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气相色谱-飞行时间质谱法测定食用植物油中 197 种农药残留

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摘要：建立了气相色谱-飞行时间质谱（GC-TOF-MS）同时测定食用植物油中 197 种农药残留的方法。样品经乙腈超声提取，冷冻除脂，C18 和 PSA 吸附剂共同净化；目标物经 HP-5MS UI 毛细管柱（30 m×0.25 mm×0.25 μm）分离，电子轰击源电离，全扫描模式采集质谱信息；MassHunter 软件对数据进行定性与定量分析，设置精确质量数偏差为±5×10^{-5}，保留时间偏差为±0.1 min。实验考察了基质效应情况和方法学性能。结果表明，大多数农药表现出基质增强效应，需采用基质标准工作溶液进行定量。在优化的条件下，174 种农药定量限可以达到 0.01 mg/kg，占全部被测农药的 88%，另外 23 种农药的定量限为 0.025～0.1 mg/kg。除联苯的线性范围为 2～100 μg/L 外，其余农药的线性范围均为定量限～200 μg/L，相关系数（R^2）均大于 0.99。在 3 个添加水平（0.1、0.25 和 0.5 mg/kg）下，有 156 种农药的回收率为 70%～120%，占全部被测农药的 79%，有 185 种农药的相对标准偏差<10%，占全部被测农药的 94%。应用该方法对 23 份市售植物油样品进行了检测，结果在 12 个样品中检出 13 种农药。该方法操作简便，一次进样即可实现近 200 种农药的同时检测，且检测结果的准确度和灵敏度良好，适用于食用植物油中 197 种农药残留的快速检测。

关键词：气相色谱-飞行时间质谱；农药残留；植物油
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Determination of 197 pesticide residues in edible vegetable oil by gas chromatography-time-of-flight mass spectrometry

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Abstract: An analysis method based on gas chromatography-time-of-flight mass spectrometry (GC-TOF-MS) with single acquisition was established for the simultaneous rapid screening and accurate confirmation of 197 pesticide residues in edible vegetable oil. First, a standard library of the 197 pesticides was established. The library contained GC-TOF-MS information such as retention time, accurate mass measurements of quantitative and quantitative ions, and ratio of the qualitative ion. According to the European Union regulation (SANTE/11945/2015), the standard for qualitative determination by HRMS was determined; that is, each compound was confirmed by at least two ions. Second, the instrument conditions and sample pretreatment conditions for the determination of different pesticides were optimized. The following observations were made: the extraction efficiency of acetonitrile was better than that of acetonitrile containing 0.1% formic acid because pesticide recovery in the former case was in the range of 70%−120%; C18 and PSA adsorbents exerted a better purification effect than did the other two purification materials (C18 and Z-Sep adsorbent or PRiME HLB column), thus ensuring good recovery of the target compounds; most pesticides showed a matrix enhancement effect, necessitating the use of a matrix-matched external calibration method for quantitation. Finally, based on the above findings, the experimental procedure was established. The edible vegetable oil samples were ultrasonically extracted with acetonitrile, and the resultant solution was

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subjected ot fat removal by freezing at −20 ℃ for 2 h. The supernatant (1.0 mL) was cleaned-up by dispersive solid phase extraction using 50 mg C18 and 50 mg PSA powder. The compounds were separated on an HP-5MS UI capillary column (30 m×0.25 mm×0.25 μm) and ionized using an electron impact ion source. Qualitative and quantitative detection of the pesticides was completed in full scan mode. The retention time, mass accuracy, and qualitative ion matching ratio were used for qualitative screening, while the peak areas of the quantitative ion were used for quantification. The limits of quantification (LOQs) of 174 pesticides were 0.01 mg/kg, and the LOQs of the other 23 pesticides ranged from 0.025 to 0.1 mg/kg. The linear ranges were LOQs to 200 μg/L for 196 pesticides, and from 2 to 100 μg/L for biphenyl, with the correlation coefficients being greater than 0.99. The recoveries of 156 pesticides were in the range of 70% to 120% at three spiked levels (0.1, 0.25, and 0.5 mg/kg), accounting for 79% of the total pesticides. The proposed method was successfully applied to the determination of pesticide residues in 23 edible vegetable oil samples. Chlorpyrifos was detected in all six peanut oil samples. Bromopropylate, fenpropathrin, oxadiazon, permethrin, tebufenpyrad, cyproconazole and pirimiphos-methyl were detected in a fourth-grade rapeseed oil sample. The results demonstrate that the developed method is accurate, reliable, and time-saving. It can be used for the high-throughput screening and quantitative determination of pesticide residues in edible vegetable oil.

Key words: gas chromatography-time-of-flight mass spectrometry (GC-TOF-MS); pesticide residues; vegetable oil

农药因具有防治病虫害的功效,在现代农业中发挥着重要作用。然而,因为不合理的使用,农药残留问题严重威胁着消费者的健康。相比水果蔬菜,植物油中的农药残留问题被关注的较少,同时由于基质的复杂性,食用植物油检测方法的报道也较少。

油脂基质会对农药残留的分析产生很大干扰[1],同时会对仪器造成污染;部分有机氯和菊酯类农药具有较强的亲脂性,难与油脂分离。如何有效去除油脂,并最大程度保证亲脂性农药的回收,成为植物油中农药残留检测的难点。传统除去油脂的方法有浓硫酸磺化法[2]和凝胶柱色谱净化法[3,4],浓硫酸磺化法需要使用强酸,不适用于对酸不稳定农药的检测,另外操作相对复杂,产生的废弃物需要经过处理才能丢弃。凝胶柱色谱净化法虽然可以实现自动化,但是净化时间较长,且要消耗大量有机溶液,不符合环保需求。基质固相分散(MSPD)技术[5]与固相萃取(SPE)技术也被用于植物油中农药残留的前处理,其中固相萃取技术常用的萃取柱有弗罗里硅土柱[6]、C18 与乙二胺-*N*-丙基硅烷(PSA)串联柱[7]、PRiME HLB 柱[8]等,近期有文献[9]报道使用自行填装的多壁碳纳米管(MWCNTs)柱进行茶油中氨基甲酸酯类农药检测,该柱可被重复利用。QuEChERS 方法因为简单快速、重复性好等优点[10],越来越受到人们的重视。QuEChERS 方法需要针对基质的不同选择去除干扰物质的吸附剂,常见的吸附剂有 C18、PSA、GCB,以及近几年开始使用的硅胶键合氧化锆(Z-Sep)及 C18 与氧化锆共同键合物(Z-Sep+)[11,12]。在实际检测中,可将其中几种进行混合使用,以获得最佳的净化效果,如 C18 和 PSA 组合[13]、PSA、GCB、C18 组合[14]和 Z-Sep+、C18[15]组合。

