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增强型脂质去除分散固相萃取净化-气相色谱-串联质谱法测定动物性食品中146种农药残留

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摘要: **目的** 建立一种基于增强型脂质去除分散固相萃取(enhanced matrix removal-lipid dispersion solid phase extraction, dSPE EMR-Lipid)净化技术结合气相色谱-串联质谱法(gas chromatography-tandem mass spectrometry, GC-MS/MS)测定动物性食品中146种农药残留量的分析方法。**方法** 在5 g样品中加入2 mL超纯水, 经乙腈提取, 冷冻10 min, QuEChERS-EN-盐包除水分离, 采用dSPE EMR-Lipid净化技术, GC-MS/MS动态多反应监测(dynamic multi-reaction monitoring, DMRM)模式监测, 基质匹配标准曲线法定量分析。**结果** 146种化合物在5~320 µg/L范围内线性关系良好, 相关系数均大于0.9939, 方法的检出限为0.04~10.91 µg/kg, 定量限为0.11~32.72 µg/kg。146种化合物在0.01、0.02和0.10 mg/kg 3个不同加标水平下的平均回收率范围在61.3%~119.3%之间, 相对标准偏差为0.15%~16.02%。**结论** 该方法操作简便快速, 灵敏准确, 能够满足多种农药残留量的同时检测需求, 适用于动物性食品中多种农药残留的定量筛查。

关键词: 动物性食品; 增强型脂质去除分散固相萃取; 气相色谱-串联质谱法; 农药残留

Determination of 146 kinds of pesticide residues in animal derived food by enhanced matrix removal-lipid dispersion solid phase extraction purification coupled with gas chromatography-tandem mass spectrometry

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ABSTRACT: Objective To establish an analytical method for the determination of 146 kinds of pesticide residues in animal derived foods by enhanced matrix removal-lipid dispersion solid phase extraction (dSPE EMR-Lipid) and purification technology coupled with gas chromatography-tandem mass spectrometry (GC-MS/MS). **Methods** The 5 g sample were added to 2 mL ultrapure water, extracted with acetonitrile, frozen for 10 min, separated with QuEChERS EN-extraction package, cleaned-up with dSPE EMR-Lipid, then was detected by GC-MS/MS in dynamic multi-reaction monitoring (DMRM) mode. The analytes were quantified by matrix-matched standard curve method. **Results** The results showed that 146 kinds of pesticides had good linearities in the concentration of 5–320 $\mu\text{g/L}$, the linear correlation coefficient of the compounds were greater than 0.9939, and the limits of detection of the method were 0.04–10.91 $\mu\text{g/kg}$, the limits of quantification were 0.11–32.72 $\mu\text{g/kg}$. The average recoveries of 146 kinds of pesticides at the spiked level of 0.01, 0.02 and 0.10 mg/kg ranged from 61.3% to 119.3%, relative standard deviations were 0.15%–16.02%. **Conclusion** The method is simple in pre-treatment, convenient in operation, rapid, sensitive and accurate in detection, can meet the simultaneous detection requirements for multiple pesticide residues. It is suitable for preliminary screening and quantitative detection of multiple pesticide residues in animal derived food.

KEY WORDS: animal derived foods; enhanced matrix removal-lipid dispersion solid phase extraction; gas chromatography-tandem mass spectrometry; pesticide residues

0 引言

化学农药在促进农产品增产的同时,不仅影响生态环境,还会通过环境、饲料、饮水、呼吸、食物链等多种途径引入到动物性食品中,造成农药在动物性食品中的残留^[1-2]。随着人们对动物性食品需求的增加,残留的农药通过食物链可能在人体内蓄积,对人体健康造成潜在危害^[3-4]。

