

# QuEChERS-三重四极杆串联质谱测定 柑橘中农药基质效应的方法研究

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**摘要:**【目的】针对柑橘中常用的农药, 采用QuEChERS方法和超高效液相色谱-三重四极杆串联质谱, 系统研究了其测定过程中的基质效应。【方法】柑橘样品利用乙酸-乙腈溶液( $V:V=1:99$ )提取、GCB净化, 采用甲醇-0.1%甲酸水溶液(含 $1\text{ mmol}\cdot\text{L}^{-1}$ 乙酸铵)作为流动相, 正离子多反应监测(MRM)模式, 基质外标法定量, 可以有效地减弱基质效应。【结果】10种农药在柑橘中主要是以基质抑制为主, 其基质效应范围为 $-18\%\sim 4\%$ , 在 $0.1\sim 100\text{ ng}\cdot\text{mL}^{-1}$ 内线性关系良好, 相关系数( $r$ )大于0.999, 检出限为 $0.08\sim 0.30\text{ }\mu\text{g}\cdot\text{kg}^{-1}$ , 回收率为 $70.5\%\sim 102\%$ , 相对标准偏差(RSD)为 $3.32\%\sim 5.76\%$ 。【结论】该方法快速简便、净化效果好, 适合柑橘中常见农药的快速测定。

关键词: 柑橘; QuEChERS; 三重四极杆串联质谱; 基质效应

中图分类号: S666

文献标志码: A

文章编号: 1009-9980(2021)04-0613-10

## A study on matrix effect of QuEChERS-triple quadrupole tandem mass spectrometry in determination of pesticides in *Citrus*

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**Abstract:** 【Objective】Currently, profenofos, chlorpyrifos, difenoconazole, imidacloprid, prochloraz, acetamiprid, carbendazim, enoylmorpholine, pyraclostrobin, malathion, etc. are commonly used in citrus cultivation. Pesticides with higher detection frequency, such as enoylmorpholine, have no limit requirements and relevant measurement method standards in China's national standards. On the other hand, the determination methods of pesticides such as prochloraz and pyraclostrobin stipulated in the national standards are gas chromatography and gas chromatography-mass spectrometry, respectively, and the detection sensitivity is not added, and the operation of these methods is complicated. The standard method for the determination of fresh amine requires the high-temperature hydrolysis of prochloraz and liquid-liquid extraction after GC-ECD determination, and pyraclostrobin needs to measure after multiple purifications using C18, Carb and NH<sub>2</sub> solid phase extraction columns. The operation steps are complicated, time-consuming and laborious. In the operation process, it is necessary to use toluene with high toxicity, which is harmful to the environment and the operator. With the continuous development of QuEChERS technology combined with ultra-high performance liquid chromatography-triple quadrupole mass spectrometer, it is currently widely used in the determination of a variety of pesticide residues in fruits and vegetables due to its quick and easy operation and high sensitivity. However, for ultra-high performance liquid chromatography-triple quadrupole mass spectrometer, matrix effect is a com-

收稿日期: 2020-06-23

接受日期: 2020-12-26

基金项目: 云南省重大专项计划项目(2018BC005-04); 2019年国家农产品质量安全风险评估项目(GJFP2019012)

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mon phenomenon in mass spectrometry analysis, especially the complex matrix of citrus, due to the more pigment and essential oil content, its matrix effect is stronger, seriously affecting the accurate quantification of related pesticides in citrus. The matrix effects in the determination of commonly pesticides used in citrus were systematically studied by using the QuEChERS method and ultra-high performance liquid chromatography-triple quadrupole tandem mass spectrometry. **【Methods】**After the citrus sample was fully crushed and homogenized by an electric mixer, 5.00 g of sample was accurately weighed in a 50 mL centrifuge tube, then 10 mL of acetic acid-acetonitrile solution ( $V:V=1:99$ ) was added, and it was vortexed for 5 min. 3.0 g NaCl was added, and then it was vortexed for 1 min, centrifuged at  $5000\text{ r}\cdot\text{min}^{-1}$  for 3 min, 2 mL of supernatant was taken in a 10 mL centrifuge tube, add 200 mg of anhydrous magnesium sulfate and 80 mg of GCB filler were added, and the mix was vortexed to extract 10 s, centrifuged at  $5000\text{ r}\cdot\text{min}^{-1}$  for 3 min, and the supernatant was filtered by  $0.22\text{ }\mu\text{m}$  microporous membrane for analysis. Methanol-0.1% formic acid aqueous solution (containing  $1\text{ mmol}\cdot\text{L}^{-1}$  ammonium acetate) was used as the mobile phase, and the positive ion multiple reaction monitoring (MRM) mode was used, and the matrix was quantified by external standard method. **【Results】**In the extraction process, the appropriate amount of acetic acid could maintain the acidity of the extract environment and increase the extraction efficiency of related acidic pesticides. In positive ion mode, the addition of formic acid and ammonium acetate could enhance the mass spectrometry response of pesticides to a certain extent. The 10 pesticides in citrus were mainly based on the matrix inhibitory effect. Compared with methanol-water solution as the mobile phase, the addition of formic acid and ammonium acetate could reduce the matrix effects of 10 pesticides to a certain extent. GCB and PSA had better effects on reducing the strong matrix effects of malathion, acetamiprid, enoilmorpholine and other pesticides, while GCB had a better effect on eliminating the matrix effects of malathion and enoilmorpholine. The citrus blank matrix extract was used to prepare 10 pesticide standard solutions of different concentrations, linear regression analysis was performed based on peak area and concentration; at the same time, 10 pesticides with appropriate concentration were added to the citrus blank matrix respectively for determination, through continuous decrease of the spiked concentration, and the spiked concentration corresponding to the signal and noise ratio (S/N) of 3 times and 10 times was used as the detection limit and quantitation limit. 10 pesticides were in the range of 0.1-100.0 ng. The correlation coefficient in the concentration range of mL was better, and the limit of quantification was better, which could meet the needs of determination of pesticide residues in citrus. According to the different quantitation limits of 10 pesticides, the quantitation limit, 5-fold and 10-fold quantitation limits were used as the three additive concentration levels for the recovery test and precision determination. The citrus blank matrix extract was used to prepare the matrix standard solution to minimize matrix effect. The six parallel experiments were performed for each spiked concentration level, with average recovery and relative standard deviation. The average recovery rate of 10 pesticides ranges from 70.5% to 102%, and the relative standard deviation ranged from 3.32% to 5.76%. **【Conclusion】**The use of acidic acetonitrile extraction, GCB purification and methanol-0.1% formic acid aqueous solution (containing  $1\text{ mmol}\cdot\text{L}^{-1}$  ammonium acetate) as the mobile phase could effectively reduce the matrix effect. The method was quick and simple, with good accuracy and precision, and was suitable for the rapid determination of pesticide residues commonly used in citrus samples.