农药残留检测常见的检测方法有气相色谱法、气相色谱-质谱法和液相色谱-串联质谱法[16]。气相色谱法通常采用的电子捕获检测器与火焰光度检测

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器的选择性及抗基质干扰能力不如质谱,且无法同时检测有机磷和有机氯农药。液相色谱-串联质谱法可以很好地排除干扰,获得理想的定量定性准确度,但是对于有机氯、拟除虫菊酯和部分有机磷农药,液相色谱-串联质谱法不能获得很好的灵敏度。与气相色谱-质谱法相比,近几年越来越普及的气相色谱-串联质谱法结合多反应监测(MRM)模式具有更好的排除干扰能力[17]。

近些年农药残留检测越来越注重检测通量,需一次进样对少则几十种,多至上百种的农药同时进行检测。串联质谱结合多反应监测模式对每个离子对的监测均需要一定的驻留时间,监测的化合物越多,总的驻留时间就越长,最终导致无法在一个色谱峰上获得足够的采集点数,无法进行准确定量。虽然采取分段采集的方法可以解决这个问题,但过多的分段无疑增加了方法建立的难度,并增加了因色谱峰漂移导致没有被采集的风险。飞行时间质谱仪采用全扫描的方式获取精确质量信息,其采集速度快,有效避免了上述问题,特别适合农药残留的高通量检测[18-20]。

本研究优化了提取与净化方法,并结合气相色谱-飞行时间质谱技术,建立了植物油中 197 种农药残留的检测方法。本方法前处理简便有效,检测通量高,且具有较高的灵敏度与准确性,可以为植物油安全监管提供技术支撑。

1　实验部分

1.1　仪器、试剂与材料

7890B-7250 气相色谱-飞行时间质谱联用仪(美国 Agilent 公司); Vortex-Genie 2 涡旋混匀器(美国 Scientific Industries 公司);超声波清洗器(英国 Prima 公司); Allegra X-15R 台式冷冻离心机(美国 Beckman 公司)。

乙腈(色谱纯,德国 Merck 公司);甲酸(色谱纯,德国 Fluka 公司); C18 粉末、PSA 粉末(中国 CNW 公司); Z-Sep 粉末(美国 Supelco 公司); PRiME HLB 柱(3 mL/60 mg,美国 Waters 公司);混合标准溶液(质量浓度为 100 mg/L)购于美国 O2Si 公司,标准物质购于德国 Dr. Ehrenstorfer 公司。花生油、橄榄油、大豆油、菜籽油与芝麻油购于武汉市场。

1.2　样品前处理

提取:准确称取 2 g 植物油样品,加入 10.0 mL 乙腈,涡旋混合 1 min,超声提取 30 min,提取液于 −20 ℃放置 2 h,以 4 000 r/min 离心 10 min,取乙腈层,待净化。

净化:将 1.0 mL 上述待净化液加入含 50 mg C18 和 50 mg PSA 粉末的离心管中,涡旋 1 min,以 4 000 r/min 离心 5 min,取上层清液过 0.22 μm 有机滤膜,待上机。

1.3　标准溶液的配制

标准物质用乙腈配制成质量浓度为 100 mg/L 的标准溶液,并与 1.1 节所述购买的混合标准溶液混合,用乙腈稀释得到质量浓度为 5 mg/L 的混合标准储备溶液。

混合标准储备溶液用经 1.2 节处理的空白植物油待测液稀释,配制成质量浓度为 2、5、10、20、50、100 和 200 ng/mL 的基质标准溶液。

1.4　分析条件

1.4.1　色谱条件

色谱柱:HP-5MS UI 柱(30 m×0.25 mm×0.25 μm);进样口温度:300 ℃,进样模式:不分流进样;载气:氦气(纯度 > 99.999%);载气流速:1.2 mL/min;升温程序:初始温度 60 ℃,保持 1min,以 40 ℃/min 升温至 170 ℃,再以 10 ℃/min 升温至 310 ℃,保持 3 min。进样量:1 μL。

1.4.2　质谱条件

电离模式:电子轰击(EI)源;离子源温度:300 ℃;传输线温度:300 ℃;电离电压:70 eV;检测模式:全扫描(m/z 50~500)。

1.4.3　数据处理

采用仪器自带 MassHunter 软件进行处理,每个化合物选择一个响应较好且无明显干扰的离子用于定量,再选择两个离子用于定性,选择的定量与定性离子见表 1。定性与定量离子的精确质量数偏差范围设置为±5×10^{-5}(50 ppm),化合物保留时间偏差范围设置为±0.1 min。

2　结果与讨论

2.1　色谱条件的优化

弱极性 HP-5 毛细管柱与中等级性的 HP-1701 毛细管柱是农药残留分析中最普遍使用的两种色谱柱。HP-1701 毛细管柱对较强极性的有机磷化合物分离效果较好,但因其最高使用温度较低,不适用于部分高沸点菊酯类及唑类农药的分析。HP-5 毛细管柱在分析极性较强化合物时易出现拖尾情况,故选择具有超高惰性的 HP-5MS UI 毛细管柱,以减少

表 1 食用植物油中 197 种农药的保留时间、定量离子、定性离子、检出限、定量限、加标回收率与相对标准偏差($n=6$)

Table 1 Retention times, quantitative ions, qualitative ions, LODs, LOQs, spiked recoveries and RSDs of the 197 pesticides in edible vegetable oil ($n=6$)