农药残留是全球重点关注的一项指标,许多国家制定了严格的动物性食品的农药最大残留限量(maximum residue limit, MRL)。随着对农药种类覆盖范围的增加,对限量值的严格要求,这对检测方法的简便、快速、灵敏及通量的需求提出了更高的要求。目前涉及动物性食品检验方法的标准和文献报道主要有气相色谱法(gas chromatograph, GC)^[5-6]、气相色谱-质谱法(gas chromatography-mass spectrometry, GC-MS)^[7-10]、气相色谱-串联质谱法(gas chromatography-tandem mass spectrometry, GC-MS/MS)^[11-12]、液相色谱-串联质谱法(liquid chromatography-tandem mass spectrometry, LC-MS/MS)^[13-17]、高分辨质谱法^[18-19]等。GC-MS和LC-MS/MS是国家标准和文献报道中最常用的方法,关于GC-MS/MS检测方法的国家标准相对较少。采用GC-MS/MS高通量检测多种农药残留,多数报道的是针对植物性食品,对检测动物性食品中多种农药残留的高通量方法相对较少,因此,对动物性食品建立准确、灵敏的高通量检测方法是非常必要的。

动物性食品中含有大量的脂肪和蛋白质,不仅会污染仪器,还可能干扰目标农药的检测,去除脂肪是动物性样品前处理的关键。目前关于动物性食品中的农药多残留

分析所报道的前处理方法中多数采用凝胶渗透色谱^[20-22]、固相萃取法^[23-24]、冷冻过滤技术^[25]、QuEChERS前处理^[26-27]等,且多数是与LC-MS/MS结合进行检测。凝胶渗透色谱设备昂贵,操作烦琐,不利于批量检测;固相萃取前处理操作复杂、耗时长;QuEChERS具有成本低、快速便捷、萃取效率高等特点,近年来虽被广泛应用,但是在多农残检测中存在净化材料选择局限性等缺点。增强型脂质去除分散固相萃取(enhanced matrix removal-lipid dispersion solid phase extraction, dSPE EMR-Lipid)作为一种新型吸附材料,能够选择性去除样品提取物中的主要脂类,不会造成分析物的损失,在兽药残留检测中去脂效果较好^[28]。鉴于此,本研究以乙腈为提取溶剂, dSPE EMR-Lipid净化,浓缩、置换溶剂复溶后以GC-MS/MS定量分析,建立一种简便、快速、准确测定动物性食品中农药多残留的分析方法,为动物性食品的质量安全提供技术保障。

1 材料与amp;方法

1.1 试剂、仪器与材料

146种农药标准品(纯度 $\geq 95\%$,天津阿尔塔科技有限公司);N-丙基乙酰胺(N-primary secondary amine, PSA)、碳十八烷基硅烷键合硅胶(C_{18})、QuEChERS-EN-提取包(内含氯化钠1 g、无水 MgSO_4 4 g、柠檬酸钠1 g、柠檬酸氢二钠0.5 g)、dSPE EMR-Lipid净化管(美国Agilent科技有限公司);羟基多壁碳纳米管(hydroxylated multi-walled carbon nanotubes, MWCNTs-OH)、多壁碳纳米管

(multi-walled carbon nanotubes, MWCNTs)(中国科学院成都有机化学有限公司); ZIP-8(兰州化物所合成); 无水硫酸镁(分析纯, 国药集团化学试剂有限公司); 乙酸乙酯、乙腈(色谱纯, 德国 Merck 公司); 丙酮(色谱纯, 科密欧化学试剂有限公司)。

7890B-7000D 气相色谱-三重四极杆质谱联用仪、HP-5 MS UI 毛细管色谱柱(30 m×0.25 mm, 0.25 μm)(美国 Agilent 科技有限公司); Milli-Q 超纯水机(美国 Millipore 公司); AUTO-EVA-60 全自动平行浓缩仪(睿科集团股份有限公司); 5810R 高速低温离心机(德国 Eppendorf 公司); VORTEX-5 涡旋混匀器(海门其林贝尔公司); T 18 匀浆机(德国 IKA 公司); JR05-300 绞肉机(浙江苏泊尔股份有限公司)。

猪肉、牛肉、羊肉、鸡肉、水产品、鸡蛋样品均为市售。

1.2 样品制备

猪肉、牛肉、羊肉、鸡肉: 将肉去筋膜, 切成小块, 绞肉机充分绞碎成糜状; 水产品: 按照 GB/T 30891—2014《水产品抽样规范》, 取可食部分用匀浆机制备; 蛋类: 去壳后用搅拌机搅匀, 制成匀浆。

