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高效液相色谱-串联质谱法测定葡萄和土壤中噻苯隆残留消解动态

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摘 要:**【目的】**评价噻苯隆在葡萄上的使用安全性。**【方法】**采用高效液相色谱-串联质谱法建立快速准确的噻苯隆在葡萄及土壤中的残留分析方法,进行2 a两地的消解动态及最终残留试验。**【结果】**建立的噻苯隆在葡萄及土壤中的残留分析方法表明:噻苯隆在0.01~1.00 mg·L^{-1}内线性关系良好,灵敏度、准确度均符合检测要求。采用该方法研究噻苯隆在葡萄中的消解动态,对葡萄及果园土壤的最终残留进行了测定,结果表明,噻苯隆在葡萄样品中的消解曲线均符合一级动力学方程,半衰期为0.8~5.7 d,最终残留试验表明,在到达安全间隔期14 d时噻苯隆在葡萄中最高残留量为0.020 0 mg·kg^{-1},远低于国家限量标准。**【结论】**噻苯隆在葡萄中属于易降解农药,降解较快。

关键词:葡萄;高效液相色谱-串联质谱;噻苯隆;最终残留;消解动态

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Study on decline and residue of thidiazuron in grape and soil by high performance liquid chromatography-tandem mass spectrometry

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Abstract: 【Objective】To understand the dynamic degradation and final residue of thidiazuron in grape fruit and grapery soil, respectively. We propose a high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) method to detect thidiazuron in grape fruit and grapery soil. The degradation of grape in the fruit followed the first order kinetic equation ($C_T=C_0e^{kT}$). Therefore, we compute the half-life ($T_{1/2}$) in the fruit of this plant growth regulators based on that equation. These results will provide guidance on the proper and safe use of this plant growth regulator for grape fruit. 【Methods】The trials were conducted in experimental fields where located in Henan province and Jiangsu province for past two years. In degradation dynamics experiment, six field plots formed one set, each with two grapevines. 0.1% thidiazuron wettable powder formulations (200 times dilution) were soaked to grape cluster (the half of the mature individuals) and each experiment was conducted in triplicate. The detailed method is described as follows. Firstly, the untreated plots were soaked with water under control. Secondly, the representative samples (grape fruit) were collected at 2 h, 1 d, 2 d, 3 d, 5 d, 7 d, 10 d, 14 d, 21 d and 28 d after thidiazuron treatment. Thirdly, the samples were placed in a freezer with -20 ℃ after sample preparation. Fourthly, the pesticide residue in the sample was collected after two hours on the day of applying was set