Pesticide	t_R/min	Quantitative ion (m/z)	Qualitative ions (m/z)	LOD/(mg/kg)	LOQ/(mg/kg)	0.1 mg/kg		0.25 mg/kg		0.5 mg/kg	
						Recovery/%	RSD/%	Recovery/%	RSD/%	Recovery/%	RSD/%
Ethiolate	4.45	100.0756	118.0685, 161.0868	0.005	0.01	40.51	8.00	39.92	18.93	43.55	33.35
Carbofuran	4.96	164.0831	131.0491, 149.0597	0.005	0.01	99.01	6.47	99.16	17.87	93.49	10.97
Dichlorobenzonitrile	5.24	170.9637	135.9948, 172.9608	0.005	0.01	55.43	5.61	57.35	11.45	56.46	15.39
Biphenyl	5.42	154.0777	152.0620, 153.0698	0.005	0.01	35.93	7.81	46.69	13.58	52.66	13.63
Etridiazole	5.83	210.9494	182.9181, 212.9464	0.005	0.01	47.54	5.78	59.39	11.53	59.6	15.92
Formothion	6.06	124.9820	93.0099, 142.9926	0.005	0.01	71.31	4.47	72.25	3.77	69.39	6.81
Methacrifos	6.06	207.9953	180.0004, 240.0215	0.005	0.01	68.25	3.67	75.42	4.10	74.47	6.91
Chloroneb	6.13	190.9661	192.9632, 205.9895	0.005	0.01	65.33	3.49	70.63	4.29	67.33	5.15
δ-Hexachlorocyolohexane (δ-BHC)	6.37	218.9110	180.9373, 182.9343	0.005	0.01	74.01	4.36	80.13	2.72	75.07	2.98
Molinate	6.38	126.0913	98.0964, 187.1025	0.005	0.01	61.19	3.24	68.76	4.40	68.01	6.56
Thionazine	6.81	143.0004	174.9725, 191.9749	0.0125	0.025	80.96	2.80	79.58	4.14	74.09	5.10
Tecnazene	6.88	260.8726	202.8797, 214.8797	0.0125	0.025	56.26	3.10	66.27	5.73	62.86	5.63
Diphenylamine	6.95	169.0886	167.0729, 168.0807	0.005	0.01	57.86	9.90	67.73	11.99	64.98	4.34
Ethoprophos	7.02	157.9619	138.9977, 200.0089	0.005	0.01	79.20	2.06	83.94	3.25	78.97	3.32
Cycloate	7.04	154.1226	83.0855, 186.0947	0.025	0.05	61.80	2.52	68.26	3.96	69.88	4.42
Chlorpropham	7.10	127.0183	171.0081, 213.0551	0.005	0.01	74.44	2.20	77.69	2.64	76.42	3.13
Ethalfluralin	7.13	316.0903	276.0590, 292.0539	0.005	0.01	72.42	3.98	80.24	5.66	76.29	2.53
Atrazine-desethyl	7.20	172.0384	174.0355, 187.0619	0.005	0.01	80.97	3.14	84.22	3.55	81.23	2.68
Trifluralin	7.23	306.0696	206.0297, 264.0226	0.025	0.05	75.25	2.28	81.72	3.48	78.54	3.23
Benfluralin	7.27	292.0539	264.0226, 318.1059	0.005	0.01	72.62	3.67	81.33	3.59	78.03	2.78
Sulfotep	7.37	322.0221	265.9595, 293.9908	0.005	0.01	77.47	1.70	83.02	3.53	80.36	3.78
Cadusafos	7.49	158.9697	157.9619, 213.0167	0.005	0.01	80.33	2.38	83.66	2.79	81.56	3.07
Phorate	7.49	230.9731	75.0263, 121.0412	0.005	0.01	56.13	7.53	58.65	16.22	56.10	22.58
α-Hexachlorocyolohexane (α-BHC)	7.63	218.9110	180.9373, 182.9343	0.005	0.01	73.10	2.59	77.47	3.12	73.26	3.44
Dimethipin	7.76	118.0083	75.9977, 90.0133	0.005	0.01	88.84	3.75	92.90	2.39	88.04	4.65
Hexachlorobenzene	7.76	283.8096	281.8125, 285.8067	0.005	0.01	33.82	3.55	37.14	5.29	39.49	3.17
Dichloran	7.79	205.9644	175.9664, 207.9615	0.005	0.01	72.44	5.63	83.38	2.66	74.42	3.69
Dimethoate	7.79	124.9820	142.9926, 228.9990	0.005	0.01	92.00	3.17	90.95	3.25	85.47	2.28
Simazine	7.81	201.0775	186.0540, 203.0748	0.005	0.01	81.09	3.47	85.66	2.96	81.73	3.02
Atrazine	7.88	200.0697	202.0697, 215.0932	0.005	0.01	78.25	3.16	83.09	3.88	78.25	2.01
Monolinuron	7.93	152.9975	125.0025, 154.9948	0.005	0.01	74.40	5.13	83.53	5.15	78.89	2.88
Propazine	7.95	214.0854	187.0619, 229.1088	0.005	0.01	73.89	2.99	84.03	3.63	80.93	2.72
Clomazone	7.98	204.1019	125.0152, 127.0123	0.005	0.01	77.45	3.52	81.66	3.26	77.75	3.78

