

QuEChERS-LC-MS/MS 测定姜油树脂、 姜精油中 8 种农药残留及膳食风险评估

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摘要:本研究建立了 QuEChERS-液相色谱-串联四极杆质谱(LC-MS/MS)法测定姜油树脂、姜精油样品中噻虫嗪、吡虫啉、噻虫胺等 8 种农药残留,通过方法优化,选择乙腈-水-正己烷体系提取样品,QuEChERS 方法净化提取液,在电喷雾离子源正离子模式下电离,多反应监测(MRM)模式下测定,并采用基质匹配标准曲线内标法进行定量分析。结果表明,8 种农药在 1~32 μg/L 浓度范围内的线性关系良好,相关系数(R^2)均大于 0.99,方法检出限和定量限分别为 0.03~0.16、0.10~0.53 mg/kg;3 种不同加标水平下的回收率均在 70%~119% 之间,相对标准偏差(RSD)均小于 20%。采用该方法测定实际样品,其中,噻虫嗪、吡虫啉、噻虫胺阳性样本的检出率较高,分别为 56%、58%、52%,残留量大于 1 mg/kg 的样本量占比分别为 12%、16%、10%,最高残留量分别为 2.16、1.92、2.01 mg/kg,其他 5 种农药的检出率均低于 20%。基于实际样品中农药残留中位值评估干姜片、姜精油和姜油树脂中噻虫嗪、吡虫啉、噻虫胺的慢性膳食摄入风险,评估结果远小于 100%,表明农药残留的慢性摄入风险较小。

关键词:姜油树脂;姜精油;农药残留;液相色谱-串联四极杆质谱(LC-MS/MS);膳食慢性摄入风险

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Determination and Dietary Risk Assessment of 8 Pesticide Residues in Ginger Oleoresin and Ginger Essential Oil by QuEChERS-LC-MS/MS

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Abstract: Ginger (*Zingiber officinale* Rosc.) is the first batch of medicinal and edible plants announced by the Ministry of Health in China. Ginger oleoresin and ginger essential oil are the products extracted from ginger, widely used as flavours and fragrances, of which the quality has a direct influence on food safety. Due to the complex composi-

tion of ginger oleoresin and ginger essential oil, the qualitative and quantitative detection of pesticide residues is challenging. In this study, a liquid-liquid extraction and QuEChERS pretreatment method of 8 pesticide residues in ginger and subsequently analysis of the extracts by liquid chromatography-tandem mass spectrometry (LC-MS/MS) were developed and validated. The sample was extracted by 1% acidic acetonitrile solution, followed by addition of an equal volume of water and a small amount of hexane to the sample. After vortexing and centrifugation, the sample underwent purification via an optimized QuEChERS technique. The purified sample was analyzed by electrospray ionization MS under positive ion mode with multiple reaction monitoring (MRM). Under optimized conditions, the results showed that the calibration curves of the 8 pesticides have good linearity within the range of 1-32 $\mu\text{g/L}$, with correlation coefficients (R^2) higher than 0.99. The limits of detection (LODs) are 0.03-0.16 mg/kg, and the limits of quantification (LOQs) are 0.10-0.53 mg/kg. The recoveries are 70%-119%, and the relative standard deviations (RSDs) are lower than 20% ($n=6$) at high, medium and low of spiking levels. The method was successfully applied to 20 ginger, 15 oleoresin, and 15 essential oil samples. The results showed that the positive detection rates of thiamethoxam, imidacloprid, and clothianidin are 56%, 58%, 52%, respectively. The detection rates of other five pesticides are lower than 20%. The proportion of residual levels greater than 1 mg/kg were found to be at a rate of 12%, 16% and 10% for thiamethoxam, imidacloprid and clothianidin with maximum levels recorded as 2.16, 1.92 and 2.01 mg/kg, respectively. Dietary exposure risk of the 3 pesticides in ginger, ginger essential oil and ginger oleoresin was evaluated based on the median value of pesticide residues. The evaluation result was far less than 100%, indicating that dietary exposure risk of pesticide residues in ginger oleoresin and ginger essential oil should be acceptable. This study provides not only an efficient and reliable quantitative method for the detection of various pesticide residues in ginger oleoresin and ginger essential oil, but also a practical technical reference for the internal quality control of plant extract enterprises and market supervision of government departments. Moreover, in view of the fact that pesticide residues have been detected in plant extract products, such as ginger oleoresin and ginger essential oil, it is recommended to formulate the maximum residue limit (MRL) standards of various plant extracts according to the acceptable daily intake (ADI) values of pesticides, MRL standards of plant extracts raw materials and extraction concentration factors to regulate the market.