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as the original reside, the residue levels in the rest samples were compared with the original residue to get the degradation rate. Lastly, the dissipation equation was fitted to the first order kinetics equation using the SigmaPlot software. In final residue experiment, according to the maximum recommended dose and 1.5 times of the maximum recommended dose, 0.1% thidiazuron wettable powder were soaked to grape cluster 1 or 2 times with an interval of 10 days, grape samples and grapery soil were collected 7, 14 and 21 d after the last treatment. The Pre-treatment methods of thidiazuron residue determination: A 10 g grapery soil or grape fruit was weighed and put into centrifuge tube. A 5 mL ultra pure water and 20 mL acetonitrile was added into grapery soil samples, a 20 mL acetonitrile was added into grape samples. After shaken vigorously by Multi-tube Vortexer for 15 min, 3 g NaCl was added into centrifuge tube and the mixture was vortexed for 1 min. The sample solutions were separated by centrifuging with 6 000 $r \cdot min^{-1}$ for 5 mins, then the supernate filtered with 0.22 μm syring filter for HPLC- MS/MS analysis.【Results】In the concentration range of 0.01-1.0 $mg \cdot L^{-1}$, the matrix-matched calibration curves showed good linearity with correlation coefficients 0.999 6. The average recoveries of thidiazuron in the grape and soil were found between 84% and 108% at 0.01-0.50 $mg \cdot kg^{-1}$, with relative standard deviations (RSD) of 0.5%-1.9%. The limit to quantification (LOQ) was 0.01 $mg \cdot kg^{-1}$. The efficiency of our proposed method in measuring trace levels of thidiazuron was monitored by analyzing the samples collected from the field trials. In degradation dynamics experiment at Henan and Jiangsu experiment fields, the original residue of thidiazuron in the grape fruit were 0.039 1-0.017 4 $mg \cdot kg^{-1}$, the thidiazuron degradation rate found 7 d after treatment were 100%, 100%, 100%, 66.4% in grape fruit for 2014 and 2015. The half-life ($T_{1/2}$) of thidiazuron in grape fruit from Henan in 2014 and 2015 were 1.7 d and 1.7 d, and from Jiangsu were 0.8 d and 5.7 d. The final residue test showed that thidiazuron was readily degraded in grape and the final residue of thidiazuron in the grapery soil was less than in the grape. In 7, 14 and 21 d after the last pesticide soak, 95.1% of the grapery soil testing data is below LOQ (0.01 $mg \cdot kg^{-1}$), while the grape is 70.1% below LOQ (0.01 $mg \cdot kg^{-1}$), the highest residue in the grape and grapery soil of all final residue test date was 0.024 7 $mg \cdot kg^{-1}$ (2014, Jiangsu high-dose group, twice treatment, 7 d), 0.020 0 $mg \cdot kg^{-1}$ (2015, Henan low-dose group, twice treatment, 14 d), respectively.【Conclusion】The result indicated that thidiazuron is readily degreaded in grape and is safe to environment and soil. In addition, the thidiazuron maximum residue limit (MRL) in grape is 0.05 $mg \cdot kg^{-1}$ and the safety period of 0.1% thidiazuron wettable powder is 14 d.

Key words: Grape; High performance liquid chromatography-tandem mass spectrometry; Thidiazuron; Final residue; Degradation dynamics

噻苯隆(thidiazuron,TDZ)是一种新型高效的植物生长调节剂(plant growth regulators,PGRs),属苯基脲类衍生物,具有较强生物活性,可诱导植物细胞分裂,延缓植物衰老,增强植株抗逆性,促进植物光合作用,增加作物产量,改善作物品质[1],在我国应用广泛[2]。

近年来,噻苯隆制剂在水果类[3]、棉花[4]等作物上取得了良好的应用效果,各国已分别制订了噻苯隆在不同作物上的最大残留限量(MRL),美国和日本规定其在棉籽中的最大残留限量值均为0.3 $mg \cdot kg^{-1}$[5];韩国规定其在甜瓜、猕猴桃和西瓜中的最大残留限量是0.1 $mg \cdot kg^{-1}$,在葡萄中为0.2 $mg \cdot kg^{-1}$[6];中国规定其在葡萄、甜瓜、黄瓜中的最大残留限量是0.05 $mg \cdot kg^{-1}$[7]。噻苯隆应用在葡萄种植过程中,主要作用为提高葡萄坐果、增大果粒、增加产量[8-10]。目前噻苯隆在作物上的残留及消解动态研究较少,主要研究作物对象为棉花[11]、甜瓜[12]等,在葡萄上其他植物生长调节剂的残留动态已有报道[13],但未见噻苯隆在葡萄上的残留及消解动态研究报道。因此,通过研究0.1%噻苯隆可湿性粉剂在葡萄中的消解

动态规律及不同施药剂量、施药次数、采收间隔期与最终残留量的关系[14],为该植物生长调节剂的科学合理使用提供依据。

噻苯隆在果蔬中的残留量检测方法已有报道,黄玉南等[15]采用了高效液相色谱法测定水果中的噻苯隆残留量,在5种水果基质中回收率为84.3%~104.7%,乔成奎等[16]、闫震等[17]分别采用改进的QuEChERS方法进行前处理,高效液相色谱-串联质谱法测定水果中噻苯隆残留量,回收率分别为87%~102%、71.71%~111.69%。笔者采用高效液相色谱-串联质谱法配合固相萃取技术,针对检测样品量大、处理繁琐等问题,简化前处理步骤,建立一种快速、准确的噻苯隆在葡萄及土壤中残留量的检测方法,该方法快速、准确,能满足噻苯隆在葡萄及土壤中残留量的检测要求。