表 1 （续）
Table （Continued）

Pesticide	t_R/min	Quantitative ion (m/z)	Qualitative ions (m/z)	LOD/(mg/kg)	LOQ/(mg/kg)	0.1 mg/kg		0.25 mg/kg		0.5 mg/kg	
						Recovery/%	RSD/%	Recovery/%	RSD/%	Recovery/%	RSD/%
β-Hexachlorocyolohexane (β-BHC)	8.02	218.9110	180.9373, 182.9343	0.005	0.01	76.14	3.98	83.23	2.78	77.22	2.02
Propetamphos	8.09	193.9823	138.0137, 222.0348	0.005	0.01	86.38	2.18	86.33	3.45	80.24	2.88
Profluralin	8.10	318.0696	264.0226, 330.1059	0.005	0.01	74.93	4.09	84.54	4.41	78.55	2.62
Terbuthylazine	8.12	214.0854	216.0825, 229.1088	0.05	0.1	74.61	2.46	84.17	3.57	81.95	2.74
γ-Hexachlorocyolohexane (γ-BHC)	8.14	218.9110	180.9373, 182.9343	0.005	0.01	75.65	4.85	83.50	3.78	79.22	2.42
Terbufos	8.15	230.9736	153.0133, 202.9418	0.005	0.01	60.36	3.90	59.57	12.15	60.19	19.35
Propyzamide	8.17	172.9555	174.9526, 254.0134	0.005	0.01	80.81	2.47	87.49	3.08	80.50	3.26
Pentachloronitrobenzene	8.21	294.8337	236.8407, 248.8407	0.0125	0.025	57.07	5.14	63.53	5.27	64.04	3.42
Fonofos	8.24	137.0184	109.0106, 246.0296	0.005	0.01	73.58	2.39	78.35	3.55	73.01	4.57
Pyrimethanil	8.27	198.1025	183.0791, 199.1104	0.005	0.01	74.25	3.34	81.86	2.78	83.46	1.51
Diazinon	8.28	179.1178	199.0630, 304.1004	0.005	0.01	73.88	2.80	77.93	3.07	74.49	2.92
Paraoxon-methyl	8.42	230.0212	200.0233, 247.0240	0.005	0.01	81.89	4.85	92.79	5.86	84.42	3.37
Isazofos	8.52	256.9785	208.0037, 285.0098	0.005	0.01	83.99	2.07	90.20	3.12	84.25	2.42
Etrimfos	8.54	292.0641	153.0658, 181.0971	0.005	0.01	79.80	2.26	84.17	3.86	80.65	3.60
Triallate	8.56	268.0324	142.9216, 270.0294	0.0125	0.025	65.26	1.96	69.49	2.47	68.68	2.00
Tebupirimfos	8.62	318.1161	261.0457, 276.0692	0.0125	0.025	74.16	1.90	83.64	3.95	78.22	3.00
Iprobenfos	8.69	204.0004	171.0205, 246.0474	0.005	0.01	84.32	1.92	97.00	3.54	90.71	2.93
Pirimicarb	8.72	166.0974	167.1004, 238.1424	0.005	0.01	84.64	10.09	97.86	4.09	87.47	3.93
Desmetryn	8.88	213.1042	171.0573, 198.0808	0.005	0.01	80.57	2.81	89.36	3.02	86.71	1.80
Pentachloroaniline	8.90	264.8595	262.8624, 266.8565	0.005	0.01	53.11	3.44	57.22	3.27	58.50	1.92
Propanil	8.93	160.9793	162.9762, 164.9735	0.005	0.01	78.38	3.26	87.65	3.61	80.94	2.59
Dichlofenthion	8.96	279.0006	222.9380, 224.9336	0.005	0.01	72.25	2.94	80.67	3.32	76.74	2.36
Metribuzin	8.99	198.0695	182.0382, 199.0697	0.005	0.01	72.68	5.09	81.44	4.52	80.63	5.63
Acetochlor	9.08	162.0913	146.0964, 223.0762	0.005	0.01	82.78	2.95	85.22	3.15	83.64	1.77
Vinclozolin	9.10	212.0028	186.9586, 284.9953	0.025	0.05	80.76	3.82	84.69	1.90	82.27	2.05
Chlorpyrifos-methyl	9.13	285.9255	124.9820, 287.9231	0.005	0.01	76.01	2.34	84.43	2.78	79.43	2.80
Parathion-methyl	9.13	263.0011	109.0049, 245.9984	0.005	0.01	80.60	4.15	89.80	3.91	85.35	3.01
Tolclofos-methyl	9.22	264.9849	174.9711, 266.9821	0.005	0.01	76.62	3.36	83.62	3.25	77.93	3.22
Ametryne	9.24	227.1199	170.0495, 212.0964	0.005	0.01	84.34	1.57	89.97	2.50	84.87	2.07
Alachlor	9.25	188.1069	146.0964, 160.1120	0.005	0.01	81.95	2.24	87.63	2.87	81.12	2.25
Prometryn	9.28	241.1355	184.0651, 226.1120	0.0125	0.025	84.17	3.22	87.28	3.86	85.26	1.98
Fenchlorphos	9.38	284.9300	286.9274, 288.9247	0.005	0.01	70.50	2.55	75.25	2.83	75.69	2.28
Fenitrothion	9.58	260.0141	109.0049, 277.0168	0.005	0.01	81.12	2.99	86.91	2.36	83.27	2.96

表 1 （续）
Table （Continued）

Pesticide	t_R/min	Quantitative ion (m/z)	Qualitative ions (m/z)	LOD/(mg/kg)	LOQ/(mg/kg)	0.1 mg/kg Recovery/%	0.1 mg/kg RSD/%	0.25 mg/kg Recovery/%	0.25 mg/kg RSD/%	0.5 mg/kg Recovery/%	0.5 mg/kg RSD/%
Pirimiphos-methyl	9.58	290.0722	276.0566, 305.0957	0.005	0.01	80.74	2.58	88.46	3.35	84.15	3.45
Ethofumesate	9.61	207.1015	161.0597, 286.0869	0.005	0.01	82.98	1.35	89.96	2.47	84.09	2.51
Bromacil	9.63	206.9578	204.9607, 230.9763	0.0125	0.025	80.56	2.58	85.97	1.63	83.79	2.66
Dipropetryn	9.71	255.1512	222.1713, 240.1277	0.005	0.01	84.39	3.28	91.14	2.80	87.10	2.80
Malathion	9.73	173.0808	157.9619, 210.9646	0.005	0.01	89.52	2.59	92.07	2.87	86.61	3.11
Thiobencarb	9.78	100.0756	125.0152, 257.0635	0.005	0.01	64.87	10.04	73.70	3.58	75.04	1.88
Phorate sulfone	9.87	199.0010	153.0133, 170.9697	0.005	0.01	86.79	3.20	87.12	2.90	84.66	2.57
Metolachlor	9.89	238.0993	162.1277, 163.1306	0.005	0.01	79.99	2.59	87.41	3.71	84.37	2.42
Fenthion	9.91	278.0194	169.0140, 245.0395	0.005	0.01	61.74	6.83	60.54	18.85	58.94	25.66
Aldrin	9.93	262.8564	264.8564, 292.9267	0.005	0.01	47.26	2.53	55.82	2.88	52.18	2.47
Chlorpyrifos	9.95	313.9568	196.9196, 257.8939	0.005	0.01	74.59	2.33	80.62	3.27	76.65	2.17
Parathion	9.96	291.0324	139.0264, 155.0035	0.005	0.01	80.12	2.44	88.78	3.51	82.53	2.36
Triadimefon	10.00	181.0163	208.0272, 210.0244	0.005	0.01	92.67	4.70	93.25	3.26	89.49	2.71
Tetraconazole	10.06	336.0521	170.9774, 338.0494	0.005	0.01	86.65	2.08	93.35	3.30	86.93	1.91
Isocarbophos	10.07	230.0001	109.9824, 289.0532	0.005	0.01	81.74	3.82	87.47	5.66	81.65	5.39
Trichloronate	10.19	296.9667	268.9354, 298.9638	0.0125	0.025	64.00	2.67	69.55	3.91	68.46	3.80
Bromophos	10.27	330.8775	328.8798, 332.8748	0.005	0.01	70.32	2.07	78.95	3.30	76.17	2.27
Pirimiphos-ethyl	10.29	318.1035	304.0879, 333.1270	0.005	0.01	87.25	3.01	88.75	2.98	85.05	2.60
Cyprodinil	10.39	224.1182	222.1025, 226.1260	0.005	0.01	81.00	2.81	92.12	3.79	85.20	4.02
Isofenphos-methyl	10.40	199.0154	230.9902, 241.0624	0.005	0.01	78.77	1.59	88.39	4.70	87.02	3.24
Pendimethalin	10.51	252.0978	191.0689, 208.0716	0.005	0.01	70.58	4.10	78.32	3.25	75.44	2.33
Penconazole	10.55	248.0948	158.9762, 160.9733	0.005	0.01	77.72	2.89	85.70	5.50	83.20	1.94
Terbufos sulfone	10.56	199.0010	124.9820, 153.0128	0.005	0.01	88.09	2.33	87.94	4.54	85.64	2.07
Chlorfenvinphos	10.66	266.9375	294.9688, 323.0001	0.005	0.01	80.40	2.42	87.11	4.09	84.63	1.97
Fipronil	10.66	366.9429	212.9480, 368.9400	0.005	0.01	87.25	1.41	91.22	4.59	91.10	4.12
Isofenphos	10.66	213.0311	184.9998, 255.0780	0.0125	0.025	80.57	3.64	85.65	5.00	80.82	2.57
Beflubutamid	10.68	176.1069	193.0271, 221.0584	0.005	0.01	80.75	6.56	87.61	4.43	83.74	1.79
Quinalphos	10.73	146.0474	156.0682, 157.0760	0.0125	0.025	73.57	13.04	84.69	4.88	80.34	1.74
Triadimenol	10.73	168.1131	128.0023, 129.9993	0.005	0.01	83.56	17.05	91.39	5.36	88.52	2.56
Procymidone	10.84	283.0161	255.0212, 285.0133	0.0125	0.025	84.16	3.07	86.84	5.53	83.00	2.72
Haloxyfop	10.95	375.0479	288.0033, 316.0346	0.005	0.01	87.18	2.24	89.16	5.26	85.80	1.96
Methidathion	10.99	145.0066	85.0394, 124.9820	0.005	0.01	81.04	1.95	88.15	3.48	87.85	5.32
γ-Chlordan	11.02	374.8225	372.8254, 376.8196	0.005	0.01	59.20	2.26	71.36	8.65	69.37	5.17