**Key words:** *Citrus*; QuEChERS; Triple quadrupole tandem mass spectrometry; Matrix effect

柑橘是橘、柑、橙、金柑,柚、枳等的总称,是我国常见的水果。近年来,随着消费量的逐年增大,种植规模不断扩大,品种也不断增多。为了增加柑橘产量、提高品质,大量的杀虫剂和杀菌剂也普遍用于柑橘的种植过程中,目前非科学施药和滥用药的现象较为突出,再加上采收安全间隔期意识的薄弱,导致了最终采收柑橘样品中部分农药检出频次较高甚至不符合GB 2763—2019《食品安全国家标准 食品中农药最大残留限量》中对于柑橘中农药残留的限量要求。

根据笔者实验室前期对于大量柑橘样品中相关农药的测定结果,丙溴磷、毒死蜱、苯醚甲环唑、吡虫啉、咪鲜胺、啉虫脒、多菌灵、烯酰吗啉、吡唑醚菌酯、马拉硫磷等在柑橘中的检出频次较高,部分农药如柑橘中的烯酰吗啉等在我国GB 2763—2019《食品安全国家标准 食品中农药最大残留限量》中还没有限量要求及相关的测定方法标准;另一方面,GB 2763—2019中规定的咪鲜胺和吡唑醚菌酯等农药的测定方法分别为气相色谱法和气相色谱-质谱法,检测的灵敏度不高,而且这些方法的操作复杂,如咪鲜胺的标准测定方法中需要将咪鲜胺高温水解、经液液萃取后GC-ECD测定<sup>[1]</sup>,而吡唑醚菌酯则需分别利用C<sub>18</sub>、Carb和NH<sub>2</sub>固相萃取柱的多次净化后测定<sup>[1]</sup>,操作步骤复杂,费时费力,且在操作过程中需要使用毒性较大的甲苯,对于环境和操作者的危害较大。

QuEChERS技术结合超高效液相色谱-三重四极杆质谱仪已广泛应用于果蔬中多种农药残留测定<sup>[2-4]</sup>。但是,对于超高效液相色谱-三重四极杆质谱仪来说,基质效应是质谱分析中普遍存在的现象<sup>[5-7]</sup>,特别是柑橘的基质复杂、含有较多的色素以及香精油,其基质效应较强,严重影响了柑橘中相关农药的准确定量<sup>[8-9]</sup>。

为了快速准确地测定柑橘中的农药残留,笔者采用QuEChERS-超高效液相色谱-三重四极杆串联质谱,对柑橘中检出频次较高的10种农药进行QuEChERS前处理条件优化,以研究其基质效应,并建立有效可靠的QuEChERS-UHPLC-MS/MS测定方法,研究结果可为柑橘中农药残留定性和定量、限量标准制修订提供依据。

## 1 材料和方法

### 1.1 仪器与试剂

API4000三重四极杆串联质谱仪(美国AB Sciex公司);1290超高效液相色谱仪(美国Agilent公司);ACQUITY UPLC BEH C<sub>18</sub>,1.7 μm,1 mm × 50 mm 色谱柱(美国Waters公司)。

乙腈、甲醇(色谱纯,德国Merck公司);无水MgSO<sub>4</sub>、NaCl(分析纯,国药集团化学试剂有限公司);乙酸、甲酸、乙酸铵(色谱纯,中国迪马科技公司);ProElut C<sub>18</sub>、PSA、GCB、Florisil填料(50 μm,中国迪马科技公司);纯净水(杭州娃哈哈公司);丙溴磷、毒死蜱、苯醚甲环唑、吡虫啉、咪鲜胺、啉虫脒、烯酰吗啉、吡唑醚菌酯、马拉硫磷标准物质(1000 μg·mL<sup>-1</sup>,农业农村部环境保护科研监测所);多菌灵标准物质(500 μg·mL<sup>-1</sup>,农业农村部环境保护科研监测所)。