1.3 样品前处理

称取 5 g(精确至 0.001 g)匀浆样品至 50 mL 离心管中, 加入 2 mL 超纯水, 充分摇匀, 准确加入 10 mL 乙腈, 超声提取 10 min, 置于 -18 °C 冷冻 10 min, 然后加入 QuEChERS-EN-提取盐包, 快速摇散, 涡旋混合 1 min, 4000 r/min 离心 5 min (4 °C 条件下), 收集上清液。准确移取 3.0 mL 上清液于预先装有净化材料的 dSPE EMR-Lipid 净化管中, 涡旋混合 1 min, 以 4000 r/min 离心 5 min (4 °C 条件下), 取净化液 2.0 mL 至 10 mL 离心管中, 于 40 °C 水浴中氮吹至近干, 准确加入 1.0 mL 乙酸乙酯复溶, 过 0.22 μm 有机滤膜, 收集滤液, 上机测试。

1.4 标准溶液的配制

标准储备溶液配制: 分别精确称取 10 mg 单个农药标准品于 10 mL 容量瓶中, 用丙酮定容至刻度; 混合标准工作溶液配制: 精密移取单个储备溶液, 用乙酸乙酯定容, 配制成 1000 μg/L 的标准工作溶液。临用时用乙酸乙酯或者空白基质样品溶液(按 1.3 方法制备)将混合标准工作液配制成系列标准溶液, 所有标准溶液均置于棕色瓶内于 -18 °C 密封保存, 备用。

1.5 仪器条件

1.5.1 色谱条件

色谱柱: HP-5 MS UI 毛细管色谱柱(30 m×0.25 mm, 0.25 μm); 程序升温: 初始温度 60 °C(保持 1 min), 以 40 °C/min 升温至 170 °C, 再以 10 °C/min 升温至 310 °C(保持 3 min); 进样口温度: 280 °C; 流速: 1.0 mL/min; 进样模

式: 不分流进样; 进样量: 1 μL。

1.5.2 质谱条件

离子源: 电子轰击(electron impact, EI)源; 电离能量: 70 eV; 离子源温度: 230 °C; 辅助传输线温度: 280 °C; 溶剂延迟 2.5 min; 监测模式: 动态多反应监测模式; 碰撞气: 氮气; 淬灭气: 氦气(纯度均≥99.999%)。图 1 为猪肉基质中 146 种农药的总离子流图。

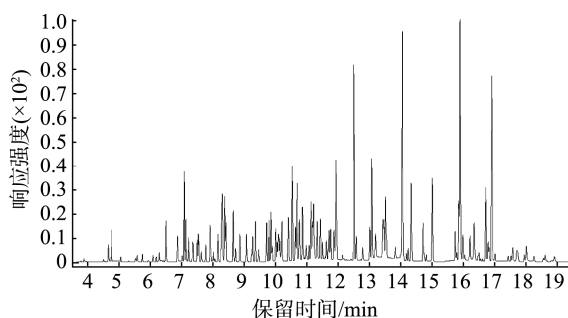


图 1 猪肉基质中 146 种农药(240 μg/L)的总离子流图
Fig.1 Total ion chromatograms of 146 kinds of pesticides (240 μg/L) in the pork matrix