Key words: ginger oleoresin; ginger essential oil; pesticide residue; liquid chromatography-tandem mass spectrometry (LC-MS/MS); dietary exposure risk

生姜是我国卫生部公布的第一批药食两用植物^[1],姜油树脂及姜精油是生姜经切片、干燥、萃取、浓缩后的产物^[2-3],其主要成分包括挥发性姜精油、姜辣素(姜酮、姜酚等)等,具有广谱、抑菌、抗氧化作用^[4-9]。为防治病虫害,在生姜种植中常喷洒农药^[10],极易造成生姜的农药残留,而且在姜浓缩提取过程中可导致农药富

集,进而引起产品安全隐患^[11-12]。

目前,已有关于鲜姜中痕量农药残留检测的报道^[13-18]。刘丹等^[13]采用QuEChERS前处理方法结合超高效液相色谱-三重四极杆串联质谱法测定高良姜中31种农药残留。梅文泉等^[17]利用固相萃取柱净化结合气相色谱-质谱联用法测定鲜姜中12种农药残留。韩梅等^[18]

采用超高效液相色谱-四极杆/静电场轨道阱高分辨质谱法,比较了未净化、QuEChERS前处理、氨基柱固相萃取的鲜姜中农药残留提取净化效果。噻唑膦、苯醚甲环唑、甲霜灵、戊唑醇是农业农村部允许在生姜种植或储存中登记使用的农药,而噻虫嗪、吡虫啉、噻虫胺等未被允许登记使用。由于姜油树脂、姜精油成分复杂,其中的挥发油、姜辣素等成分严重干扰农药残留的定性和定量分析^[19],给植物提取物的质量控制和市场监管带来困难。

本研究拟通过优化姜油树脂、姜精油的前处理方式以及仪器检测参数,建立液相色谱-串联四极杆质谱法检测干姜片、姜精油、姜油树脂等样品中8种农药残留,并评估噻虫嗪、吡虫啉、噻虫胺的慢性膳食摄入风险。

1 材料与方法

1.1 仪器与装置

Acquity UPLC-TQD液相色谱-质谱联用仪:美国Waters公司产品,配有电喷雾离子源(ESI)和MassLynxV4.1数据处理软件;H-2050R高速冷冻离心机:湖南湘仪实验室仪器开发有限公司产品;SCI-RM涡旋混合器:美国Scientific Industries公司产品;BSA224S电子天平:德国Sartorius公司产品;Millipore超纯水处理系统:德国Merck公司产品。

1.2 材料与试剂

Waters BEH C18柱:美国Waters公司产品;乙腈、正己烷、甲醇、异丙醇:色谱级,美国Fisher公司产品;甲酸、乙酸铵、乙酸:色谱级,上海安谱实验科技股份有限公司产品;乙酸钠、硫酸镁、石墨化碳黑吸附剂(GCB)、N-丙基乙二胺固相吸附剂(PSA)、十八烷基键合硅胶吸附剂(C18):上海安谱实验科技股份有限公司产品;超纯水:由Millipore超纯水处理系统制备;多菌灵、多菌灵-D3、噻虫嗪、吡虫啉、噻虫胺、噻唑膦、戊唑醇-D9、甲霜灵、戊唑醇、苯醚甲环唑农药标准溶液(1 000 mg/L):天津阿尔塔科技公司产品;0.22 μm有机滤膜:天津艾杰尔公司产品。