柑(金柑)、橘(砂糖橘)、橙(冰糖橙)、柚子(沙田柚)、柠檬(尤力克)等柑橘试验材料均购于云南省昆明市当地农贸市场。

### 1.2 方法

1.2.1 标准溶液的配制 分别将丙溴磷、毒死蜱、苯醚甲环唑、吡虫啉、咪鲜胺、啉虫脒、烯酰吗啉、吡唑醚菌酯、马拉硫磷标准物质利用甲醇稀释为40 μg·mL<sup>-1</sup>质量浓度的标准储备液,多菌灵标准物质利用甲醇稀释为20 μg·mL<sup>-1</sup>的标准贮备液,各农药再分取适当体积,用甲醇稀释得到10 μg·mL<sup>-1</sup>的10种农药混合标准溶液,4℃下避光保存。

1.2.2 样品前处理 柑橘样品经电动搅拌机充分粉碎匀浆均匀后,于50 mL离心管中准确称取5.00 g样品,再加入10 mL乙酸-乙腈溶液(V:V=1:99),涡旋提取5 min后,加入3.0 g NaCl,涡旋1 min后,5000 r·min<sup>-1</sup>高速离心3 min后,取上清液2 mL于10 mL离心管中,加入200 mg无水硫酸镁和80 mg GCB填料,涡旋提取10 s后5000 r·min<sup>-1</sup>离心3 min,上清液经0.22 μm微孔滤膜过滤后待分析。

1.2.3 色谱条件 流动相A为甲醇,B为1 mmol·L<sup>-1</sup>乙酸铵水溶液(含0.1%甲酸),梯度洗脱条件:0~2.5 min,5% A~95% A,2.5~5 min,95% A~95% A,5~5.2 min,95% A~5% A,5.2~8.0 min,5% A;流速为200 μL·min<sup>-1</sup>;柱温35℃;进样量1 μL。

1.2.4 质谱条件 采用ESI正离子多反应监测模式(MRM),其中气帘气流速为20 L·h<sup>-1</sup>,雾化气流速为55 L·h<sup>-1</sup>,辅助气流速为55 L·h<sup>-1</sup>,辅助加热温度为550℃,喷雾电压为5500 V。10种农药的质谱参数

参考文献[10-13]并根据实验室仪器条件进行相应的优化(表1)。

表 1 柑橘中 10 种农药的质谱参数

Table 1 Mass spectrometric parameters of 10 pesticides in citrus

农药 Pesticide	保留时间 Retention time/min	母离子 Precursor ion/(m/z)	子离子 Product ion/(m/z)	去簇电压 Declustering potential/V	碰撞电压 Collision energy/V
多菌灵 Carbendazim	2.52	192.1	160.1*/132.1	56.0/56.0	27.0/41.0
吡虫啉 Imidacloprid	2.67	256.2	175.1*/209.0	61.0/61.0	23.0/23.0
啉虫脒 Acetamiprid	2.79	223.1	126.2*/99.1	56.0/56.0	29.0/47.0
烯酰吗啉 Dimethomorph	3.56	388.1	301.0*/165.1	66.0/66.0	25.0/45.0
马拉硫磷 Malathion	3.60	331.0	127.1*/99.1	46.0/46.0	17.0/31.0
吡唑啉菌酯 Pyraclostrobin	3.77	388.0	194.0*/163.0	31.0/31.0	19.0/29.0
咪鲜胺 Prochloraz	3.82	376.2	308.1*/70.0	41.0/41.0	17.0/37.0
苯醚甲环唑 Difenoconazole	3.85	406.2	251.1*/337.1	76.0/76.0	37.0/28.0
丙溴磷 Profenofos	3.99	375.2	305.1*/347.0	75.0/75.0	26.0/16.0
毒死蜱 Chlorpyrifos	4.13	350.0	198.0*/96.9	41.0/41.0	25.0/41.0

注:\*. 定量离子。

Note: \*. Quantitative ion.

1.2.5 基质效应考察 基质效应的测定方法和评判标准参照文献[14]中的方法,其计算公式为:

$$ME/\% = \left( \frac{S_m}{S_s} - 1 \right) \times 100$$

其中,  $S_m$  和  $S_s$  分别表示利用橘、柑、橙、柚子、柠檬等柑橘类水果空白基质提取液配制的标准曲线和溶剂配制的标准曲线斜率。当  $ME < 0$  时表示基质抑制效应,  $ME > 0$  时表示基质增强效应,其中当  $ME$  的绝对值为 0%~20% 时为弱基质效应;  $ME$  的绝对值为 20%~50% 时为中等基质效应; 当  $ME$  的绝对值 > 50% 时为强基质效应。