1　材料和方法

1.1　仪器和试剂

Agilent 1290-6460高效液相-三重四级杆串联质谱仪;电子分析天平0.01 g(奥豪斯仪器上海有限公司);电子分析天平0.000 1 g(Precisa Gravimetrics AG/Switzerla <0.001);台式高速冷冻离心机(上海力申科学仪器有限公司);多管涡旋振荡器(北京踏锦科技有限公司)。

噻苯隆标准品100 mg·L^{-1}(农业部环境质量监督测试中心);乙腈(Fisher Scientific,色谱纯),其他试剂为分析纯;滤膜(上海安谱科学仪器有限公司,0.22 μm有机相);实验室用水为超纯水(Mili-2Q)等。

供试农药0.1%噻苯隆可湿性粉剂为中国农业科学院郑州果树研究所研制,中国农业科学院植物保护研究所廊坊农药中试厂生产。

1.2　分析方法

1.2.1　样品前处理　称取样品(土壤、葡萄均为10 g)于50 mL离心管中,土壤样品加入5 mL水和20 mL乙腈,葡萄样品加入20 mL乙腈,涡旋震荡提取15 min,加入3 g NaCl盐析促使有机相和水相分层,涡旋1 min,将离心管置于6 000 r·min^{-1}的转速下离心5 min移取上清液经0.22 μm有机系膜过滤后,转入进样小瓶中,待检测。

1.2.2　仪器条件　(1)色谱条件。色谱柱:ZORB-AX SB-C18 2.1 mm×100 mm×1.8 μm,柱温:30 ℃,流动相:乙腈-0.1%甲酸水梯度洗脱,流速:0.3 mL·min^{-1},进样体积:5.0 μL。(2)质谱条件。电喷雾离子源(ESI):正离子模式;多反应监测(MRM)方式检测;干燥气温度350 ℃;干燥气流速8 L·min^{-1};噻苯隆的定性离子为m·z^{-1} 221.2→102(定量离子)和m·z^{-1} 221.2→127.8。

1.3　田间试验设计

田间试验设计参照《农药残留试验准则》进行[18]。

1.3.1　供试葡萄来源　分别为2种不同气候类型:河南省郑州市中牟县的葡萄品种'夏黑'和江苏省南京市江宁区秣陵镇的葡萄品种'白罗莎'。两地分2 a(2014、2015年)同时进行消解动态试验和最终残留试验。

1.3.2　消解动态试验　葡萄:根据推荐使用方法,在葡萄果实谢花期至果实膨大期施药(浸蘸果穗)1次,施药时应保证用于动态试验的葡萄均匀着药。消解动态施药剂量是最高推荐剂量的1.5倍即200倍液(5.00 g·kg^{-1}),施药后2 h,1 d、2 d、3 d、5 d、7 d、14 d、21 d、28 d采葡萄样品,每小区为2株葡萄树,每个处理3次重复,处理间设保护隔离区,另设清水空白对照。

土壤:选一块不种植作物的10 m^{2}空白地块进行土壤的消解动态试验,施药剂量按最高推荐剂量的15倍进行,即质量分数为50.0 g·kg^{-1}(20倍液)喷雾,10 m^{2}施药量为37.5 g制剂/0.750 L水,施药后2 h、1 d、2 d、3 d、5 d、7 d、14 d、21 d、28 d采样,每个处理3次重复,处理间设保护隔离区,另设清水空白对照。