1.3 实验条件

1.3.1 色谱条件 Waters BEH-C18色谱柱(2.1 mm×100 mm×1.7 μm);柱温40 °C;流动相:A为0.1%甲酸-水-5 mmol/L乙酸铵溶

液,B为0.1%甲酸-甲醇-5 mmol/L乙酸铵溶液;梯度洗脱程序:0~0.25 min(98%A),0.25~16 min(98%~1%A),16~17 min(1%A),17~18 min(1%~98%A),18~20 min(98%A);流速0.35 mL/min;进样量5 μL。

1.3.2 质谱条件 电喷雾离子源正离子模式(ESI⁺),多反应监测(MRM)模式,电离电压1 kV,离子源温度120 °C,脱溶剂气温度420 °C,脱溶剂气流速650 L/h,锥孔气体流速50 L/h。

1.4 样品前处理

称取适量干姜片原料,粉碎,过20目筛,充分混合均匀;姜油树脂经60 °C加热后,充分摇匀,待称量。

分别称取2 g姜粉、0.5 g姜油树脂、0.5 g生姜精油样品,加入20 mL 1%乙酸乙腈、20 mL超纯水、2 mL正己烷,置于涡旋混合器,以1 800 r/min涡旋混合3 min,以4 000 r/min离心5 min,弃去正己烷层及悬浮杂质;移取20 mL萃取液,加入QuEChERS净化盐包(6 g硫酸镁,1.5 g乙酸钠),迅速摇匀后离心;移取8 mL乙腈层至QuEChERS净化管(1 200 mg MgSO₄,400 mg GCB,400 mg PSA,400 mg C18)中,涡旋混合3 min,以4 000 r/min离心5 min,精确吸取1 mL上清液,加入40 μL(0.1 mg/kg)同位素内标溶液,涡旋混匀后过0.22 μm滤膜,待UPLC-MS/MS检测。

1.5 标准溶液配制

分别量取100 μL 1 000 mg/L多菌灵、噻虫嗪、吡虫啉、噻虫胺、噻唑膦、甲霜灵、戊唑醇、苯醚甲环唑标准溶液,用乙腈定容至25 mL,配制成4 mg/L混合标准工作溶液,于-18 °C密封保存,备用,即得标准储备溶液。

分别量取25 μL 100 mg/L多菌灵-D3、戊唑醇-D9标准溶液,用乙腈定容至25 mL,配制成0.1 mg/L混合标准工作溶液,于-18 °C密封保存,备用,即得同位素内标混合工作溶液。

基质标准工作溶液配制:将阴性样品经优化的提取净化方法处理后,得到空白基质溶液;用空白基质溶液稀释混合标准储备液,配制成1、2、4、8、16、20、24、32 μg/L基质标准工作溶液,现用现配。

1.6 基质效应

采用液相色谱-串联质谱测定时,样品中的

内源性或外源性物质会影响分析物的离子化效率,使目标物的质谱响应升高或降低,从而产生基质效应(matrix effect, ME)^[20-21],对结果准确性产生影响。参考文献[22]的方法进行基质效应评价,示于式(1):

$$Me = \left(\frac{\text{基质匹配标准曲线的斜率} - 1}{\text{溶剂标准曲线的斜率}} \right) \times 100\% \quad (1)$$

其中, $Me > 0$ 为基质增强效应,会造成实际测量值偏高; $Me < 0$ 为基质抑制效应,会导致实际测量值偏低; $|Me| < 20\%$ 表示弱基质效应,可忽略; $20\% \leq |Me| \leq 50\%$ 表示中等基质效应; $|Me| > 50\%$ 表示强基质效应。当 $|Me| \geq 20\%$ 时,需使用基质标准曲线作为回归方程校准测量值,以消除基质效应的影响^[23-24]。