溶剂标准曲线配制方法: 采用  $10 \mu\text{g} \cdot \text{mL}^{-1}$  的 10 种农药混合标准溶液, 分别利用乙腈将其稀释为 0.01、0.05、0.1、0.5 和  $1.0 \mu\text{g} \cdot \text{mL}^{-1}$  标准曲线。基质标准曲线配制方法: 采用  $10 \mu\text{g} \cdot \text{mL}^{-1}$  的 10 种农药混合标准溶液, 分别吸取 0.001、0.005、0.01、0.05 和 0.1 mL, 利用氮气吹干后, 分别加入 1 mL 柑橘类水果(橘、柑、橙、柚子、柠檬等)的空白基质提取溶液混匀后过  $0.22 \mu\text{m}$  滤膜, 配制成质量浓度为 0.01、0.05、0.1、0.5 和  $1.0 \mu\text{g} \cdot \text{mL}^{-1}$  的基质标准曲线。

## 2 结果与分析

### 2.1 色谱条件的优化

本实验利用乙腈和柑橘空白基质乙腈提取液分别将  $10 \mu\text{g} \cdot \text{mL}^{-1}$  的 10 种农药混合标准溶液稀释配制为 0.01、0.05、0.1、0.5 和  $1.0 \mu\text{g} \cdot \text{mL}^{-1}$  标准曲线进样, 分

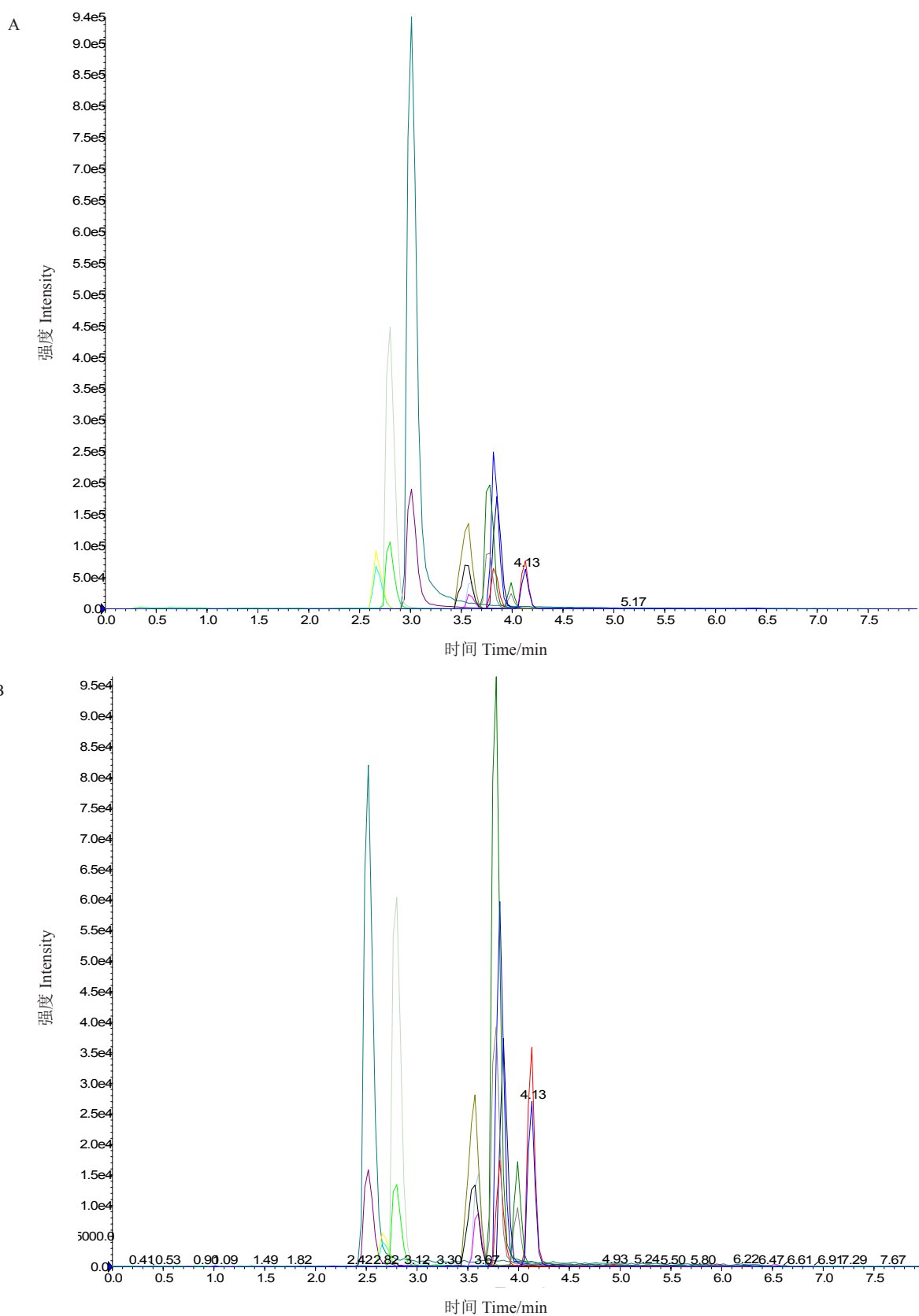
别比较了甲醇-水和甲醇-0.1% 甲酸水溶液(含  $1 \text{mmol} \cdot \text{L}^{-1}$  乙酸铵) 2 种常用流动相相对于各种农药基质效应的响应情况, 如图 1 所示。

