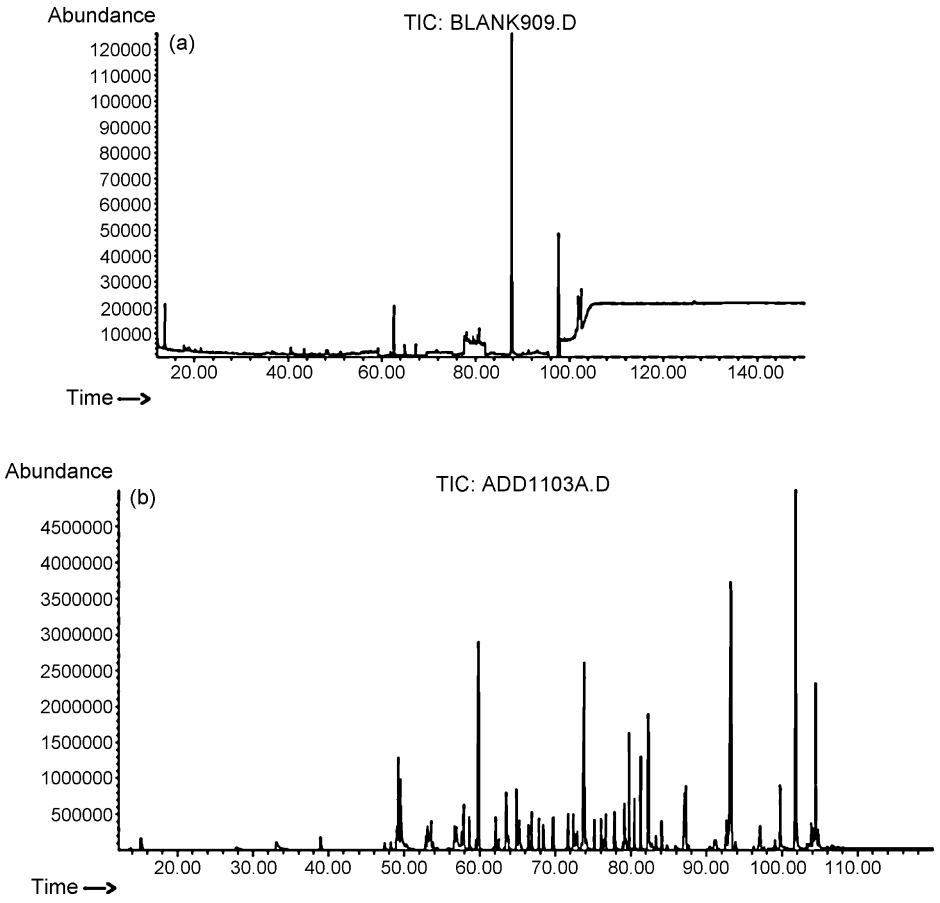

Fig. 1. (a) SIM chromatogram for a typical blank tea sample. (b) SIM chromatogram of the typical blank green tea spiked with 0.1 mg/kg of the target analyte.

equipped with a cosmosil packed column (250 × 10 mm I.D., 5 μm, 300–15,000 mesh; Nacalai Tesque, Japan). The reconstituted solution was injected into the GPC column and eluted with hexane–ethyl acetate (1:1 v/v) at a 3 mL/min flow rate. The eluent was just collected between 3–5.7 and 8–9.7 min, because there is no pesticide eluted between 5.7 and 8 min, and concentrated to about 1 mL for the SPE clean-up.

2.4.3. SPE procedure

The SPE columns used in the experiment were Supelco Envi^{TM}-Carb SPE cartridges (3 mL and 250 mg; Supelco, USA). A 1 mL of the concentrated eluent was introduced into the SPE column, which was preconditioned with 6.0 mL acetone–ethyl acetate–*n*-hexane (1:2:1 v/v/v), while the retained pesticides on the column were eluted with 6.0 mL acetone–ethyl acetate (1:2 v/v). The eluents were collected and then evaporated to dryness with nitrogen stream at 45 °C. Finally, the residue was redissolved in 0.5 mL ethyl acetate for GC–MS analysis.

3. Results and discussion

3.1. Validation procedure

Tea samples free of pesticides were used for the preparation of a blank matrix. The typical chromatogram of a blank tea sample is shown in Fig. 1a. No matrix interference GC peaks were detected in the SIM chromatograms for targeted pesticides obtained in analyses of blank tea samples from five producing areas in China, demonstrating that the method has good selectivity. The selection of the extracting solvent in sample pretreatment process with a proper polarity to match the analyte of interest were beneficial to improve process efficiency and minimize potential interferences from tea, and little matrix effect on MS detection of low level tea samples was found under the optimized extraction and chromatographic conditions (Fig. 1b).