1.6 数据处理

采用 Agilent MassHunter 软件对农药化合物定性和定量分析, 采用 Excel 2019 软件对数据进行统计分析、制表及绘图。

2 结果与分析

2.1 加水量的选择

前处理技术是分析痕量组分过程中极为重要的环节, 主要是提取、净化、浓缩和复溶等步骤。我国 2018 年以后发布的多个农药残留检测标准和文献[12]报道多数以乙腈为提取溶剂。肉类样品具有一定的黏性, 脂肪在乙腈中的溶解度较小, 蛋白质在乙腈作用下会变性沉淀, 这会使目标物被包裹难以释放^[29], 加水后可将样品分散均匀, 增强乙腈对样品的渗透性, 有利于目标物提取^[30], 同时考虑到后期还需加盐除去多余水分, 本研究考察 5 g 样品分别加入 0、2、5 mL 超纯水, 经前处理后对目标化合物回收率的影响(见图 2)。结果显示, 未净化时, 回收率在 60%~120% 范围内化合物数量从高到低为 2 mL>0 mL>5 mL, 加水量 2 mL 时, 回收率低于 60%或高于 120%的数量最少。净化后, 不同加水量的平均回收率均高于未净化, 加水量 2 mL 时, 目标化合物整体平均回收率最高, 不加水时, 回收率高于 120%的化合物偏多, 加水量 5 mL 时, 回收率低于 60%的化合物数量增加。因此, 本研究以 5 g 样品中加入 2 mL 超纯水为宜。

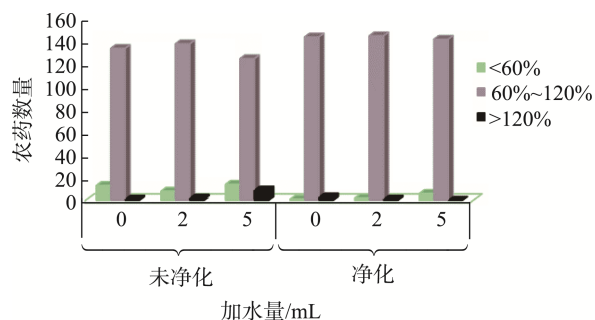


图2 加水量对农药化合物回收率的影响

Fig.2 Effects of water addition on the recoveries of pesticide compounds

2.2 净化条件的选择

动物性食品的基质成分复杂, 萃取液中的杂质不仅会影响目标化合物的离子化效率和响应强度, 导致灵敏度下降, 还会造成仪器堵塞, 降低色谱柱寿命。通过对提取液有效净化, 可降低检测干扰和仪器污染。目前常用的净化材料有 C_{18} 、PSA、碳基纳米材料 (MWCNTs、MWCNTs-OH), 以及去脂材料 dSPE EMR-Lipid 等。本研究考察 C_{18} 、PSA、MWCNTs、MWCNTs-OH、dSPE EMR-Lipid 以及实验室自备合成的 ZIP-8 净化材料等实验方案(如方案: ① $MgSO_4$ 450 mg+PSA 30 mg、② $MgSO_4$ 450 mg+ C_{18} 30 mg、③ $MgSO_4$ 450 mg+PSA 15 mg+ C_{18} 15 mg、④ $MgSO_4$ 450 mg+MWCNTs 30 mg、⑤ $MgSO_4$ 450 mg+MWCNTs-OH 30 mg、⑥ dSPE EMR-Lipid、⑦ ZIP-8 30 mg) 对农药化合物净化效果的影响(图3)。图3结果显示, 比较回收率在 60%~120%的农药数量, 方案③和⑥较其他方案均好, 且在此范围内方案⑥的平均回收率(91.3%)较方案③的平均回收率(89.3%)高。同时考虑到要实际应用于大批量样本的快速处理, 最终选择 dSPE EMR-Lipid 净化填料为本研究的净化方案。