1.7 慢性膳食摄入风险评估

依照农药毒理学数据对人体摄入膳食量进行慢性膳食风险评估,示于式(2):

$$\%ADI = \frac{C \times F}{b.w. \times ADI} \times 100 \quad (2)$$

式中, C 为农药残留中位值; F 为姜油树脂或姜精油摄入量,按酱油类计算^[25]; $b.w.$ 为我国平均体重^[26]; ADI 为每日允许摄入量,各农药的 ADI 数值来源于国家标准 GB2763—2021^[27],姜油树脂和姜精油的每日膳食摄入量采用最大风险值^[25]。

2 结果与讨论

2.1 样品提取及净化方式优化

姜油树脂、姜精油是生姜切片、干燥、萃取、浓缩而成^[2-3],其基质比生姜复杂。为降低基质干扰,提取溶剂及净化方式的选择尤为重要。本研究对比了3种不同萃取方式及净化方式的净化效果,分别是:1) 环己烷-乙酸乙酯(1:1, V/V)萃取,凝胶净化色谱(GPC)净化;2) 1%乙酸-乙腈萃取,QuEChERS净化;3) 乙腈-水-正己烷萃取,QuEChERS净化,结果示于图1。第1种方式萃取净化后的基质效应非常明显,样品回收率在52%~83%之间,不满足相关标准要求^[28],主要原因可能是GPC更适用于去除油脂、糖类等大分子物质,而姜酚、姜酮类化合物以及精油中的组成成分均属于小分子化合物,与目标农药的分子质量接近,因此净化效果较差;第2种方式萃取净化后的待测液颜色仍

较深,样品回收率在51%~77%之间,不满足相关标准要求,主要原因可能是姜油树脂和姜精油的基质复杂,部分姜酮、姜酚类化合物以及色素物质溶于乙腈,即使将QuEChERS净化材料用量增加至1200 mg MgSO₄+400 mg GCB+400 mg PSA+400 mg C18,仍不能吸附全部杂质,净化效果较差;第3种方式萃取净化后的待测液颜色较浅,样品回收率在72%~90%之间,符合相关标准要求,噻虫胺、噻虫嗪和吡虫啉的回收率显著提升。因此,本研究选择第3种萃取和净化方式。

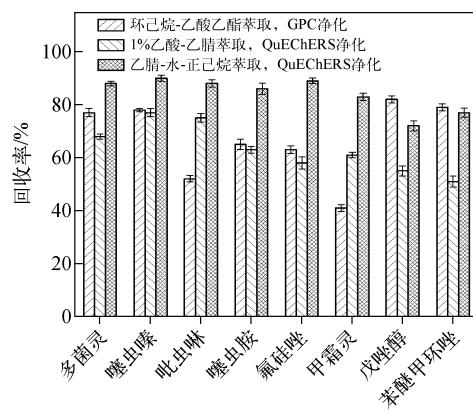


图1 不同提取净化方式对8种农药回收率的影响

Fig. 1 Effect of different extraction and purification methods on the recoveries of eight pesticides