Quantitative analysis was carried out using an external standard. The calibration curve was obtained by analyzing blank samples spiked with the pesticides at five different tea levels. The concentrations of the calibration standards were selected for each pesticide considering the MRLs established by the EU legislations. Good linearity of the MS detector response was found for all pesticides at concentrations within the test intervals, with linear regression coefficients (R^2) higher than 0.990, except for 4-*t*-pentylphenol ($R^2 > 0.910$) and Mefenacet ($R^2 > 0.905$). The signals from the chromatograms of 10 blank tea samples extracted and injected were evaluated as recommended [29] to estimate the lower limits of detection (LOD) and quantification (LLOQ). Although some MRL values were lower than the first calibration level, the LLOQ of the method is lower than EU MRL. So, we think it will not affect the determination of the pesticide residues (Table 2).

Table 2
Validation parameter 1: calibration range, correlation coefficient and LLOQ of GC–MS quantitation for 102 pesticides in tea

Peak no.	Pesticide selected	Linear range[a] (μg/mL)	Correlation coefficient (R^2)	LLOQ[b] (ug/mL)	EU MRL (mg/kg)	Peak no.	Pesticide selected	Linear range (μg/mL)	Correlation coefficient (R^2)	LLOQ (ug/mL)	EU MRL (mg/kg)
1	DCIP	0.100–2.000	0.9974	0.050	0.2	52	Mecarbam	0.202–7.000	0.9999	0.101	0.1
2	Dichlorvos	0.128–6.400	0.9931	0.064	0.1	53	Procymidone	0.119–4.950	0.9947	0.059	0.1
3	Dichlobenil	0.182–9.100	0.9999	0.091	ND[c]	54	Endosulfan	1.136–113.6	0.9998	0.568	30
4	Chlormephos	0.118–5.260	0.9998	0.053	ND	55	Triflumizole	3.050–152.7	0.9972	1.527	15
5	Heptenophos	0.128–6.400	0.9999	0.064	ND	56	Butachlor	0.128–6.400	0.9965	0.064	ND
6	Tecnazene	0.114–5.650	0.9944	0.057	0.1	57	Dieldrin	0.028–5.400	0.9997	0.014	0.02
7	Diphenylamine	0.092–5.600	0.9995	0.046	0.05	58	Fenamophos	0.132–6.100	0.9967	0.061	0.1
8	Fenobucarb	0.102–5.100	0.9982	0.051	0.05	59	Profenofos	0.104–5.200	0.9954	0.052	0.1
9	Baygon	0.104–5.200	0.9975	0.052	0.1	60	DDT	0.090–4.500	0.9988	0.045	0.2
10	Hexaflumuron	0.090–2.260	0.9946	0.045	15	61	Myclobutanil	0.268–107.0	0.9976	0.134	20
11	4-t-pebylphenol	0.103–5.150	0.9977	0.052	0.05	62	Buprofezin	0.026–2.750	0.9987	0.013	0.02
12	Bendiocarb	0.104–5.200	0.9109	0.052	ND	63	Perthane	0.095–4.750	0.9882	0.048	0.1
13	HCH	0.101–5.050	0.9989	0.051	0.2	64	Binapacryl	0.113–5.650	0.9912	0.057	0.1
14	Phorate	0.108–5.650	0.9993	0.054	0.1	65	Chlorobenzilate	0.124–12.45	0.9995	0.062	0.1
15	Trifluralin	0.109–5.450	0.9978	0.054	0.05	66	Ethion	0.500–25.00	0.9995	0.25	3
16	Hexachloroenzene	0.020–1.274	0.9981	0.0099	0.01	67	Sulprophos	1.000–50.00	0.9967	0.5	5
17	Thiometon	0.154–7.700	0.9963	0.077	0.1	68	Mepromil	0.107–5.350	0.9999	0.0535	0.06
18	Dimethoate	0.131–6.550	0.9976	0.066	0.2	69	Triazophos	0.106–6.300	0.9974	0.053	0.05
19	Lindane(β-HCH)	0.097–4.850	0.9982	0.049	0.2	70	Edifenphos	0.138–6.900	0.9970	0.069	0.1