1.3.3　最终残留试验　设2个施药剂量:低剂量为最高推荐剂量300倍液(3.33 g·kg^{-1}),高剂量为1.5倍最高推荐剂量200倍液(5.00 g·kg^{-1});各设1次施药和2次施药2个处理,每个处理设3次重复,小区面积2株葡萄树,按照试验设计时间开始施药,施药间隔期10 d。采样时间距离最后一次施药的间隔时间为7、14、21 d,随机在试验小区内采集葡萄和土壤样品。另设清水空白对照,处理间设保护带。

1.3.4　试验样品的采集制备及保存　葡萄样本:随机在试验小区内不同部位采集生长正常、无病害的葡萄果实(不少于2 kg),装入样品容器中包扎妥当,贴好标签。

土壤样本:随机取点(葡萄植株范围内)10个以上,采用土钻采集0~10 cm(消解动态样本)、0~15

cm(最终残留样本)的土壤1~2 kg,装入样本容器中,贴好标签。

样品8 h内运回实验室,葡萄样品立即用匀浆机打碎,土壤样品碾碎过筛,制备成实验室样品-20 ℃冷冻保存至检测。

2 结果与分析

2.1 方法线性范围

将1.0 g·L^{-1}的噻苯隆标准溶液用乙腈逐级稀释配得了0.01、0.05、0.10、0.50、1.00 mg·L^{-1} 5种质量浓度的系列标准溶液,在1.2.2中的仪器条件下进行测定,以噻苯隆标准溶液浓度为横坐标,定量离子峰面积为纵坐标绘制标准曲线。标准溶液线性方程为y=1.7×10^5 x+175 7,相关系数R^2为0.999 6。结果表明,在0.01~1.00 mg·L^{-1}内,噻苯隆质量浓度与峰面积呈良好线性关系,本方法中,噻苯隆在葡萄中的定量限远低于目前各国现行的残留限量标准,满足噻苯隆残留检测的要求。

2.2 方法准确度、检出限与定量限

分别在空白葡萄和土壤样品中添加3档浓度的噻苯隆标准溶液,每档5次重复,用上述1.2中分析方法测定回收率,结果见表1,噻苯隆在葡萄和土壤上的回收率为84%~107%,相对标准偏差为0.5%~1.9%,符合农药残留分析要求。

根据信噪比S/N=3计算仪器检出限(LOD),噻苯隆的仪器检出限(LOD)为5.67×10^{-5} mg·L^{-1}×5 μL=2.835×10^{-4} ng;以最小添加浓度为定量限(LOQ),噻苯隆在葡萄和土壤中的定量限均为0.01 mg·kg^{-1}。

表1 葡萄果实和园地土壤中噻苯隆的添加回收率(n=5)

Table 1 Recoveries of thidiazuron in grape fruit and grapery soil (n=5)

样品类型 Sample type	添加水平 Adding level/(mg·kg^{-1})	平均回收率 Average recovery/%	相对标准偏差 RSD/%
葡萄果实 Grape fruit	0.01	107	1.0
	0.05	91	1.7
	0.50	89	1.7
土壤 Soil	0.01	90	1.9
	0.05	87	1.3
	0.50	84	0.5

2.3 田间消解动态试验结果

噻苯隆在葡萄果实中的消解动态曲线见图1。结果显示,2014、2015年噻苯隆在河南、江苏两地葡萄中的原始沉积量分别为0.017 4、0.034 9、0.039 1、0.038 1 mg·kg^{-1}。2 a两地葡萄中的原始沉积量基本一致,2 a两地半衰期略有差异,从0.8~5.7 d,2 a两地的消解动态动力学方程及半衰期见表2。