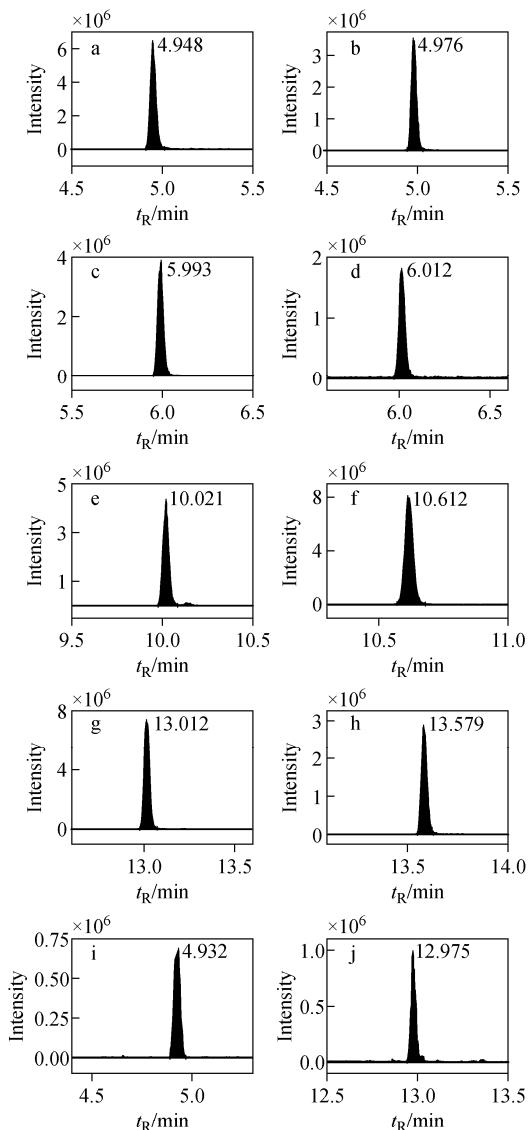
2.2 色谱条件优化

本研究考察了3种色谱流动相体系,分别为:1) A为0.1%甲酸-乙腈,B为0.1%甲酸-水;2) A为0.1%甲酸-甲醇,B为0.1%甲酸-水;3) A为0.1%甲酸-甲醇-5 mmol/L乙酸铵,B为0.1%甲酸-水-5 mmol/L乙酸铵。结果表明,前2种流动相体系检测标准样品的响应值和精密度较差,而添加少量乙酸铵能促进目标物的电离,显著提升了质谱信号强度,因此选择第3种流动相体系。8种农药标准溶液及2种内标溶液的MRM谱图示于图2。

2.3 质谱条件优化

分别配制8种农药的标准溶液(0.5 mg/L),以注射泵直接进样,采用电喷雾正、负离子模式扫描,优化质谱锥孔电压、碰撞电压以及最优离子对。结果表明,8种目标化合物在ESI⁺模式下的响应均显著高于ESI⁻模式。在ESI⁺模式

下,确定各农药的母离子 $[M+H]^+$ 。在最优化孔电压下扫描二级质谱图,优化碰撞电压,并筛选2个相对丰度较高且稳定的特征碎片离子分别作为定性、定量离子。最佳质谱参数列于表1。



注: a. 多菌灵; b. 噻虫嗪; c. 吡虫啉; d. 噻虫胺;
e. 噻唑膦; f. 甲霜灵; g. 戊唑醇; h. 苯醚甲环唑;
j. 多菌灵-D3(内标); k. 戊唑醇-D9(内标)

图2 8种农药标准溶液和2种内标溶液的MRM谱图

Fig. 2 MRM spectra of 8 pesticide standard solutions and 2 internal standard solutions

2.4 基质效应评价

基质效应评价结果列于表2。干姜片、姜精油、姜油树脂中8种农药的检测基质效应在-17.45%~-56.08%之间,多表现为中等抑制效应。

为消除基质效应的影响,采用基质匹配标准曲线内标法对样品的农药残留进行定量分析^[23,29]。

2.5 线性范围、检出限和定量限

在定量分析过程中,多菌灵、噻虫嗪、吡虫啉、噻虫胺以多菌灵-D3为内标物,噻唑膦、甲霜灵、戊唑醇和苯醚甲环唑以戊唑醇-D9为内标物,以目标物和内标物的浓度比为横坐标,响应面积比为纵坐标绘制标准曲线。8种农药在1~32 μg/L浓度范围内的线性关系良好,相关系数(R^2)均在0.995 0~0.999 8之间。分别以3倍和10倍信噪比(S/N)所对应的浓度确定检出限(LOD)和定量限(LOQ),结果列于表2。

2.6 加标回收率及精密度验证

本研究选择干姜片、姜精油、姜油树脂的空白基质样品,分别添加0.1、1.0、2.0 mg/kg 3种浓度水平的8种农药,每一浓度做6次平行实验,考察方法的回收率和精密度,结果列于表3。干姜片、姜精油、姜油树脂中8种农药的3个加标水平的平均回收率在70%~119%之间,相对标准偏差(RSD)<20%,方法回收率满足相关要求^[28]。