20	Carbofuran	0.128–6.440	0.9999	0.064	0.1	71	Propiconazole	0.116–5.800	0.0004	0.058	0.1
21	Atrazine	0.106–5.300	0.9891	0.053	0.1	72	Hexazinone	0.183–9.150	0.9993	0.092	0.1
22	Chlorbufam	0.108–5.400	0.9943	0.054	0.1	73	Propargite	1.000–50.00	0.9965	2.45	5
23	Fonfos	0.128–6.400	0.9999	0.064	ND	74	Phosmet	0.115–5.950	0.9983	0.0575	ND
24	Terbumeton(Terbufos)	0.112–5.600	0.9984	0.056	ND	75	Acarol; Bromopropylate	0.087–4.350	0.9984	0.044	0.1
25	Propyzamid	0.096–7.800	0.9963	0.048	0.05	76	EPN	0.104–5.200	0.9884	0.052	0.1
26	Disulfoton	0.106–5.300	0.999	0.053	0.05	77	Tertramethrin	0.145–5.200	0.9992	0.073	ND
27	Diaznion	0.090–9.500	0.9037	0.045	0.05	78	Methoxychlor	0.130–7.250	0.9853	0.065	0.1
28	Chlorothalnil	0.105–5.250	0.997	0.053	0.1	79	Bifenthrin	0.989–24.74	0.9992	0.5	5
29	Etrimofos	0.117–5.850	0.9997	0.117	ND	80	Fenpropathrin	0.024–4.850	0.9986	0.012	0.02
30	Pirimicarb	0.103–5.150	0.995	0.052	0.05	81	Phenothrin	0.117–5.850	0.9998	0.0585	0.1
31	Metribuzin	0.206–10.30	0.9985	0.103	0.1	82	Phosalone	0.103–5.150	0.9992	0.052	0.1
32	Heptachlor	0.042–5.050	0.991	0.021	0.02	83	Furathiocarb	0.104–5.200	0.9951	0.052	0.1
33	Acetochlor	0.112–5.600	0.9058	0.056	ND	84	Mefenacet	0.114–5.700	0.9067	0.057	ND
34	Methyl-chlorpyrifos	0.098–4.900	0.9939	0.049	0.1	85	Fenarimol	0.105–5.750	0.9881	0.05	0.05
35	Methyl-parathion	0.173–10.80	0.998	0.087	0.1	86	Lambda-cyhalothrin	0.246–10.92	0.9983	0.12	15
36	Vinclozolin	0.100–5.000	0.9964	0.050	0.1	87	Tebufenzide	0.500–2500	0.999	0.25	2
37	Fenchlorphos	0.198–9.900	0.9984	0.099	0.1	88	Pyraclofos	0.106–10.60	0.9906	0.053	5
38	Ametryn	0.119–5.950	0.9998	0.0595	ND	89	Bitertanol	0.118–5.900	0.9979	0.059	0.1
39	Metalaxyl	0.104–5.200	0.9984	0.052	0.1	90	Pyridaben	2.000–100.0	0.9996	1	10
40	Prometrye	0.125–6.250	0.9997	0.0625	ND	91	Permethrin	0.094–4.690	0.9926	0.047	2
41	Fenitrothion	0.167–8.350	0.9973	0.047	0.05	92	Baythroid	0.102–6.050	0.9977	0.051	0.1
42	Aidrin	0.024–2.500	0.9994	0.012	0.01	93	Cypermethrin	0.495–24.75	0.9904	0.25	0.5
43	Methyl-pirimiphos	0.110–5.500	0.9889	0.05	0.05	94	Flucythrinate	0.112–2.800	0.9856	0.056	0.1
44	Malathion	0.124–6.150	0.9874	0.062	0.1	95	Etofenprox	0.512–25.60	0.9985	0.26	10
45	Chlorpyrifos	0.124–6.000	0.9985	0.062	ND	96	Silnfluofen	0.102–127.5	0.9987	1.275	35
46	Parathion	0.105–5.250	0.9971	0.053	0.3	97	Fenvalerate	0.060–2.980	0.9987	0.030	0.05
47	Bromophos	0.174–8.700	0.9955	0.087	0.1	98	S–fenvalerate	0.030–1.490	0.9936	0.015	0.05
48	Chlorfenvimphos	0.105–5.250	0.9999	0.0525	0.06	99	Mavrik	0.141–7.050	0.9964	0.071	0.1
49	Pyrifenox	0.112–5.600	0.9954	0.056	5	100	Difenoconazole	0.212–50.00	0.9989	0.106	10
50	Quinalphos	0.112–5.600	0.9968	0.056	0.1	101	Deltamethrin	0.106–5.300	0.9959	0.053	5
51	Methidathion	0.095–4.750	0.9957	0.048	ND	102	Azoxystrobin	0.098–4.900	0.9913	0.049	0.1

[a] Range covering tea samples with 5 different spiked levels ($n = 5$).
[b] LLOQ, lower limitation of quantification.
[c] ND, no detected level of MRL by EU regulations.