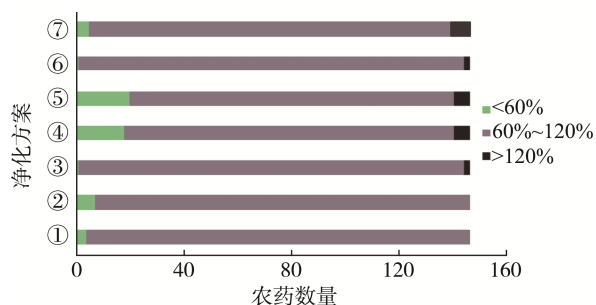


图3 净化方案对农药化合物回收率的影响

Fig.3 Effects of purification schemes on the recoveries of pesticide compounds

2.3 基质效应

基质效应(matrix effect, ME)是基质匹配标准曲线斜

率与溶剂标准曲线斜率之差与溶剂标准曲线斜率的百分比。当 ME 为正时, 表现为基质增强效应; 负时则为基质抑制效应。当 $|ME|$ 低于 20% 时, ME 可忽略不计; $|ME|$ 高于 50% 时, 表现为强 ME; $|ME|$ 介于 20%~50% 之间, 则为中等 ME^[18](图4)。考察了 146 种农药在空白猪肉中的 ME 结果表明, 92.5% 的农药表现为基质增强效应, 7.5% 的农药表现为基质抑制效应。其中 24.7% 的农药 ME 可忽略, 37.0% 的农药为中等 ME, 38.3% 的农药为强 ME。考虑到定量的准确度, 则需绘制基质匹配标准曲线来降低 ME 的影响。

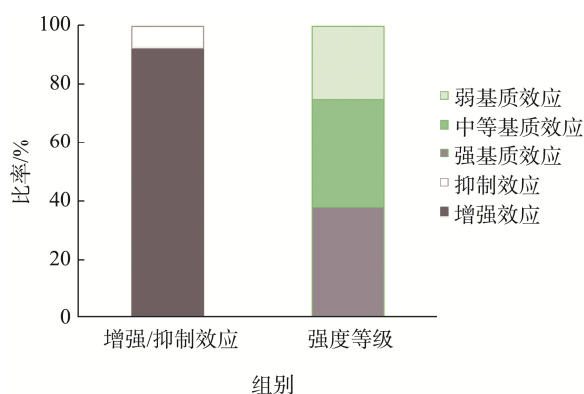


图4 空白猪肉基质中目标化合物的 MEs 及强度等级比率

Fig.4 Ratio distribution of MEs and strength levels of target compounds in blank pork matrix

2.4 方法学考察

采用系列基质混合标准工作液(5~320 $\mu\text{g/L}$)定量分析, 以农药质量浓度(X , $\mu\text{g/L}$)为横坐标, 农药浓度响应的峰面积(Y)为纵坐标, 绘制标准曲线, 通过线性拟合得到回归方程和相关系数。按照 GB 5009.295—2023《食品安全国家标准 化学分析方法验证通则》采用空白猪肉基质样品加标稀释测定, 分别以信噪比为 3 和 10 时表示方法的估算检出限(limit of detection, LOD)和估算定量限(limit of quantification, LOQ)。加标回收率实验设置 3 水平(0.01、0.02、0.10 mg/kg), 每个水平平行测定 6 次考察该方法的准确度和精密度。146 种农药的相关系数、LODs、LOQs、回收率和精密度结果见表 1。结果表明, 146 种农药的线性关系良好, 相关系数均不低于 0.9939, 化合物的 LODs 为 0.04~10.91 $\mu\text{g/kg}$, LOQs 为 0.11~32.72 $\mu\text{g/kg}$, 146 种化合物在 3 个水平下的回收率范围为 61.3%~119.3%, 其中 3 个水平下回收率在 70%~120% 的化合物分别占 91.1%、97.3% 和 96.6%。相对标准偏差(relative standard deviation, RSD)为 0.15%~16.02%, 结果表明该方法的 LOD 和 LOQ 可以满足日常监测需求; 虽然有少数化合物的回收率不是很理想, 但该方法可以满足动物源性食品中多数农药化合物的定量筛查。

表 1 146 种农药化合物的 LODs、LOQs、平均回收率及 RSDs (n=6)