2.7 实际样品检测

利用本方法测定不同厂家的20份干姜片、15份姜油树脂和15份姜精油样品,结果列于表4。噻虫嗪、吡虫啉、噻虫胺阳性样品的检出率较高,平均值分别为56%、58%、52%。其中,残留量大于1 mg/kg的样品量分别占12%、16%、10%,最高残留量分别为2.16、1.92、2.01 mg/kg;其他5种农药的检出率低于20%,且残留量较低。鉴于目前各国家和组织尚未明确规定姜油树脂、姜精油类植物提取物产品的最高残留限量(MRL)标准,建议根据农药的ADI值、提取物原料的MRL标准并结合提取浓缩因子,制定各类植物提取物的MRL标准。

2.8 慢性膳食风险评估

国家标准^[26]规定,噻虫嗪、吡虫啉、噻虫胺的每日允许摄入量分别为0.08、0.06和0.10 mg/kg·b.w.,本研究基于实际样品中农药残留中位数计算干姜片、姜精油和姜油树脂中噻虫嗪、吡虫啉、噻虫胺慢性膳食摄入风险,结果列于表5。3种农药的慢性膳食风险评估结果在0.01%~0.23%之间,慢性摄入风险远低于

表 1 8 种农药和 2 种内标溶液的最佳质谱参数

Table 1 Optimal MS/MS parameters of 8 pesticides and 2 internal standard solutions

化合物 Compound	保留时间 Retention time/min	母离子 Parent ion (m/z)	子离子 Product ion (m/z)	锥孔电压 Cone voltage/V	碰撞电压 Collision voltage/V
多菌灵	4.95	192.1	132.1	28	30
			160.0 *	18	30
多菌灵-D3(内标)	4.93	195.1	132.1 *	20	20
			160.0	15	20
噻虫嗪	4.98	291.9	181.0	20	25
			211.1 *	10	25
吡虫啉	5.99	255.9	175.1	18	25
			209.1 *	15	25
噻虫胺	6.01	249.9	131.9	15	20
			169.0 *	12	20
噻唑膦	10.02	284.2	104.0 *	20	25
			228.0	10	25
甲霜灵	10.61	280.0	192.1	18	28
			220.1 *	13	28
戊唑醇-D9(内标)	12.98	317.1	70.1 *	23	35
			125.0	40	35
戊唑醇	13.01	308	70.1	23	35
			125.0 *	40	35
苯醚甲环唑	13.58	406.0	251.0 *	25	40
			337.0	15	40

注: * 表示定量离子

表 2 8 种目标化合物的标准曲线、基质效应、检出限和定量限

Table 2 Linear equations, matrix effects, limits of quantification and limits of detection of 8 target compounds

化合物 Compound	样品基质 Sample matrix	线性方程 Linear equation	相关系数 Correlation coefficient (R^2)	基质效应 Matrix effect/%	检出限 LOD/ (mg/kg)	定量限 LOQ/ (mg/kg)
多菌灵	干姜片	$y=0.2599x-0.0211$	0.9994	-17.45	0.05	0.17
	姜精油	$y=0.4698x-0.0313$	0.9994	-18.92	0.08	0.27
	姜油树脂	$y=0.4616x-0.0140$	0.9998	-19.57	0.08	0.27
噻虫嗪	干姜片	$y=0.3398x-0.0082$	0.9995	-23.22	0.03	0.10
	姜精油	$y=0.2896x-0.0204$	0.9997	-28.57	0.10	0.30
	姜油树脂	$y=0.2398x-0.0122$	0.9984	-30.84	0.10	0.30
吡虫啉	干姜片	$y=0.2006x-0.0125$	0.9997	-19.76	0.08	0.27
	姜精油	$y=0.1353x-0.0059$	0.9992	-19.03	0.10	0.30
	姜油树脂	$y=0.1207x-0.0750$	0.9978	-21.15	0.10	0.30