Table 3
Validation parameter 2: intra- and inter-laboratory recovery and precision of GC–MS quantitation for 102 pesticides in tea

Peak no.	Pesticide selected	Intra-lab recovery and precision									Inter-lab recovery and precision ($n = 15$ labs)					
		Spiking level 1			Spiking level 2			Spiking level 3			Spiking level 1			Spiking level 2		
		Conc. (mg/kg)	Recovery[a] (%)	RSD (%)	Conc. (mg/kg)	Recovery(%)	RSD (%)	Conc. (mg/kg)	Recovery (%)	RSD (%)	Conc. (mg/kg)	Recovery (%)	RSD (%)	Conc. (mg/kg)	Recovery (%)	RSD (%)
1	DCIP	0.05	67.2	12.0	0.10	65.1	8.9	0.50	78.8	7.6	0.050	70.00	11.7	0.250	81.16	8.60
2	Dichlorvos	0.05	86.1	9.3	0.10	100.8	3.6	2.50	77.8	8.2	0.064	85.22	8.9	1.600	85.75	3.50
3	Dichlobenil	0.05	87.2	9.0	0.10	80.0	15.5	3.50	77.9	7.6	0.091	81.80	10.5	2.280	78.40	15.40
4	Chlormephos	0.05	93.9	10.2	0.10	76.4	13.8	2.50	87.3	3.3	0.053	86.21	6.2	1.320	80.38	8.40
5	Heptenophos	0.05	122.5	7.9	0.10	136.7	3.2	3.50	98.6	7.1	0.064	101.01	8.1	1.600	89.30	14.50
6	Tecnazene	0.05	60.7	6.3	0.10	83.0	8.9	2.50	78.6	1.6	0.057	78.63	9.1	1.410	81.01	8.10
7	Diphenylamine	0.05	64.1	8.8	0.10	71.7	8.7	2.50	84.8	7.7	0.046	73.86	22.2	1.400	81.60	10.40
8	Fenobucarb	0.05	83.9	7.5	0.10	85.1	11.5	2.50	84.9	9.8	0.051	88.20	26.1	1.280	92.30	16.70
9	Baygon	0.05	91.5	6.9	0.10	107.1	10.9	2.50	107.5	10.9	0.052	80.15	13.9	1.300	83.06	8.90
10	Hexaflumuron	0.05	76.9	9.7	0.10	78.7	1.1	1.00	74.1	4.1	0.045	70.10	17.5	0.565	82.83	5.80
11	4-t-pentylphenol	0.05	60.4	13.2	0.10	66.6	10.7	2.50	90.4	3.3	0.052	70.20	12.2	1.300	84.79	12.60
12	Bendicarb	0.05	109.6	6.4	0.10	103.8	13.3	2.50	105.3	9.9	0.052	104.54	3.0	1.300	97.85	9.60
13	HCH	0.05	98.4	10.5	0.10	82.1	16.0	2.50	87.9	4.4	0.051	87.24	5.6	1.260	80.00	8.80
14	Phorate	0.05	67.1	27.7	0.10	77.4	16.7	2.50	81.7	6.3	0.054	70.88	24.0	1.410	87.23	6.20
15	Trifluralin	0.05	68.2	14.0	0.10	75.9	19.1	1.50	80.7	13.3	0.055	70.60	23.5	1.360	81.33	8.40
16	Hexachlorobenzene	0.005	62.0	8.2	0.01	65.5	7.2	0.50	76.0	6.2	0.099	65.20	9.8	0.320	81.10	5.70
17	Thiometon	0.05	69.1	7.3	0.10	76.4	6.9	3.50	79.2	3.4	0.077	70.90	9.0	1.930	85.60	4.10
18	Dimethoate	0.05	71.5	5.5	0.10	91.3	5.0	2.50	83.2	6.1	0.066	79.10	25.2	1.640	79.51	8.60
19	Lindane(β-HCH)	0.05	78.4	3.9	0.10	92.4	19.0	2.50	80.7	8.7	0.049	82.50	10.2	1.220	89.39	11.50
20	Carbofuran	0.05	114.1	10.1	0.10	93.6	5.6	3.50	109.7	8.1	0.064	106.7	3.0	1.610	107.41	6.90
21	Atrazine	0.05	96.6	7.7	0.10	93.6	8.7	2.50	104.3	6.9	0.053	97.40	4.9	1.330	96.74	10.70
22	Chlorbufam	0.05	75.2	13.3	0.10	62.2	9.0	2.50	95.6	10.8	0.054	79.20	3.2	1.350	88.30	6.10
23	Fonfos	0.05	85.6	12.1	0.10	85.5	18.4	2.50	72.0	6.0	0.064	78.67	19.9	1.600	88.10	4.20
24	Terbumeton	0.05	75.0	11.8	0.10	72.0	11.3	2.50	85.8	2.2	0.056	71.80	9.4	1.400	85.00	7.60
25	Propyzamid	0.05	106.7	3.2	0.10	105.2	6.1	3.50	93.8	11.8	0.048	120.9	13.0	2.000	100.00	8.90
26	Disulfoton	0.05	94.3	11.7	0.10	102.8	15.0	2.50	82.3	7.7	0.053	88.80	11.0	1.330	80.00	10.00