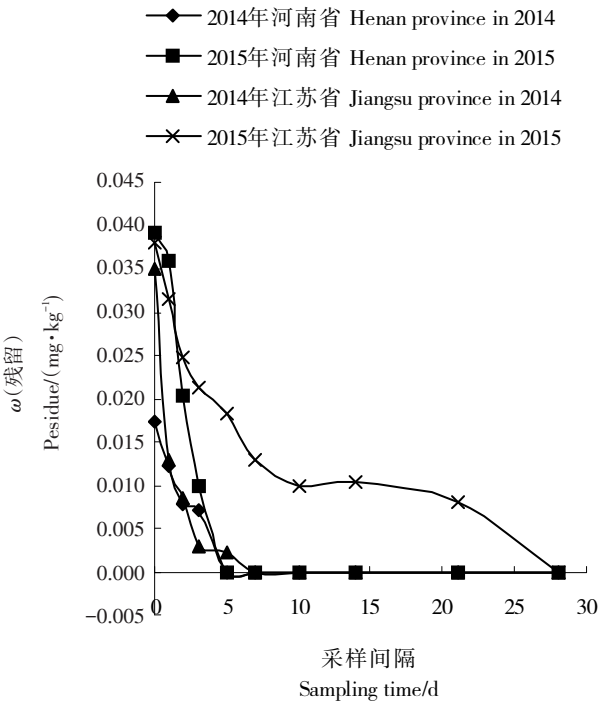

图1 噻苯隆在葡萄果实中的消解动态曲线

Fig. 1 Degradation dynamic curve of thidiazuron in grape fruit

表2 噻苯隆在葡萄果实中的降解动态方程、半衰期

Table 2 Degradation dynamic equations and half-lives of thidiazuron in grape fruit

年份 Year	地点 Site	消解动态方程 Degradation dynamics equations	半衰期 Half-lives/d
2014	河南 Henan	C_T=0.017 8e$^{-0.41T}$, R^2=0.972 8	1.7
	江苏 Jiangsu	C_T=0.034 4e$^{-0.84T}$, R^2=0.990 1	0.8
2015	河南 Henan	C_T=0.043 3e$^{-0.42T}$, R^2=0.947 6	1.7
	江苏 Jiangsu	C_T=0.034 7e$^{-0.12T}$, R^2=0.936 3	5.7

注:T. 消解时间/d;C_T. T 时间时噻苯隆残留量/(mg·kg^{-1})。消解动态方程由 SigmaPlot 软件拟合。

Note: T. Time of degradation/d, C_T. Residue of thidiazuron at T day/(mg·kg^{-1}). The regressive equation fitting by SigmaPlot.

噻苯隆在土壤中的消解动态试验结果显示,2014年噻苯隆在河南、江苏两地土壤中的原始沉积量分别为0.007 3、0.019 1 mg·kg^{-1};2015年噻苯隆在河南、江苏两地土壤中的原始沉积量分别为0.017 9、0.012 7 mg·kg^{-1}。由于残留量较低,2 a两地土壤中噻苯隆的消解趋势不规律,未拟合消解曲线方程。

2.4 最终残留试验结果

试验结果表明,将0.1%噻苯隆可湿性粉剂按最

高推荐剂量和1.5倍最高推荐剂量分别施药1次和施药2次的情况下,按距最后一次施药后间隔7、14、21 d采集葡萄样品,葡萄样品中检出的残留量最高值为0.019 5 mg·kg^{-1}(2014年江苏高剂量施药2次7 d葡萄样品),70.1%的检测数据低于最低检测值(LOQ)0.01 mg·kg^{-1},最终残留数据见表3。

表3　噻苯隆在葡萄和土壤中的最终残留量

Table 3　The residues of thidiazuron in grape and grapery soil　　ω/(mg·kg^{-1})