续表 2

化合物 Compound	样品基质 Sample matrix	线性方程 Linear equation	相关系数 Correlation coefficient (R^2)	基质效应 Matrix effect/%	检出限 LOD/ (mg/kg)	定量限 LOQ/ (mg/kg)
噻虫胺	干姜片	$y=0.1726x-0.0045$	0.9995	-38.96	0.10	0.30
	姜精油	$y=0.1287x-0.0045$	0.9998	-54.21	0.16	0.53
	姜油树脂	$y=0.1334x-0.0099$	0.9965	-56.08	0.16	0.53
噻唑膦	干姜片	$y=4.1208x-0.2722$	0.9950	-21.32	0.03	0.10
	姜精油	$y=8.6200x-1.1221$	0.9989	-47.40	0.08	0.27
	姜油树脂	$y=6.5018x-0.3128$	0.9986	-49.87	0.08	0.27
甲霜灵	干姜片	$y=2.8635x-0.1135$	0.9996	-27.52	0.05	0.17
	姜精油	$y=5.3884x-0.1830$	0.9982	-48.12	0.08	0.27
	姜油树脂	$y=3.8332x+0.0469$	0.9977	-51.29	0.08	0.27
戊唑醇	干姜片	$y=1.2485x-0.1486$	0.9991	-29.64	0.08	0.27
	姜精油	$y=1.0937x+0.2028$	0.9973	-55.65	0.10	0.30
	姜油树脂	$y=1.3796x-0.0114$	0.9981	-54.47	0.10	0.30
苯醚甲环唑	干姜片	$y=1.0171x-0.0770$	0.9989	-23.77	0.08	0.27
	姜精油	$y=1.3754x-0.0557$	0.9980	-43.96	0.10	0.30
	姜油树脂	$y=0.9441x-0.0029$	0.9968	-49.53	0.10	0.30

表 3 8种农药在不同加标水平下的回收率及相对标准偏差($n=6$)

Table 3 Average recoveries and relative standard deviations (RSDs) of 8 pesticides at different spiking levels ($n=6$)

化合物 Compound	加标水平 Spiked/ (mg/kg)	干姜片 Dried ginger		姜精油 Ginger essential oil		姜油树脂 Ginger oleoresin	
		回收率 Recovery/%	相对标准偏差 RSD/%	回收率 Recovery/%	相对标准偏差 RSD/%	回收率 Recovery/%	相对标准偏差 RSD/%
		Recovery/%	RSD/%	Recovery/%	RSD/%	Recovery/%	RSD/%
多菌灵	0.1	95	5.8	86	16.7	95	19.2
	1.0	81	9.3	77	6.3	70	8.6
	2.0	86	5.0	82	3.2	76	4.7
噻虫嗪	0.1	115	19.0	119	15.9	99	13.4
	1.0	93	7.7	89	5.9	80	8.2
	2.0	90	6.4	86	3.0	75	5.1
吡虫啉	0.1	107	15.4	112	19.1	98	19.1
	1.0	88	10.4	91	7.5	75	8.4
	2.0	90	4.3	93	4.0	85	2.8
噻虫胺	0.1	103	10.3	117	15.6	100	13.9
	1.0	92	9.3	90	6.7	72	10.2
	2.0	89	6.6	91	3.8	85	6.4