27	Diaznion	0.05	84.4	5.4	0.10	76.3	15.4	3.50	80.0	4.3	0.095	78.70	3.8	2.380	85.20	20.70
28	Chlorothalnil	0.05	101.1	6.3	0.10	109.5	12.5	2.50	92.6	6.9	0.053	93.90	6.2	1.310	95.57	6.80
29	Etrimofos	0.05	100.0	8.3	0.10	95.2	1.9	3.50	124.2	5.4	0.059	94.82	15.3	1.460	107.90	8.10
30	Pirimicarb	0.05	107.3	4.3	0.10	96.7	6.1	2.50	101.7	4.4	0.052	84.31	18.0	1.290	91.33	11.10
31	Metribuzin	0.05	89.3	5.4	0.10	97.2	2.2	5.00	102.1	2.6	0.103	93.37	8.9	2.580	93.31	4.60
32	Heptachlor	0.01	71.3	5.7	0.05	73.1	8.1	2.50	89.7	3.8	0.021	79.21	12.2	1.260	87.86	12.50
33	Acetochlor	0.05	77.5	6.4	0.10	81.2	3.8	5.00	88.1	7.4	0.056	83.80	11.9	3.650	88.86	6.10
34	Methyl-chlorpyrifos	0.05	76.3	10.3	0.10	62.8	13.1	2.50	72.0	1.7	0.049	81.67	11.4	1.230	79.10	12.40
35	Methyl-parathion	0.05	65.0	7.4	0.10	74.8	6.5	5.00	88.0	3.7	0.087	70.36	16.7	2.700	83.29	5.90
36	Vinclozolin	0.05	82.0	6.8	0.10	68.8	4.6	2.50	83.3	5.7	0.050	92.92	11.3	1.250	92.02	20.20
37	Fenchlorphos	0.05	68.1	8.9	0.10	73.7	9.7	3.50	70.4	6.4	0.099	78.05	11.7	2.480	83.39	7.50
38	Ametryn	0.05	80.0	7.7	0.10	103.9	14.2	2.50	100.4	11.2	0.062	99.64	20.4	1.490	97.40	20.40
39	Metalaxyl	0.05	98.1	9.5	0.10	95.8	13.4	2.50	105.6	10.2	0.052	84.80	15.9	1.300	101.98	15.40
40	Prometrye	0.05	77.5	6.2	0.10	86.9	4.1	2.50	99.1	5.0	0.063	73.54	14.8	1.560	77.38	16.80
41	Fenitrothion	0.05	122.4	6.2	0.10	111.0	6.9	3.50	97.5	8.3	0.084	110.84	18.1	2.090	89.57	14.30
42	Aldrin	0.05	66.7	6.3	0.10	73.2	11.3	3.50	82.9	3.6	0.012	75.31	15.1	2.900	82.39	15.20
43	Methyl-pirimiphos	0.05	85.1	5.8	0.10	63.3	7.6	2.50	81.3	4.2	0.051	68.62	17.0	1.380	81.41	14.00
44	Malathion	0.05	105.5	10.4	0.10	114.7	9.9	2.50	89.3	8.2	0.062	87.15	5.8	1.540	101.08	8.00
45	Chlorpyrifos	0.05	63.9	10.5	0.10	67.1	11.5	2.50	83.3	4.9	0.062	74.48	13.8	1.500	82.75	9.50
46	Parathion	0.05	84.9	6.8	0.10	82.5	11.8	2.50	76.1	5.6	0.053	90.26	23.4	1.310	97.27	11.20
47	Bromophos	0.05	90.1	2.9	0.10	84.8	3.1	3.50	84.3	4.3	0.087	98.90	5.9	2.180	95.41	8.40
48	Chlorfenvimphos	0.05	83.4	7.6	0.10	92.0	13.6	2.50	93.4	4.3	0.053	76.63	19.0	1.310	102.24	4.50
49	Pyrifenox	0.05	111.8	8.9	0.10	125.4	3.0	2.50	93.0	7.6	0.056	97.42	21.4	1.400	88.76	8.50
50	Quinalphos	0.05	80.4	8.2	0.10	185.7	11.4	2.50	84.3	6.1	0.056	72.38	22.0	1.400	86.43	9.60
51	Methidathion	0.05	75.4	9.2	0.10	76.5	13.2	4.50	95.5	4.3	0.048	78.29	8.4	2.400	76.20	19.20
52	Mecarbam	0.05	86.8	11.3	0.10	74.6	9.9	4.50	85.4	8.2	0.101	99.50	8.5	2.780	90.19	13.80
53	Procymidone	0.05	127.5	5.9	0.10	112.4	5.7	2.50	97.1	11.6	0.059	110.40	11.3	1.490	81.58	13.70
54	Endosulfan	0.50	73.7	9.9	1.00	101.7	12.7	45.0	78.2	5.2	0.568	75.34	11.3	28.400	80.00	15.00
55	Triflumizole	1.00	89.9	7.6	2.00	61.3	14.0	60.00	80.7	4.2	1.530	72.74	8.5	38.200	81.79	9.70
56	Butachlor	0.05	71.0	7.8	0.10	73.7	5.2	2.50	77.7	6.7	0.064	68.33	14.6	1.600	80.88	3.60
57	Dieldrin	0.01	75.2	6.3	0.05	78.9	5.6	2.50	78.3	6.2	0.014	72.24	6.6	1.350	80.20	8.40
58	Fenamophos	0.05	95.7	12.6	0.10	132.1	7.0	3.50	113.2	8.9	0.061	117.20	15.5	1.530	118.78	4.90