表 1 （续）
Table （Continued）

Pesticide	t_R/min	Quantitative ion (m/z)	Qualitative ions (m/z)	LOD/(mg/kg)	LOQ/(mg/kg)	0.1 mg/kg		0.25 mg/kg		0.5 mg/kg	
						Recovery/%	RSD/%	Recovery/%	RSD/%	Recovery/%	RSD/%
o,p′-Dichlorodiphenyldichloroethylene (o,p′-DDE)	11.07	245.9997	247.9969, 317.9346	0.0125	0.025	50.94	2.46	55.16	5.81	55.07	3.92
Paclobutrazol	11.09	236.0585	125.0152, 238.0561	0.005	0.01	82.49	4.47	86.59	4.95	85.40	2.16
Tetrachlorvinphose	11.15	328.9298	109.0049, 330.9270	0.005	0.01	79.11	2.47	82.80	2.80	80.28	3.23
Butachlor	11.20	176.1069	160.1120, 188.1069	0.005	0.01	80.88	3.99	80.39	3.78	76.75	2.36
α-Endosulfan	11.25	338.8725	236.8407, 238.8378	0.005	0.01	63.60	8.36	71.00	4.61	67.69	4.02
Ditalimfos	11.29	242.9749	271.0062, 299.0375	0.005	0.01	79.24	7.43	84.19	3.87	83.42	3.56
Chlorfenson	11.36	174.9615	176.9580, 301.9565	0.005	0.01	76.70	2.25	78.89	4.85	76.81	1.70
Butamifos	11.37	286.1025	231.9827, 258.0712	0.005	0.01	79.72	2.34	88.65	3.46	82.11	2.84
Flurodifen	11.37	190.0110	126.0149, 146.0212	0.005	0.01	77.09	1.70	82.77	3.06	82.43	2.33
Flutriafol	11.37	123.0240	164.0618, 219.0616	0.005	0.01	80.03	3.51	83.13	5.18	82.86	1.49
Bromfenvinphos	11.38	294.9688	169.9684, 323.0001	0.005	0.01	81.43	2.16	89.26	3.68	81.80	1.58
Flutolanil	11.39	173.0208	281.0658, 323.1127	0.005	0.01	87.18	1.43	94.90	5.30	90.37	4.46
Napropamide	11.41	271.1566	100.1120, 115.0542	0.005	0.01	83.97	4.78	89.61	4.23	87.00	3.03
Hexaconazole	11.45	213.9933	215.9904, 231.0338	0.005	0.01	84.40	1.06	84.79	3.10	79.80	2.59
Prothiofos	11.49	308.9934	238.9151, 310.9904	0.005	0.01	62.74	5.94	73.68	4.30	68.99	3.14
Isoprothiolane	11.50	188.9674	231.0144, 290.0640	0.005	0.01	85.34	5.64	86.33	5.15	82.46	3.78
Profenofos	11.54	338.9637	268.8854, 336.9657	0.025	0.05	76.34	3.26	80.98	4.38	78.18	3.19
Fludioxonil	11.55	248.0391	154.0525, 182.0474	0.005	0.01	86.40	1.80	89.04	5.94	87.62	5.11
Pretilachlor	11.58	238.0993	202.1226, 262.1801	0.005	0.01	81.22	1.88	84.69	3.31	83.06	3.62
Tribufos	11.59	168.9905	146.9152, 226.0609	0.0125	0.025	68.23	2.53	72.92	4.06	68.89	2.18
p,p′-Dichlorodiphenyldichloroethylene (p,p′-DDE)	11.61	245.9997	247.9969, 317.9346	0.005	0.01	53.84	2.32	63.17	4.39	62.22	1.84
Oxadiazon	11.64	174.9586	258.0321, 344.0689	0.005	0.01	76.84	2.39	84.94	4.92	83.92	3.41
Dieldrin	11.71	262.8564	264.8535, 344.8983	0.005	0.01	66.87	2.31	70.93	5.56	70.94	2.66
Flusilazole	11.71	233.0592	206.0544, 234.0620	0.0125	0.025	81.40	3.13	83.75	4.78	83.24	3.09
Oxyfluorfen	11.71	252.0392	300.0033, 361.0323	0.005	0.01	82.17	2.85	85.68	3.09	81.58	2.18
Myclobutanil	11.74	179.0244	150.0105, 206.0731	0.005	0.01	84.82	2.14	84.72	5.73	84.50	3.75
o,p′-Dichlorodiphenildichloroethane (o,p′-DDD)	11.78	235.0075	165.0698, 237.0047	0.005	0.01	64.72	1.93	72.33	5.75	72.99	4.02
Bupirimate	11.81	273.1015	193.1447, 208.1444	0.005	0.01	85.89	5.13	89.22	4.98	86.57	3.86
Kresoxim-methyl	11.81	116.0494	131.0729, 206.0811	0.005	0.01	79.67	2.74	81.93	6.10	79.11	1.93
Isoxathion	11.93	177.0242	159.0137, 313.0532	0.005	0.01	81.48	3.41	88.15	3.31	79.22	3.85
Cyflufenamid	11.97	188.0118	207.0101, 294.0774	0.005	0.01	82.04	3.61	92.94	5.73	82.52	3.58
Fluazifop-butyl	11.98	282.0736	254.0423, 383.1338	0.005	0.01	83.73	2.88	88.28	4.30	83.45	2.24
Nitrofen	12.00	282.9797	202.0179, 284.9766	0.005	0.01	70.28	3.19	78.74	3.29	74.24	3.49