由图 2 可知, 甲酸和乙酸铵的加入可在一定程度上增强农药的质谱响应。10 种农药在柑橘中主要是以基质抑制效应为主, 相对于甲醇-水溶液作为流动相, 甲酸和乙酸铵的加入可以在一定程度上减弱 10 种农药的基质效应(绝对值)(图 1), 在甲醇-水为流动相时, 10 种农药的基质效应为 7%~94%, 烯酰吗啉、马拉硫磷、吡虫啉等存在较强的基质效应, 当采用甲醇-0.1% 甲酸水溶液(含  $1 \text{mmol} \cdot \text{L}^{-1}$  乙酸铵) 时, 基质效应范围为 1%~67%, 甲酸和乙酸铵的加入能够有效地减弱相关农药的基质效应, 但是对于马拉硫磷、烯酰吗啉、啉虫脒等农药, 仍然存在着较强的基质效应, 还需要借助相关的前处理净化技术进行研究。

### 2.2 提取方法的优化

本实验以加标回收的方式, 加标量为  $0.02 \text{mg} \cdot \text{kg}^{-1}$ , 分别比较了常用的乙腈和乙酸-乙腈溶液( $V:V=1:99$ )<sup>[15]</sup> 2 种提取溶液的提取效果(图 3)。采用纯乙腈提取时, 马拉硫磷、啉虫脒、苯醚甲环唑、烯酰吗啉、咪鲜胺和吡唑啉菌酯的提取率较低, 根据这些化合物的化学结构, 化合物呈现出中等酸性, 同时如马拉硫磷、啉虫脒在碱性环境中存在一定程度的水解, 因此, 1% 乙酸的加入可保持提取液环境的酸性并提高相关酸性农药的提取效率。





A 流动相为甲醇-水溶液;B 流动相为甲醇-0.1%甲酸水溶液(含  $1 \text{ mmol} \cdot \text{L}^{-1}$  乙酸铵)。

A. The mobile phase is methanol-aqueous solution; B. The mobile phase is methanol-0.1% formic acid aqueous solution (containing  $1 \text{ mmol} \cdot \text{L}^{-1}$  ammonium acetate).

图 1 不同流动相条件下柑橘中 10 种农药的色谱图

Fig. 1 Chromatograms of 10 pesticides in *Citrus* under the same mobile phase conditions