Table 3 (*Continued.*)

Peak no.	Pesticide selected	Intra-lab recovery and precision									Inter-lab recovery and precision ($n = 15$ labs)					
		Spiking level 1			Spiking level 2			Spiking level 3			Spiking level 1			Spiking level 2		
		Conc. (mg/kg)	Recovery[a] (%)	RSD (%)	Conc. (mg/kg)	Recovery(%)	RSD (%)	Conc. (mg/kg)	Recovery (%)	RSD (%)	Conc. (mg/kg)	Recovery (%)	RSD (%)	Conc. (mg/kg)	Recovery (%)	RSD (%)
59	Profenofos	0.05	77.3	8.4	0.10	114.6	10.5	2.50	85.6	8.8	0.050	86.92	6.4	1.300	83.63	6.20
60	DDT	0.05	99.6	7.6	0.10	74.4	5.9	2.50	80.1	6.5	0.045	87.11	11.7	1.130	81.70	2.30
61	Myclobutanil	0.10	109.7	4.3	0.25	95.7	9.5	50.0	101.9	7.0	0.134	108.60	6.2	26.80	91.54	8.60
62	Buprofezin	0.01	80.0	5.3	0.05	77.7	8.1	1.00	73.1	5.5	0.013	78.49	10.4	1.280	80.95	5.20
63	Perthane	0.05	73.5	9.0	0.10	69.6	3.4	1.00	80.0	9.8	0.055	84.80	12.2	0.690	76.70	3.70
64	Binapacryl	0.05	84.2	10.4	0.10	82.3	5.4	2.50	94.4	7.8	0.057	93.77	16.4	1.410	95.70	9.10
65	Chlorbenzilate	0.05	74.2	11.8	0.10	81.9	8.6	5.00	83.1	5.4	0.062	84.89	13.8	3.110	88.72	5.50
66	Ethion	0.25	80.7	6.9	0..50	77.1	10.7	10.00	84.9	10.9	0.250	82.56	8.0	6.250	80.20	9.90
67	Sulprophos	0.50	89.1	8.9	1.00	86.7	10.7	25.00	83.5	3.7	0.500	86.71	12.1	12.50	80.00	10.40
68	Mepromil	0.05	122.2	6.9	0.10	86.7	14.5	2.50	99.2	7.5	0.054	114.20	23.0	1.340	96.00	7.40
69	Triazophos	0.05	101.6	11.4	0.10	108.5	8.5	2.50	88.0	8.1	0.053	105.84	19.3	1.580	85.11	10.70
70	Edifenphos	0.05	95.1	6.5	0.10	96.1	3.4	3.50	95.2	7.6	0.069	92.77	14.1	1.730	91.80	11.80
71	Propiconazole	0.05	96.6	8.7	0.10	91.6	4.6	2.50	85.5	3.2	0.058	90.30	25.1	1.450	91.50	10.40
72	Hexazinone	0.10	111.7	7.7	0.10	91.7	4.0	4.50	92.8	5.6	0.092	94.83	18.1	2.300	90.10	6.10
73	Propargite	1.50	68.8	3.2	2.50	70.50	6.4	25.00	71.8	4.4	2.450	70.29	5.4	12.300	85.88	5.80
74	Phosmet	0.05	121.6	5.3	0.10	105.5	6.0	3.00	99.9	6.4	0.060	106.20	14.4	1.490	89.98	12.70
75	Bromopropylate	0.05	86.8	5.0	0.10	92.1	5.6	2.00	90.9	6.3	0.044	81.40	20.0	1.090	90.90	16.20
76	EPN	0.05	82.7	5.7	0.10	93.3	5.9	2.00	81.1	6.0	0.052	79.90	15.6	1.300	83.93	8.50
77	Tertramethrin	0.05	77.7	13.3	0.10	80.5	5.8	2.50	83.4	5.3	0.052	70.01	24.0	1.300	82.41.	15.90
78	Methoxychlor	0.05	80.0	7.9	0.10	91.7	2.8	3.00	81.4	5.2	0.073	87.40	6.9	1.810	88.47	5.00