表 1 (续)

Table (Continued)

Pesticide	t_R/min	Quantitative ion (*m/z*)	Qualitative ions (*m/z*)	LOD/(mg/kg)	LOQ/(mg/kg)	0.1 mg/kg		0.25 mg/kg		0.5 mg/kg	
						Recovery/%	RSD/%	Recovery/%	RSD/%	Recovery/%	RSD/%
Cyproconazole	12.03	222.0428	138.9945, 224.0401	0.005	0.01	84.22	2.96	82.81	5.64	84.81	3.27
Chlorobenzilate	12.17	251.0025	138.9945, 252.9997	0.005	0.01	75.38	1.61	82.37	5.00	81.74	3.83
β-Endosulfan	12.27	338.8725	236.8407, 238.8378	0.005	0.01	75.93	2.36	77.18	5.25	73.56	2.92
Diniconazole	12.32	232.0272	270.0010, 268.0039	0.005	0.01	83.57	2.47	84.15	4.17	83.35	4.02
p,p'-Dichlorodiphenildichloroethane (*p,p'*-DDD)	12.36	235.0075	165.0698, 237.0047	0.005	0.01	53.32	3.68	56.95	4.55	56.70	4.87
Fenthion sulfone	12.37	310.0093	246.0474, 311.0120	0.005	0.01	90.15	1.76	91.15	4.39	88.21	3.00
Aclonifen	12.38	264.0296	212.0580, 266.0271	0.005	0.01	74.21	1.87	79.99	2.91	77.79	4.14
Ethion	12.42	230.9731	153.0133, 174.9105	0.005	0.01	76.65	2.32	81.69	3.77	82.46	2.84
o,p'-Dichlorodiphenyltrichloroethane (*o,p'*-DDT)	12.43	235.0075	165.0698, 237.0047	0.005	0.01	66.26	2.56	73.84	4.88	75.70	4.48
Chlorthiophos	12.48	268.9257	270.9227, 324.9883	0.005	0.01	75.31	2.12	75.18	5.26	74.69	3.87
Triazophos	12.65	257.0018	177.0355, 285.0331	0.025	0.05	82.93	2.33	88.75	5.60	86.20	3.42
Famphur	12.80	218.0161	245.0174, 280.9701	0.0125	0.025	82.71	2.09	87.54	5.02	88.13	3.92
Carbophenothion	12.82	156.9873	295.9856, 341.9733	0.005	0.01	75.14	2.24	76.24	5.22	77.30	4.82
Benalaxyl	12.87	148.1120	206.1175, 266.1539	0.005	0.01	88.16	2.03	89.25	4.83	88.49	3.10
Quinoxyfen	12.91	237.0584	272.0272, 306.9961	0.005	0.01	74.08	5.98	74.48	4.38	74.43	4.01
Edifenphos	12.93	310.0245	172.9820, 201.0133	0.005	0.01	82.84	6.14	81.88	5.48	79.00	4.66
Trifloxystrobin	12.97	116.0495	145.0259, 172.0368	0.025	0.05	105.04	5.05	93.06	3.47	84.15	3.43
p,p'-Dichlorodiphenyltrichloroethane (*p,p'*-DDT)	13.03	235.0075	165.0698, 237.0047	0.005	0.01	54.75	5.76	57.21	5.64	56.97	5.83
Propiconazole	13.06	259.0287	172.9555, 261.0259	0.005	0.01	85.85	2.53	88.78	4.23	85.02	3.57
Diclofop-methyl	13.28	340.0263	252.9817, 281.013	0.005	0.01	77.21	2.23	81.90	3.95	80.04	3.71
Tebuconazole	13.29	250.0741	163.0309, 274.1105	0.005	0.01	81.48	3.28	85.03	5.08	84.75	5.21
Piperonyl butoxide	13.38	176.0831	149.0597, 177.0910	0.005	0.01	74.31	3.47	71.62	15.87	72.86	13.73
Epoxiconazole	13.58	278.1088	192.0336, 194.0307	0.005	0.01	86.61	4.41	83.17	7.13	80.47	3.82
Iprodione	13.71	316.0066	314.0093, 271.0035	0.005	0.01	78.35	6.16	77.43	3.60	81.65	6.21
Pyridaphenthion	13.82	340.0641	199.0865, 204.0351	0.005	0.01	85.77	3.13	90.48	2.39	87.43	3.39
Endrin	13.87	316.9034	280.9267, 318.9005	0.005	0.01	71.31	8.48	78.07	6.56	85.66	6.29
Phosmet	13.90	160.0393	133.0284, 161.0433	0.005	0.01	84.09	2.37	90.37	5.86	89.71	5.08
Bifenthrin	13.92	181.1011	165.0698, 166.0777	0.005	0.01	70.85	2.83	71.80	3.99	71.11	3.57
Bromopropylate	13.92	340.8994	182.9440, 338.9014	0.005	0.01	76.72	2.30	73.90	4.96	74.96	4.48
Tetramethrin	13.93	164.0706	165.0739, 135.044	0.025	0.05	78.22	2.22	86.98	4.39	87.50	4.02
Tsumaphos	13.94	156.9871	141.0099, 169.0412	0.005	0.01	80.67	1.45	79.24	4.28	80.42	4.03
Piperophos	14.03	122.0964	140.1069, 170.9334	0.005	0.01	83.95	1.90	82.84	4.58	84.23	4.52
Bifenazate	14.04	258.0999	300.1468, 196.0757	0.005	0.01	115.78	27.28	101.18	8.29	84.82	19.89

表 1 (续)

Table (Continued)