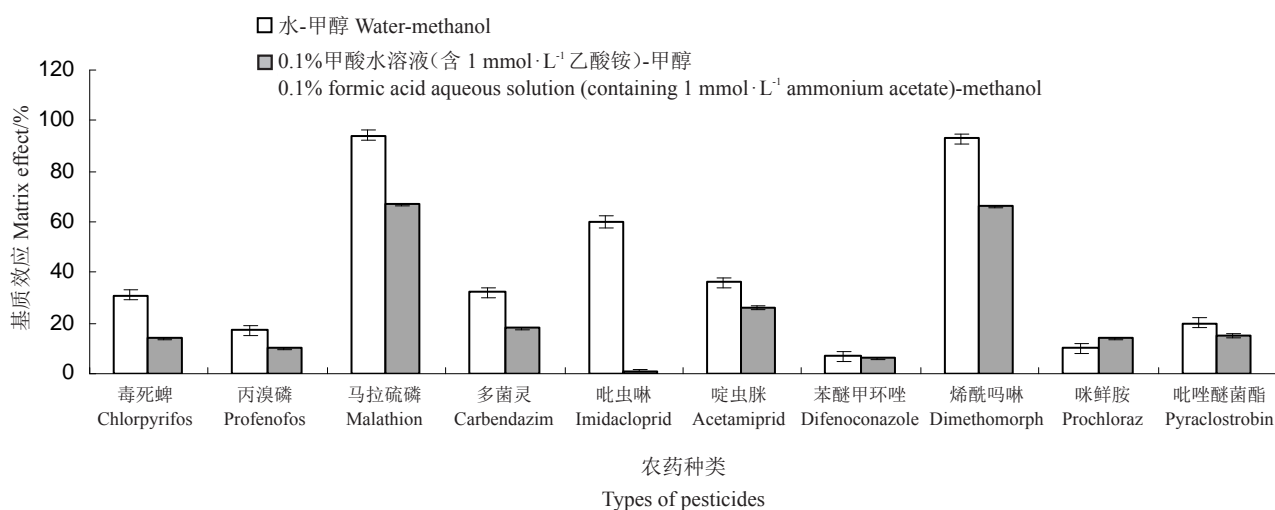


图 2 柑橘中 10 种农药在不同流动相中的基质效应

Fig. 2 Matrix effects of 10 pesticides in citrus in different mobile phases

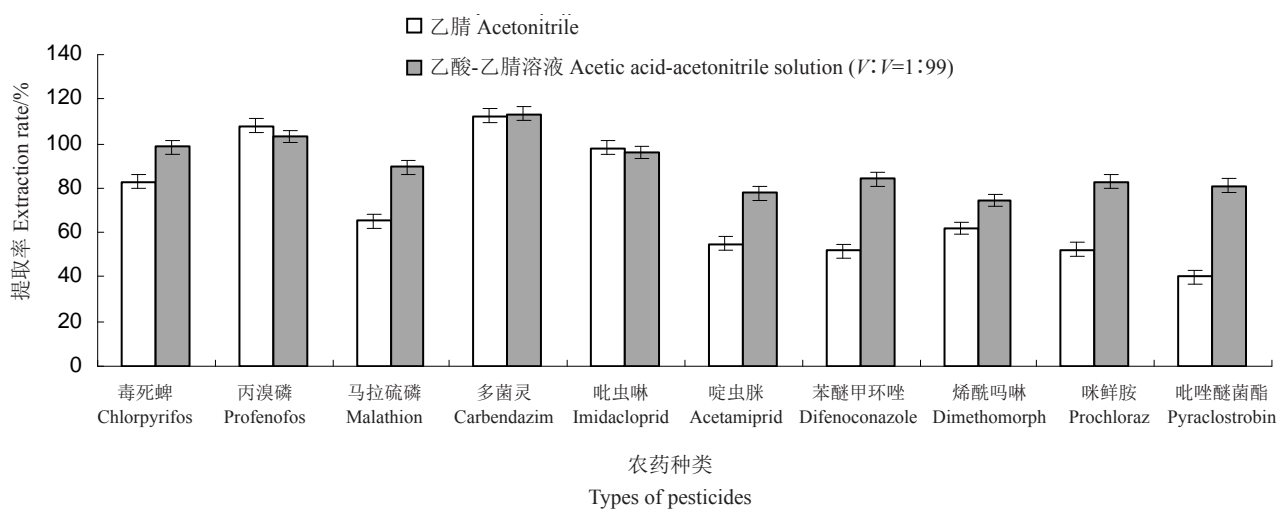


图 3 不同提取溶剂对柑橘中 10 种农药的提取效果

Fig. 3 Extraction effect of different extraction solvents on 10 pesticides in citrus

### 2.3 净化方法的选择

为了系统地研究不同净化填料对于柑橘中 10 种农药测定时的基质效应,选取了 C<sub>18</sub>、PSA、GCB、Florisil 填料,分别称取 500 mg 各填料,并加入 10 mL 柑橘空白提取溶液,经涡旋净化后,取上清液分别配制 0.01、0.05、0.1、0.5 和 1.0 μg·mL<sup>-1</sup> 的经不同填料净化的柑橘基质标准曲线,同时配制相同质量浓度的乙腈溶剂标准曲线,按照 1.2.5 的基质效应评价方法对 4 种净化填料的效果进行评价。

试验结果表明,除吡虫啉在 Florisil、GCB 和 PSA 净化填料中呈现出基质增强作用,其余农药在 4 种填料中均呈现出基质抑制效应,各农药的基质效应(绝对值)结果如图 4 所示,GCB 和 PSA 对于减

弱马拉硫磷、啶虫脒、烯酰吗啉等强基质效应的农药具有较好的效果,而 GCB 对于马拉硫磷和烯酰吗啉基质效应的消除效果更好,综合考虑,选取在 2 mL 乙酸-乙腈溶液(V:V=1:99)提取溶液中加入 80 mg GCB 净化填料。

### 2.4 线性范围和检出限

利用柑橘空白基质提取液配制不同质量浓度的 10 种农药标准溶液,以峰面积和质量浓度进行线性回归分析;同时,利用柑橘的空白基质,加入适当质量浓度的 10 种农药,采用以上方法进行测定,通过不断降低加标浓度,分别在 3 倍和 10 倍信噪比(S/N)下所对应的加标浓度作为检出限和定量限,如表 2 所示,10 种农药在 0.1~100 ng·mL<sup>-1</sup> 内相关系数较

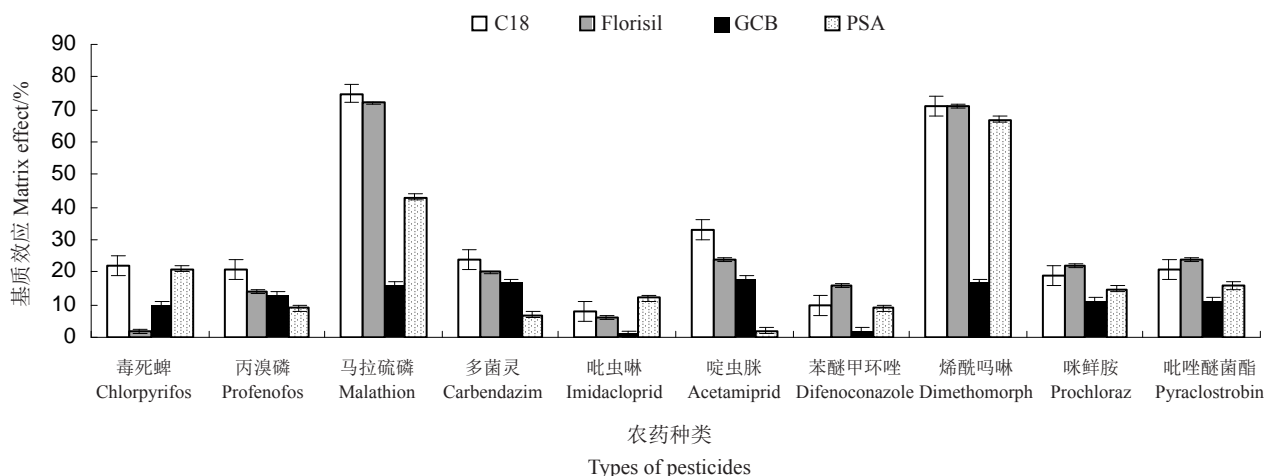


图4 不同净化填料对柑橘中10种农药的基质效应

Fig. 4 Matrix effect of different purification fillers on 10 pesticides in citrus