试验小区 Test plots	葡萄 Grape				土壤 Soil			
	2014		2015		2014		2015	
	河南 Henan	江苏 Jiangsu	河南 Henan	江苏 Jiangsu	河南 Henan	江苏 Jiangsu	河南 Henan	江苏 Jiangsu
L1-21 d	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
L2-21 d	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
H1-21 d	<LOQ	<LOQ	<LOQ	0.010 3	<LOQ	<LOQ	<LOQ	<LOQ
H2-21 d	<LOQ	<LOQ	<LOQ	0.015 7	<LOQ	<LOQ	<LOQ	<LOQ
L1-14 d	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
L2-14 d	<LOQ	0.011 1	<LOQ	<LOQ	<LOQ	<LOQ	0.013 8	<LOQ
H1-14 d	<LOQ	0.010 6	<LOQ	0.012 1	<LOQ	<LOQ	<LOQ	<LOQ
H2-14 d	<LOQ	0.017 2	<LOQ	0.013 2	<LOQ	<LOQ	<LOQ	<LOQ
L1-7 d	<LOQ	0.010 7	<LOQ	0.010 1	<LOQ	<LOQ	<LOQ	<LOQ
L2-7 d	<LOQ	0.011 2	0.010 8	0.012 6	0.010 5	0.012 8	<LOQ	<LOQ
H1-7 d	<LOQ	0.010 1	<LOQ	0.013 5	<LOQ	<LOQ	<LOQ	<LOQ
H2-7 d	0.010 7	0.019 5	0.012 6	0.018 1	<LOQ	<LOQ	<LOQ	<LOQ

注:H 指高剂量,L 指低剂量,d 表示间隔天数。如 L2-7 d 表示以低剂量施药 2 次后,间隔 7 d 采样,以此类推。噻苯隆定量限(LOQ)在葡萄和土壤中为 0.01 mg·kg^{-1}。

Note: H means high dose, L means low dose, d means days. For example, L2-7d means after 2 times treat with low dose, then sampling after 7 days, and by this analogy. The limits of quantification (LOQ) for thidiazuron in grape and grapery soil was 0.01 mg·kg^{-1}.

园区土壤样品中检出的残留量最高为0.013 8 mg·kg^{-1}(2015年河南低剂量施药2次14 d土壤样品),95.1%的检测数据低于最低检测量(LOQ)0.01 mg·kg^{-1}。

3　讨　论

噻苯隆残留分析方法研究中发现乔成奎等[16]、闫震等[17]报道中前处理过程在多种果蔬基质下加入PSA等吸附材料进行净化处理,本研究中对照发现葡萄及土壤基质下不使用PSA等材料进行净化处理,在高效液相色谱-串联质谱(HPLC-MS/MS)调整梯度洗脱比例进行检测时基线噪音并未变化,且连续多针进样平行性良好;同时由于减少了吸附材料对噻苯隆的吸附,得到良好的添加回收率。本研究中噻苯隆残留分析方法简化了前处理步骤,且具有较高的准确度和灵敏度。

通过噻苯隆在2 a两地葡萄中的消解动态试验,发现噻苯隆在葡萄果实中的残留消解半衰期为0.8~5.7 d,消解动态曲线均符合一级动力学方程,属于易降解农药。从最终残留数据可以看出,噻苯隆在葡萄及果园土壤中的整体残留量较低,在葡萄上的残留比土壤中高。造成这样的结果推测为,葡萄施药方法为浸蘸果穗,施药后葡萄中着药量相对较高,土壤未直接着药,残留较少,总体上来看,施药量与残留量呈正相关关系:施药量越大,残留量也越大。

合理使用建议:0.1%噻苯隆可湿性粉剂,按照推荐剂量及推荐的施药次数,最高施药剂量(有效成分)为3.33 mg·kg^{-1}(300倍液);最多施药2次,施药间隔为10~15 d;安全间隔期(最后一次施药距采收时的时间)为14 d。

本研究利用HPLC-MS/MS建立了葡萄及土壤中噻苯隆的检测方法。通过回收率、检出限、精密度等指标考察,表明该方法操作简单、结果准确、重现性好,适用于葡萄及土壤中噻苯隆的定性、定量分析测定。

通过噻苯隆葡萄动态试验及最终残留试验,表明噻苯隆属于易降解农药,在合理施用下,安全间隔期后采收,噻苯隆在葡萄中的残留远低于中国最大残留限量标准(0.05 mg·kg^{-1})[7]。

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