Pesticide	t_R/min	Quantitative ion (*m/z*)	Qualitative ions (*m/z*)	LOD/(mg/kg)	LOQ/(mg/kg)	0.1 mg/kg Recovery/%	0.1 mg/kg RSD/%	0.25 mg/kg Recovery/%	0.25 mg/kg RSD/%	0.5 mg/kg Recovery/%	0.5 mg/kg RSD/%
Fenpropathrin	14.05	181.0647	197.0597, 265.0733	0.005	0.01	81.90	1.88	80.54	5.14	83.02	4.15
Etoxazole	14.09	330.1300	300.1194, 359.1691	0.005	0.01	83.84	2.26	86.03	4.25	84.84	3.91
Tebufenpyrad	14.11	318.1367	276.0898, 333.1602	0.005	0.01	75.37	2.71	76.89	5.22	76.66	3.71
Fenamidone	14.16	268.0903	237.1022, 238.1100	0.005	0.01	76.53	20.53	78.83	4.94	82.67	7.47
Bifenox	14.22	340.9852	309.9668, 342.9825	0.005	0.01	79.26	2.92	80.28	4.11	81.30	6.66
Anilofos	14.28	226.0451	124.9820, 183.9982	0.005	0.01	84.04	2.81	80.00	5.35	80.98	5.60
Tetradifon	14.41	355.8808	226.8886, 228.8856	0.005	0.01	67.64	1.73	69.53	6.52	70.95	5.90
Azinphos-methyl	14.42	132.0443	104.0494, 160.0505	0.005	0.01	91.69	5.05	90.72	5.51	86.38	4.86
Phosalone	14.59	182.0000	183.9975, 366.9863	0.005	0.01	82.73	2.70	79.99	5.54	82.46	4.73
Pyriproxyfen	14.62	136.0756	186.0675, 226.0988	0.005	0.01	75.43	1.82	79.14	6.35	78.35	5.10
Leptophos	14.64	376.8983	171.0027, 374.9005	0.005	0.01	59.15	2.12	62.83	4.64	62.90	5.15
Mefenacet	14.79	136.0215	192.0113, 120.0807	0.005	0.01	83.70	13.44	75.71	7.43	72.89	5.88
λ-Cyhalothrin	14.88	181.0647	209.0835, 197.0339	0.005	0.01	82.22	2.08	88.22	5.61	86.87	6.09
Acrinathrin	15.03	181.0647	209.0835, 289.0657	0.005	0.01	87.77	1.67	88.83	3.96	93.46	6.46
Fenarimol	15.09	251.0025	138.9945, 219.0319	0.005	0.01	73.56	3.08	71.31	7.35	71.12	5.30
Pyrazophos	15.13	221.0795	232.1080, 265.0879	0.005	0.01	89.37	2.57	84.93	6.75	86.15	6.19
Bitertanol	15.61	170.0726	141.0698, 171.0766	0.005	0.01	77.70	3.64	76.11	7.41	73.32	4.40
Permethrin	15.61	183.0800	127.0309, 163.0075	0.005	0.01	70.83	2.02	66.27	6.81	69.28	4.89
Pyridaben	15.78	147.1168	117.0698, 309.0822	0.005	0.01	66.33	4.33	66.66	6.10	69.44	5.61
Spirodiclofen	15.78	312.0314	212.9504, 259.0520	0.005	0.01	74.91	6.46	76.32	2.91	77.59	5.09
Coumaphos	15.86	362.0139	225.9849, 364.0112	0.005	0.01	81.29	3.46	77.05	5.61	79.42	4.77
Fluquinconazole	15.86	340.0395	108.0244, 342.0366	0.005	0.01	76.39	3.86	68.00	11.12	68.06	10.19
Fenbuconazole	16.22	129.0573	125.0152, 198.0900	0.005	0.01	75.75	8.30	71.48	9.44	69.17	6.56
Boscalid	16.59	139.9897	141.9873, 344.0321	0.005	0.01	68.46	6.41	61.81	8.03	60.01	7.27
Cypermethrin	16.70	181.0647	169.0647, 209.0835	0.005	0.01	74.26	1.23	68.51	3.03	67.64	4.23
Etofenprox	16.70	163.1117	107.0491, 135.0804	0.005	0.01	68.47	3.27	65.56	6.12	64.13	5.62
Flucythrinate	16.88	199.0929	157.0459, 225.0784	0.005	0.01	76.52	3.23	67.79	6.48	69.43	5.17
Fenvalerate	17.41	125.0152	225.0784, 419.1282	0.005	0.01	60.66	7.53	55.86	8.63	58.63	6.28
Fluvalinate	17.62	250.0604	206.0003, 252.0576	0.005	0.01	64.04	7.76	57.09	8.58	60.15	7.79
Difenoconazole	17.88	264.9817	266.9794, 323.0236	0.005	0.01	65.21	4.05	57.14	8.23	56.18	6.42
Deltamethrin	18.12	181.0647	209.0835, 252.9045	0.005	0.01	55.38	3.67	48.85	3.59	52.84	5.66
Azoxystrobin	18.36	344.1029	372.0978, 388.0928	0.005	0.01	64.95	7.95	57.23	8.93	59.74	12.54

拖尾的发生。经过优化，确定了 1.4.1 节所述色谱条件，该条件下 197 种农药分析时间短，峰形较好，10 ng/mL 基质标准溶液提取离子色谱图见图 1。

2.2　前处理条件的优化

2.2.1　提取条件的选择

植物油基质主要干扰物质为甘油三酯，选择不与甘油三酯互溶的有机试剂，可以简化后续处理步骤。乙腈在农药残留检测中应用广泛，考虑到部分农药可能对 pH 值敏感，同时考察了用含 1% 甲酸的乙腈提取的情况。为了避免基质效应的影响，各组均采用基质标准溶液进行定量分析。结果表明，采用乙腈与含 1% 甲酸的乙腈提取时，197 种农药的回收率分布差异不大；乙腈提取情况下回收率小于 50% 的农药数量更少一些（见图 2），同时根据实验室前期[21]积累的数据，乙腈提取液在-20 ℃下冷冻 2 h 后离心，可以在一定程度上除去脂类干扰物。故最终选择使用乙腈进行提取。

2.2.2　净化方式的选择

对于冷冻除脂后的样品，考察了 PRiME HLB 柱（3 mL/60 mg），以及参照 AOAC 2007.01 方法中适用于含脂肪果蔬的 50 mg C18+50 mg PSA 粉末和 50 mg C18+50 mg Z-Sep 粉末作为净化剂进行净化的效果。其中，PRiME HLB 柱无需活化，直接取待净化液加入 PRiME HLB 柱中，收集流出液。在选定的仪器条件下，采用基质标准溶液进行定量分析，比较不同净化剂净化后的回收率情况。结果表明，采用 50 mg C18+50 mg PSA 粉末净化时，回收率为 70%～120% 的农药数量最多，同时回收率小于 50% 的农药数量最少（见图 3）。故选择采用 50 mg C18+50 mg PSA 粉末进行净化。

2.3　基质效应

实验对 197 种农药的基质效应（基质效应 = 基质标准溶液响应/溶剂标准溶液响应）进行了考察，93% 的农药基质效应大于 1.2，表现为基质增强效应；3% 的农药基质效应小于 0.8，表现为基质减弱效应；只有 4% 的农药基质效应在 0.8～1.2 之间，表现为较弱的基质效应。故采用空白基质配制标准溶液的方式进行定量。