表2 柑橘中10种农药的线性范围、  
相关系数( $r$ )、检出限和定量限Table 2 Linear ranges, correlation coefficients ( $r$ ), limits of detection (LODs) and limits of quantitation (LOQs) of the 10 of pesticides in citrus

农药 Pesticide	线性范围 Linear range/ ( $\text{ng} \cdot \text{mL}^{-1}$ )	相关 系数 $r$	检出限 LOD/ ( $\mu\text{g} \cdot \text{kg}^{-1}$ )	定量限 LOQ/ ( $\mu\text{g} \cdot \text{kg}^{-1}$ )
多菌灵 Carbendazim	0.30~100	0.999 7	0.20	0.60
吡虫啉 Imidacloprid	0.20~100	0.999 3	0.15	0.40
啶虫脒 Acetamiprid	0.20~100	0.999 5	0.15	0.40
烯酰吗啉 Dimethomorph	0.10~100	0.999 4	0.08	0.20
马拉硫磷 Malathion	0.40~100	0.999 6	0.30	0.80
吡唑醚菌酯 Pyraclostrobin	0.10~100	0.999 8	0.08	0.20
咪鲜胺 Prochloraz	0.20~100	0.999 5	0.15	0.40
苯醚甲环唑 Difenoconazole	0.10~100	0.999 6	0.08	0.20
丙溴磷 Profenofos	0.10-100	0.999 4	0.08	0.20
毒死蜱 Chlorpyrifos	0.30~100	0.999 8	0.20	0.60

好,定量限较好,可满足柑橘中农药多残留的测定需求。

### 2.5 回收率和精密度

根据10种农药的不同的定量限,以定量限、5倍和10倍定量限作为3个添加浓度水平进行回收试验和精密度测定,采用柑橘空白基质提取液配制基质标准溶液,以尽量减弱基质效应。每个加标浓度水平分别进行6次平行试验,并计算平均回收率和相对标准偏差。由表3可知,10种农药的平均回收率为70.5%~102%,相对标准偏差为3.32%~5.76%。

### 2.6 净化填料回收效果验证

利用空白柑橘基质中加标回收实验,在 $0.02 \text{ mg} \cdot \text{kg}^{-1}$ 加标浓度下,分别比较了2 mL乙酸-乙腈( $V:V=1:99$ )提取溶液中加入20、40、60、80、100、120和140 mg GCB净化填料对于10种农药的吸附情况,结果如表4所示,随着GCB的加入量的增大,当加入量分别为20、40和60 mg时,10种农药,特别是马拉硫磷、多菌灵、吡虫啉、烯酰吗啉等农药的基质效应明显降低,加入量为80 mg时最佳,回收率为70.5%~102%,但是随着GCB加入量的继续增加,超过100 mg后,多菌灵、毒死蜱、丙溴磷、咪鲜胺、吡唑醚菌酯等农药会被GCB大量吸附,回收效果较差。因此,选择在2 mL乙酸-乙腈溶液( $V:V=1:99$ )提取溶液中加入80 mg GCB净化填料。

## 3 讨论

GCB是目前样品前处理过程中常用的净化填料之一,能够有效地去除色素、甾醇类和非极性干扰物<sup>[16-17]</sup>。柑橘中含有大量的类黄酮、酚酸等物质<sup>[18-20]</sup>,而柑橘皮中更是含有大量的萜烯类、醇类、醛类、酯类、酮类及酚类等挥发油成分<sup>[21-22]</sup>,这些成分在分析测定时都会带来较强的基质效应,而GCB的加入能够较好地吸附色素和挥发油等低极性化合物,从而有效地减小基质效应<sup>[23-24]</sup>;但是GCB对具有平面结构的农药具有一定的吸附能力<sup>[25]</sup>,如本实验中测定的多菌灵、毒死蜱、丙溴磷、咪鲜胺、吡唑醚菌酯等农药,都属于含有苯环的平面结构农药,易被过量

表3 柑橘中10种农药的回收率和相对标准偏差 ( $n=6$ )Table 3 Recoveries, relative standard deviations and matrix effect of 10 of pesticides in citrus ( $n=6$ )