| 化合物 | LODs ($\mu\text{g}/\text{kg}$) | LOQs ($\mu\text{g}/\text{kg}$) | 回收率(RSDs)% | | |
|---------------|-------------------------------------|-------------------------------------|--------------|--------------|--------------|
| | | | 0.01 mg/kg | 0.02 mg/kg | 0.10 mg/kg |
| | | | | | |
| 甲胺磷 | 1.42 | 4.25 | 62.7 (8.12) | 75.8 (6.47) | 63.8 (5.08) |
| 敌敌畏 | 0.57 | 1.70 | 65.0 (4.76) | 71.2 (6.81) | 72.4 (3.51) |
| 克菌丹 | 0.90 | 2.70 | 68.9 (11.42) | 80.4 (5.25) | 78.3 (3.88) |
| 禾草敌 | 1.34 | 4.03 | 99.9 (4.62) | 90.4 (1.83) | 87.9 (0.54) |
| 四氯硝基苯 | 0.32 | 0.95 | 87.4 (1.01) | 85.1 (1.81) | 88.3 (1.12) |
| 氟铃脲 | 0.32 | 0.96 | 94.1 (4.22) | 96.6 (2.71) | 95.2 (2.10) |
| 二苯胺 | 0.18 | 0.54 | 78.9 (2.51) | 82.3 (0.45) | 90.6 (0.75) |
| 硫线磷 | 1.29 | 3.87 | 87.6 (2.61) | 92.4 (1.24) | 99.5 (1.32) |
| 灭线磷 | 0.17 | 0.52 | 84.5 (2.15) | 89.6 (0.61) | 98.4 (0.54) |
| 氯苯胺灵 | 0.38 | 1.13 | 85.0 (1.45) | 91.2 (0.16) | 99.7 (0.81) |
| 氟乐灵 | 0.09 | 0.28 | 114.4 (0.54) | 100.3 (0.43) | 98.0 (0.54) |
| 治螟磷 | 1.00 | 3.00 | 83.6 (2.06) | 88.6 (0.81) | 97.5 (0.36) |
| 甲拌磷 | 0.16 | 0.49 | 89.9 (0.35) | 86.9 (1.69) | 92.6 (0.15) |
| α -六六六 | 0.24 | 0.71 | 78.7 (3.00) | 85.2 (1.24) | 92.3 (1.10) |
| 六氯苯 | 0.30 | 0.91 | 68.1 (5.43) | 68.5 (0.39) | 75.2 (1.16) |
| 乐果 | 0.82 | 2.47 | 72.5 (9.24) | 83.7 (6.94) | 76.7 (6.13) |
| 氯硝胺 | 0.80 | 2.40 | 88.2 (2.95) | 94.5 (1.48) | 100.3 (0.82) |
| 莠去津 | 0.05 | 0.15 | 87.5 (1.34) | 88.3 (2.04) | 94.4 (0.84) |
| 噻节因 | 0.74 | 2.22 | 63.8 (2.19) | 75.2 (5.11) | 67.2 (6.24) |
| β -六六六 | 0.31 | 0.93 | 70.1 (6.65) | 82.7 (1.28) | 90.6 (1.51) |
| 特丁津 | 0.54 | 1.62 | 88.2 (0.71) | 88.0 (1.12) | 93.2 (0.81) |
| γ -六六六 | 0.44 | 1.31 | 64.8 (7.54) | 78.6 (1.63) | 85.4 (2.74) |
| 特丁硫磷 | 0.13 | 0.40 | 87.2 (1.52) | 86.8 (0.32) | 95.3 (0.63) |
| 炔苯酰草胺 | 0.34 | 1.01 | 92.2 (0.76) | 92.4 (1.38) | 96.0 (1.66) |