79	Bifenthrin	0.05	70.0	6.4	0.10	73.1	3.5	10.00	89.8	5.1	0.050	80.81	15.9	6.190	80.60	17.20
80	Fenpropathrin	0.01	78.3	5.8	0.05	76.7	9.9	2.00	75.5	5.3	0.012	81.30	7.9	1.210	83.37	11.00
81	Phenothrin	0.05	89.2	2.9	0.10	71.4	13.3	2.50	73.4	5.9	0.059	87.06	11.7	1.460	88.45	10.30
82	Phosalone	0.05	100.4	11.6	0.10	90.5	8.2	2.50	88.4	7.6	0.052	100.6	12.3	1.290	91.70	12.60
83	Furathiocarb	0.05	89.6	9.7	0.10	91.5	8.4	2.5	80.0	6.0	0.052	78.50	15.5	1.300	85.18	12.20
84	Mefenacet	0.05	77.9	7.6	0.10	71.4	7.3	2.5	86.2	6.1	0.057	81.90	8.1	1.430	84.82	13.00
85	Fenarimol	0.05	98.5	7.1	0.10	96.4	6.6	2.5	98.2	4.5	0.053	113.2	11.4	1.440	82.92	15.30
86	Lambda-cyhalothrin	0.10	78.0	10.4	0.20	79.8	10.2	4.00	73.1	6.7	0.123	77.50	12.9	2.730	90.60	8.70
87	Tebufenzide	0.20	90.6	6.5	0.50	100.0	6.5	10.0	80.9	3.9	0.250	82.90	8.6	6.250	85.50	4.70
88	Pyraclofos	0.05	99.2	5.6	0.10	106.8	12.2	5.00	112.4	11.9	0.053	73.96	22.2	2.650	88.90	13.10
89	Bitertanol	0.05	85.4	5.7	0.10	80.8	9.10	2.50	83.9	5.5	0.059	87.21	9.0	1.480	85.63	5.00
90	Pyridaben	0.10	68.3	5.6	1.50	69.7	9.8	40.0	84.8	3.5	0.256	85.23	6.0	25.00	86.77	8.10
91	Permethrin	0.05	71.5	8.3	0.10	71.0	8.8	2.00	83.4	2.4	0.047	76.60	20.5	1.170	83.71	8.30
92	Baythroid	0.05	89.4	8.4	0.10	81.5	12.5	2.50	82.2	6.6	0.051	89.60	8.5	1.510	83.58	8.80
93	Cypermethrin	0.20	81.8	5.5	0.50	85.9	14.0	10.00	75.0	4.9	0.248	78.06	9.7	6.190	82.65	8.80
94	Flucythrinate	0.05	76.8	3.7	0.10	72.7	7.2	1.00	83.3	4.9	0.056	65.36	8.7	0.700	84.67	11.80
95	Etofenprox	0.10	68.3	12.4	0.35	68.4	14.0	10.0	78.4	6.9	0.256	76.40	14.4	6.400	75.67	7.90
96	Silnfluofen	1.00	71.1	6.2	2.00	77.4	8.6	55.0	86.7	3.1	1.280	82.03	10.1	31.90	81.09	6.10
97	Fenvalerate	0.02	73.3	7.2	0.05	76.7	5.5	1.00	80.9	2.8	0.030	83.02	9.6	0.745	89.52	5.50
98	S-fenvalerate	0.01	81.3	12.2	0.02	72.4	4.8	0.50	82.3	5.7	0.015	82.21	11.7	0.372	86.42	11.90
99	Mavrik	0.05	83.1	9.0	0.10	72.9	12.6	2.50	73.7	4.6	0.071	81.90	6.7	1.760	77.72	15.10
100	Difenoconazole	0.50	75.4	7.9	1.00	99.6	6.5	20.0	95.8	24.0	0.500	80.19	10.8	10.60	85.50	11.10
101	Deltamethrin	0.10	83.0	8.5	0.20	81.1	9.6	2.50	84.6	6.7	0.088	111.80	13.9	2.650	88.90	10.00
102	Azoxystrobin	0.05	87.8	12.2	0.10	101.8	10.9	2.50	120.0	7.3	0.053	86.20	30.8	1.230	93.10	12.30

[a] covering tea samples with 3 different spiked levels ($n = 5$).