农药名称 Pesticide name	加标水平 Spiked level/ ( $\mu\text{g}\cdot\text{kg}^{-1}$ )	回收率 Recovery/ % (RSD/%)	加标水平 Spiked level/ ( $\mu\text{g}\cdot\text{kg}^{-1}$ )	回收率 Recovery/ % (RSD/%)	加标水平 Spiked level/ ( $\mu\text{g}\cdot\text{kg}^{-1}$ )	回收率 Recovery/% (RSD/%)	基质效应 Matrix effect/%				
							橘 <i>Citrus reticulata</i>	柑 <i>Fortunella margarita</i>	橙 <i>Citrus sinensis</i>	柚子 <i>Citrus maxima</i>	柠檬 <i>Citrus limon</i>
多菌灵 Carbendazim	0.60	76.5 (5.33)	3.00	80.1 (4.53)	6.00	82.4 (4.13)	-16	-12	-14	-5	-10
吡虫啉 Imidacloprid	0.40	91.5 (4.29)	2.00	92.8 (3.91)	4.00	95.8 (3.51)	3	1	4	2	3
啶虫脒 Acetamiprid	0.40	70.5 (5.76)	2.00	71.4 (5.57)	4.00	75.1 (4.53)	-15	-16	-12	-8	-9
烯酰吗啉 Dimethomorph	0.20	77.6 (3.65)	1.00	79.5 (4.64)	2.00	81.4 (4.52)	-18	-15	-16	-10	-8
马拉硫磷 Malathion	0.80	79.5 (4.54)	4.00	83.6 (4.32)	8.00	84.6 (3.55)	-14	-12	-10	-5	-7
吡唑啉菌酯 Pyraclostrobin	0.20	75.3 (4.54)	1.00	78.4 (3.59)	2.00	83.6 (4.50)	-15	-11	-11	-9	-6
啉鲜胺 Prochloraz	0.40	80.7 (4.12)	2.00	82.6 (5.38)	4.00	85.9 (4.34)	-13	-11	-15	-9	-10
苯醚甲环唑 Difenoconazole	0.20	92.5 (3.43)	1.00	96.1 (4.61)	2.00	102.0 (4.32)	4	6	2	3	7
丙溴磷 Profenofos	0.20	82.3 (5.21)	1.00	85.5 (3.47)	2.00	89.1 (4.48)	-12	-7	-9	-5	-8
毒死蜱 Chlorpyrifos	0.60	75.2 (4.32)	3.00	74.6 (3.46)	6.00	76.6 (4.27)	-13	-11	-6	-7	-15

表4 不同GCB加入量对柑橘中10种农药的回收效果

Table 4 The recovery effect of 10 pesticides in *Citrus* with different GCB addition

农药名称 Pesticide name	GCB加入量 GCB add amount/mg						
	20	40	60	80	100	120	140
多菌灵 Carbendazim	80.8	82.8	89.2	85.6	83.2	70.3	68.9
吡虫啉 Imidacloprid	120.4	114.8	106.3	98.6	97.9	95.4	96.1
啶虫脒 Acetamiprid	69.2	73.8	85.8	87.9	88.3	85.2	87.0
烯酰吗啉 Dimethomorph	62.5	69.9	85.2	93.7	95.6	90.7	91.4
马拉硫磷 Malathion	70.1	75.3	83.2	81.5	84.3	85.2	80.8
吡唑啉菌酯 Pyraclostrobin	73.4	75.1	73.9	70.5	69.1	64.6	59.1
啉鲜胺 Prochloraz	79.3	85.9	84.7	83.3	79.3	67.9	62.5
苯醚甲环唑 Difenoconazole	114.0	107.0	101.0	102.0	106.0	99.8	103.0
丙溴磷 Profenofos	69.3	72.1	77.3	78.9	76.9	74.1	65.4
毒死蜱 Chlorpyrifos	73.9	77.2	76.9	79.1	73.3	67.1	63.7

GCB吸附,从而影响了其回收效果。因此,GCB的加入量应根据不同基质及不同农药而进行具体研究。

PSA也是目前常用的净化填料之一,能够有效去除柑橘样品中的糖类物质等<sup>[26]</sup>,在一定程度上可降低基质效应,本试验中PSA对于丙溴磷、多菌灵、啶虫脒和苯醚甲环唑等的去除基质效应效果较好,但是对于马拉硫磷、烯酰吗啉等农药的去除基质效应不佳,推测柑橘样品中的色素、挥发油等物质对于基质效应的影响较大。

超高效液相色谱-三重四极杆串联质谱分析过程中,流动相的选择对于色谱峰的峰形和响应强度影响较大。通常情况下,有机流动相常选择甲醇和乙腈,由于乙腈的毒性大,对于环境的污染较大,一般情况下首选甲醇作为有机流动相;对于相关的酸性农药,水相中加入适量的甲酸,能够较好地减弱出峰拖尾现象,同时加入适量乙酸铵,溶液中大量的铵根离子能够有效抑制质谱电离时 $[M+K]^+$ 和 $[M+Na]^+$ 离子的产生,伴随着甲酸中电离的大量 $H^+$ 离子,从



而促进[M+H]<sup>+</sup>离子的产生,可在一定程度上增强其质谱响应。

## 4 结 论

柑橘中的农药种类较多,基质效应复杂,在分析测定时常出现较强的基质效应。笔者针对柑橘中检出频次较高的10种农药,采用经典的QuEChERS前处理方法并根据柑橘的基质情况作相应的方法改进,利用超高效液相色谱-三重四极杆串联质谱,系统研究了不同提取溶液、净化填料以及流动相条件等对柑橘测定过程中基质效应的影响。结果表明,采用乙酸-乙腈溶液(*V:V=1:99*)提取、GCB的净化和甲醇-0.1%甲酸水溶液(含1 mmol·L<sup>-1</sup>乙酸铵)作为流动相,可以有效地减弱基质效应。方法快速简便,准确度和精确度较好,适合柑橘样品中常用农药残留的快速测定。

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