| 五氯硝基苯 | 0.26 | 0.78 | 109.5 (2.02) | 95.1 (0.33) | 88.3 (1.09) |
| 地虫硫磷 | 0.50 | 1.49 | 86.9 (1.72) | 89.9 (0.92) | 98.8 (0.64) |
| 敌百虫 | 0.29 | 0.86 | 83.3 (2.53) | 87.0 (0.77) | 98.5 (0.40) |
| 二嗪磷 | 0.09 | 0.27 | 81.8 (1.67) | 87.6 (0.48) | 95.5 (1.18) |
| 噻霉胺 | 0.23 | 0.70 | 81.0 (2.84) | 83.4 (1.83) | 86.7 (1.37) |
| δ -六六六 | 0.34 | 1.02 | 83.2 (5.00) | 87.5 (1.06) | 92.1 (1.09) |
| 氯唑磷 | 1.67 | 5.01 | 92.5 (1.84) | 93.4 (0.90) | 99.5 (0.90) |
| 久效磷 | 0.75 | 2.26 | 62.2 (4.80) | 86.6 (5.45) | 91.7 (5.41) |
| 乙炔菌核利 | 0.15 | 0.46 | 95.8 (2.88) | 98.6 (1.56) | 104.8 (0.84) |
| 甲基毒死蜱 | 0.20 | 0.59 | 83.7 (1.51) | 85.9 (1.89) | 93.7 (0.16) |
| 甲基对硫磷 | 0.85 | 2.56 | 111.2 (2.46) | 100.2 (1.06) | 99.5 (1.30) |
| 氟甲腈 | 0.13 | 0.38 | 91.8 (3.26) | 88.7 (1.08) | 89.6 (1.60) |
| 甲基立枯磷 | 0.10 | 0.30 | 86.8 (1.49) | 87.6 (1.85) | 93.5 (0.40) |
| 莠灭净 | 0.43 | 1.28 | 75.4 (2.12) | 80.3 (1.92) | 79.3 (2.00) |
| 甲霜灵 | 0.45 | 1.36 | 73.7 (3.21) | 81.1 (2.84) | 83.9 (2.11) |
| 七氯 | 0.08 | 0.24 | 62.2 (4.79) | 72.0 (3.92) | 83.2 (4.62) |
| 甲基噻啉磷 | 0.04 | 0.12 | 78.1 (1.46) | 79.9 (1.45) | 82.4 (1.41) |
| 杀螟硫磷 | 0.25 | 0.75 | 112.0 (0.44) | 96.5 (1.34) | 96.0 (1.43) |
| 戊草丹 | 0.20 | 0.61 | 80.5 (2.00) | 85.0 (1.18) | 93.4 (0.84) |
| 马拉硫磷 | 0.44 | 1.32 | 77.9 (0.86) | 89.7 (0.81) | 102.3 (1.05) |
| 乙霉威 | 0.11 | 0.32 | 84.2 (2.97) | 86.5 (0.73) | 94.7 (0.52) |
| 甲拌磷亚砷 | 1.82 | 5.46 | 86.3 (2.20) | 92.8 (1.77) | 95.7 (2.65) |
| 倍硫磷 | 0.52 | 1.57 | 82.6 (1.59) | 82.5 (2.21) | 90.3 (1.20) |
| 艾氏剂 | 1.09 | 3.27 | 80.7 (6.72) | 76.5 (6.25) | 83.2 (0.88) |
| 毒死蜱 | 0.16 | 0.48 | 85.8 (2.24) | 83.3 (1.27) | 88.8 (0.61) |
| 三唑酮 | 0.29 | 0.88 | 79.7 (1.23) | 85.3 (0.75) | 92.5 (1.70) |
| 四氟醚唑 | 0.18 | 0.53 | 89.3 (6.24) | 86.7 (2.11) | 86.0 (2.82) |
| 对硫磷 | 0.70 | 2.11 | 117.8 (0.97) | 98.5 (1.26) | 95.7 (1.03) |
| 水胺硫磷 | 1.17 | 3.52 | 78.3 (5.22) | 88.4 (0.36) | 95.1 (2.54) |