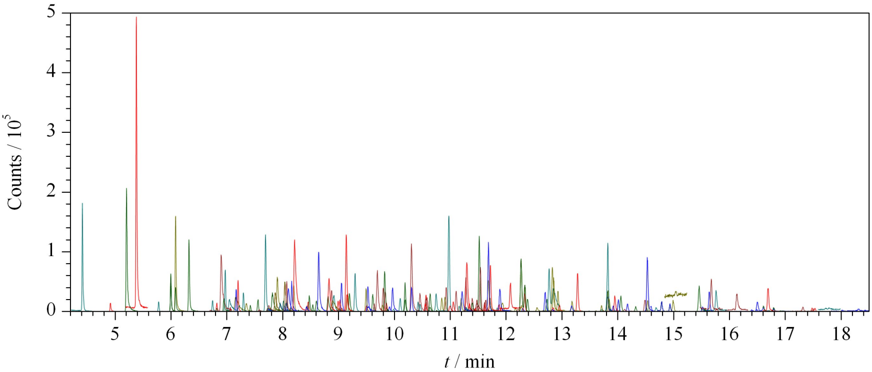

图 1　197 种农药（10 ng/mL）基质标准溶液的提取离子色谱图

Fig. 1　Extract ion chromatograms of the 197 pesticides (10 ng/mL) in matrix standard solution

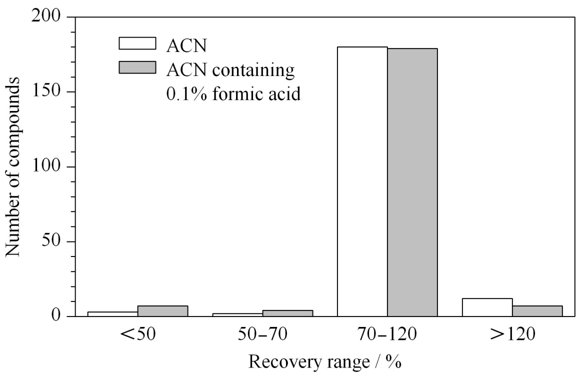

图 2　不同提取溶剂提取时 197 种农药的回收率分布

Fig. 2　Distribution of recoveries of the 197 pesticides extracted by different extraction solvents

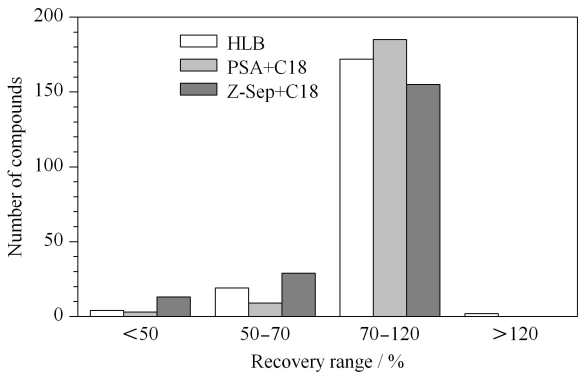

图 3　不同净化材料净化时 197 种农药的回收率分布

Fig. 3　Distribution of recoveries of the 197 pesticides purified by different purification materials

2.4　方法学考察

称取 2 g 空白植物油样品,添加一定浓度的混合标准溶液,制备不同浓度的加标样品。对加标样品进行检测,以 3 倍信噪比作为检出限、10 倍信噪比作为定量限,发现 197 种农药中有 174 种农药定量限可以达到 0.01 mg/kg,占总数量的 88%; 15 种农药的定量限为 0.025 mg/kg, 7 种农药的定量限为 0.05 mg/kg,仅特丁津的定量限为 0.1 mg/kg。

联苯在 2~100 μg/L 范围内,其余农药在定量限~200 μg/L 范围内,其各自质量浓度与对应的峰面积均呈良好的线性关系,相关系数大于 0.99。

我国现行国家标准 GB 2763-2019 规定了 54 种农药在不同种类植物油中共计 84 项残留与再残留限量,其中 46 项限量在 0.1~1 mg/kg 范围内,同时考虑各农药定量限情况,选择 0.1、0.25 和 0.5 mg/kg 3 个水平进行加标回收试验,考察 197 种农药的准确度与精密度。3 个水平下,回收率为 70%~120% 的农药占总数的 79% 以上,相对标准偏差<10% 的农药占总数的 94% 以上,说明方法整体准确度与精密度良好,结果见表 1。

2.5　实际样品检测

实验对 23 份市售植物油样品进行了检测,结果在 12 份样品中检出 13 种农药。其中,6 份花生油样品中均检出毒死蜱,含量为 0.021~0.176 mg/kg; 1 份四级菜籽油样品中检出联苯菊酯、溴螨酯、乙酯杀螨醇、甲氰菊酯、噁草酮、氯菊酯和吡螨胺 7 种农药,详细检出情况见表 2。

与我国现行国家标准 GB 2763-2019 比较,上述检出农药均未超过规定的最大残留限量值,或暂未制定对应的最大残留限量值。

表 2　市售食用植物油中农药残留检出情况

Table 2　Detection of pesticide residues in edible vegetable oils on the market

No.	Sample	Pesticide	Content/(mg/kg)	No.	Sample	Pesticide	Content/(mg/kg)
1	peanut oil	chlorpyrifos	0.021	9	rapeseed oil (grade 1)	bifenthrin	0.017
2	peanut oil	chlorpyrifos	0.221	10	rapeseed oil (grade 3)	chlorobenzilate	0.016
3	peanut oil	acetochlor	0.007	11	rapeseed oil (grade 4)	bifenthrin	0.035
		chlorpyrifos	0.098			bromopropylate	0.009
4	peanut oil	chlorpyrifos	0.156			chlorobenzilate	0.015
5	peanut oil	acetochlor	0.060			fenpropathrin	0.014
		chlorpyrifos	0.255			oxadiazon	0.008
6	peanut oil	chlorpyrifos	0.176			permethrin	0.009
7	olive oil	oxyfluorfen	0.093			tebufenpyrad	0.007
		trifloxystrobin	0.012	12	rapeseed oil (grade 3)	cyproconazole	0.009
8	olive oil	oxyfluorfen	0.008			pirimiphos-methyl	0.006

3　结论

本方法优化了适用于食用植物油基质的提取和净化条件,结合气相色谱-飞行时间质谱技术建立了食用植物油中 197 种农药残留的测定方法。该方法利用飞行时间质谱的高质量分辨率特点,可以在保证灵敏度的基础上大大提高检测通量,简化前处理步骤,对于大部分农药残留定量限达到 0.01 mg/kg,同时方法准确度及精密度良好,满足食用植物油中农药残留高通量检测的要求。

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