续表 3

化合物 Compound	加标水平 Spiked/ (mg/kg)	干姜片		姜精油		姜油树脂	
		Dried ginger		Ginger essential oil		Ginger oleoresin	
		回收率 Recovery/%	相对标准偏差 RSD/%	回收率 Recovery/%	相对标准偏差 RSD/%	回收率 Recovery/%	相对标准偏差 RSD/%
噻唑膦	0.1	89	9.9	94	12.8	86	16.2
	1.0	82	7.7	86	6.9	79	8.1
	2.0	94	5.4	89	3.0	80	3.9
甲霜灵	0.1	101	10.3	109	14.8	72	7.9
	1.0	87	9.2	83	7.5	77	9.0
	2.0	72	6.1	77	4.1	70	5.6
戊唑醇	0.1	93	6.2	97	5.4	81	8.3
	1.0	96	5.2	107	8.1	92	8.0
	2.0	99	7.2	86	8.2	92	8.6
苯醚甲环唑	0.1	95	6.7	99	8.4	99	8.4
	1.0	103	8.9	110	7.6	94	7.6
	2.0	110	10.0	92	10.9	91	10.9

表 4 市售样品中 8 种农药残留检测

Table 4 Detection of 8 pesticide residues in commercial samples

化合物 Compound	干姜片		姜精油		姜油树脂	
	农药残留量 Pesticide residue/ (mg/kg)	检出率 Rate of positive sample/%	农药残留量 Pesticide residue/ (mg/kg)	检出率 Rate of positive sample/%	农药残留量 Pesticide residue/ (mg/kg)	检出率 Rate of positive sample/%
	Pesticide	sample/%	Pesticide	sample/%	Pesticide	sample/%
多菌灵	<0.05~0.09	15	<0.08~0.13	13	<0.08~0.16	13
噻虫嗪	<0.03~1.21	55	<0.10~1.59	53	<0.10~2.16	60
吡虫啉	<0.08~1.14	50	<0.10~1.73	60	<0.10~1.92	60
噻虫胺	<0.10~1.21	50	<0.16~1.81	53	<0.16~2.01	53
噻唑膦	<0.03~0.16	20	<0.08~0.42	13	<0.08~0.56	13
甲霜灵	<0.05~0.36	15	<0.08~0.46	13	<0.08~0.52	7
戊唑醇	<0.08~0.18	5	<0.10~0.36	7	<0.10~0.42	13
苯醚甲环唑	<0.08~0.19	15	<0.10~0.32	7	<0.10~0.39	14

100%，表明姜油树脂和姜精油中农药残留的慢性摄入风险较小。

3 结论

本研究建立了液-液萃取结合 QuEChERS 净化，并与 LC-MS/MS 方法联用测定姜油树脂、姜精油中 8 种农药残留。8 种农药在 1~32 μg/L 浓度范围内的线性关系良好，相关系数均大于 0.99，方法检出限为 0.03~0.16 mg/kg，

3 种不同加标水平下的回收率均在 70%~119% 之间，相对标准偏差均小于 20%。基于实际样品中农药残留中位值评估了干姜片、姜精油和姜油树脂中噻虫嗪、吡虫啉、噻虫胺的慢性膳食摄入风险，结果表明，姜油树脂和姜精油中农药残留的慢性膳食暴露风险较小。本研究为姜油树脂、姜精油中多种农药残留的检测、风险评估提供了高效可靠的检测方法，为植物提取物质量控制以及市场监管提供了技术参考。

表5 噻虫嗪、吡虫啉、噻虫胺慢性膳食摄入风险评估计算结果
Table 5 Calculation results for risk assessment of chronic dietary intake
of thiamethoxam, imidacloprid and clothianidin

样品 Sample	膳食量 Dietary amount/g	噻虫嗪		吡虫啉		噻虫胺	
		Thiamethoxam		Imidacloprid		Clothianidin	
		农药残留 中位数 Media pesticide residue/ (mg/kg)	慢性膳食 风险 Chronic dietary intake/%	农药残留 中位数 Median pesticide residue/ (mg/kg)	慢性膳食 风险 Chronic dietary intake/%	农药残留 中位数 Median pesticide residue/ (mg/kg)	慢性膳食 风险 Chronic dietary intake/%
干姜片	9.00	0.10	0.02	0.09	0.02	0.09	0.01
姜精油	9.00	0.81	0.15	0.92	0.22	0.87	0.12
姜油树脂	9.00	0.89	0.16	0.96	0.23	0.91	0.13

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