Analysis validation was evaluated by establishing the precision and recovery of the analysis on quality control samples in two separate performances: within-laboratory (intra-lab) and between-laboratory (inter-lab) analyses. The precision represents an estimate of the variability of measurements and the reproducibility of the test method, and the recovery test for each pesticide at different fortified levels was carried out to assess the accuracy of the presented method. Intra-lab precision and single-laboratory recovery were examined using a single calibration curve for the three different QC samples, while the inter-lab variability and multi-laboratory recovery were tested for each QC level in three different laboratories using multi-laboratory calibration curves constructed in different equipment, operators and laboratory environments. Every spiking level was repeated five times. The precision of the method was described as the value of relative standard deviation (RSD, the standard deviation as a percentage of the mean calculated concentration), and the recovery of the assay was calculated from the percentage of the mean calculated concentration to the nominal spiking value. The concentration of the different spiking levels, average recovery data and RSD values obtained are shown in Table 3. Recoveries of the analytes ranged from 60.7 to 136.7%. Repeatability of peak areas for all pesticides expressed as RSD was in the range of 3.0–30.8%. Table 3 shows that the intra- and inter-lab recovery and precision of the multi-residual analysis method were quite good for almost of the test pesticides. The stabilities of the targeted analytes in stock solution and QC samples were evaluated, and the analytes were all acceptably stable under the tea sample analysis conditions.

3.2. Application to tea samples

In the method development and validation, the proposed method was proven to show sensitive and robust determination of almost all of the analytes for spiked tea samples at very low levels, e.g. 0.1 mg/kg matrix-matched standard from a green tea sample (Fig. 1b), even for a spiked tea sample from an intra- and inter-laboratory comparison test for pesticide residue analysis (Table 3). Validation parameters of the method are presented in terms of specificity, linearity, LLOQ, recovery, precision and stability, which comply with the acceptability of validation criteria by EU regulatory organizations for pesticide residue analysis in food samples [29].

The applicability of the proposed method was also assessed for the analysis of 3042 real tea samples including 1532 green teas, 620 black teas, 727 oo-long teas and 163 flower teas. From the analytical results, the pesticide residues which frequently appeared in tea included fenvalerate, cypermethrin, fenpropathrin, buprofezin, triazophos, etc. The concentration ranges of residues were 0.050–0.250 (fenvalerate), 0.010–0.050 (cypermethrin), 0.030–0.300 (fenpropathrin), 0.060–0.250 (buprofezin) and 0.020–0.200 mg/kg (triazophos), respectively. Within different type of teas, pesticide residues were found most frequently in the oo-long teas and flower teas. The frequency of concentration of fenvalerate residue, which is higher than EU MRL, is 73.4% in the oo-long teas and 52.3% in the flower teas. The frequency of concentration of fenpropathrin residue, which is higher than EU MRL, is 57.6% in the oo-long teas and 30.2% in the flower teas. In green teas and black teas, there was a low frequency of pesticide residues correspondingly. The frequency of concentration of fenpropathrin residue, which is higher than EU MRL, is 16.4% in the green teas and 22.7% in the black teas. 82.3% of the disqualification tea samples were made from small or private tea corporations.

In its application to blind tea tests organized by the National Entry–Exit Inspection and Quarantine Bureau of China in 2003, 2005, the developed method has successfully analyzed and evaluated the pesticide residues in all of the disqualification tea samples. The proficiency testing of the method was accomplished in practical applications to interlaboratory comparisons (including 15 laboratories) with robust statistical analysis. RSD of determination concentration of fenvalerate, cypermethrin, fenpropathrin, buprofezin and triazophos in the samples was 1.32–12.5%, 3.2–5.8%, 4.7–13.2%, 7.8–13.9%, 5.4–24.7%, respectively. These satisfactory test results confirm the feasibility of the proposed method, which can be easily implemented in laboratories for routine testing and monitoring of pesticides residues in tea samples.

4. Conclusions

A multi-residue analysis method based on RTL-GC–MS for robust and sensitive identification and determination of 102 pesticides in Chinese teas has been demonstrated in this work. The liquid–liquid extraction using a mixture of acetone–ethyl acetate–hexane was optimized as the typical solvent for extracting multi-class pesticides from tea samples. With further clean-up by GPC and SPE, the pretreatment provides high extraction efficiency and low matrix effects, thus allowing adaptation of this sensitive and selective method for routine multi-residue analysis of pesticides in various tea matrices. The quality-assurance evaluation procedure complied with the acceptability of validation criteria by EU regulatory organizations for pesticide residue analysis in food samples. The method described here was found to have good practicability for routine residue analysis of pesticides in various herbal tea matrices.

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