表 1(续)

| 化合物 | LODs ($\mu\text{g}/\text{kg}$) | LOQs ($\mu\text{g}/\text{kg}$) | 回收率(RSDs)% | | |
|--------------|-------------------------------------|-------------------------------------|--------------|--------------|--------------|
| | | | 0.01 mg/kg | 0.02 mg/kg | 0.10 mg/kg |
| | | | | | |
| 双苯酰草胺 | 0.59 | 1.77 | 77.3 (3.36) | 82.2 (0.23) | 86.0 (2.37) |
| 噻菌环胺 | 0.59 | 1.78 | 78.8 (1.89) | 79.9 (1.16) | 79.8 (1.56) |
| 甲基异柳磷 | 0.19 | 0.56 | 83.4 (0.80) | 87.4 (1.93) | 96.3 (0.88) |
| 氟虫腈 | 0.04 | 0.11 | 81.9 (3.21) | 79.9 (0.49) | 85.2 (1.21) |
| 二甲戊灵 | 0.84 | 2.52 | 116.1 (1.25) | 107.7 (3.26) | 98.3 (0.91) |
| 戊菌唑 | 0.07 | 0.20 | 80.5 (0.61) | 84.6 (0.63) | 88.6 (0.99) |
| 甲拌磷砷 | 1.31 | 3.92 | 78.6 (5.73) | 87.2 (6.65) | 96.4 (1.58) |
| 特丁硫磷砷 | 2.65 | 7.96 | 78.9 (5.42) | 89.2 (6.43) | 96.3 (1.58) |
| 甲基硫环磷 | 0.28 | 0.83 | 84.6 (8.16) | 84.2 (6.11) | 76.7 (3.45) |
| 硫环磷 | 0.69 | 2.07 | 84.6 (8.15) | 84.1 (6.12) | 76.7 (3.45) |
| α -硫丹 | 6.55 | 19.65 | 73.4 (0.79) | 69.8 (16.02) | 90.7 (1.21) |
| 氟虫腈亚砷 | 2.32 | 6.96 | 66.8 (8.12) | 67.7 (5.46) | 80.7 (0.30) |
| 噻硫磷 | 0.85 | 2.55 | 83.2 (2.76) | 85.9 (3.44) | 97.0 (1.17) |
| 三唑醇 | 6.52 | 19.56 | 102.4 (2.56) | 100.2 (2.95) | 97.3 (1.85) |
| 苯酰菌胺 | 4.59 | 13.77 | 97.4 (9.26) | 80.0 (7.37) | 75.9 (6.62) |
| 氟菌唑 | 4.01 | 12.03 | 93.6 (6.91) | 90.0 (2.20) | 80.9 (1.85) |
| 腐霉利 | 1.61 | 4.84 | 82.2 (2.94) | 85.2 (3.36) | 88.6 (0.65) |
| 氟吡甲禾灵 | 0.65 | 1.96 | 80.2 (1.36) | 80.9 (2.47) | 87.3 (0.45) |
| 杀扑磷 | 0.13 | 0.39 | 74.5 (1.62) | 84.4 (0.76) | 94.0 (2.11) |
| 氧丹 | 2.73 | 8.20 | 89.4 (4.18) | 78.5 (4.98) | 75.4 (3.32) |
| 精噁唑禾草灵 | 0.19 | 0.56 | 76.9 (1.15) | 84.2 (3.23) | 92.6 (1.45) |
| 2,4'-滴滴伊 | 0.10 | 0.31 | 72.9 (2.12) | 70.9 (1.11) | 76.4 (0.26) |
| 噻菌胺 | 0.93 | 2.80 | 72.6 (1.28) | 73.3 (0.72) | 83.1 (0.28) |
| 氟节胺 | 0.83 | 2.50 | 102.0 (4.23) | 93.4 (1.04) | 89.5 (1.21) |
| 狄氏剂 | 0.58 | 1.74 | 76.0 (9.56) | 83.9 (6.91) | 83.1 (0.74) |
| β -硫丹 | 4.23 | 12.70 | 97.4 (9.17) | 76.8 (3.80) | 81.0 (2.69) |
| 啉氧菌酯 | 0.47 | 1.41 | 81.4 (3.35) | 84.4 (0.82) | 88.9 (1.17) |
| 苯线磷 | 1.23 | 3.69 | 81.2 (3.57) | 86.7 (3.24) | 95.6 (1.37) |
| 己唑醇 | 3.93 | 11.78 | 74.2 (1.99) | 78.6 (1.15) | 84.9 (1.58) |
| 稻瘟灵 | 0.08 | 0.25 | 82.8 (1.60) | 83.9 (1.95) | 89.8 (1.35) |
| 丙溴磷 | 0.40 | 1.20 | 90.2 (1.46) | 88.5 (2.80) | 95.6 (1.25) |
| 丙草胺 | 0.77 | 2.31 | 82.9 (0.68) | 87.2 (0.78) | 92.7 (1.43) |
| 4,4'-滴滴伊 | 0.18 | 0.53 | 83.5 (3.59) | 77.0 (1.28) | 80.7 (0.44) |
| 异狄氏剂 | 1.94 | 5.83 | 76.7 (0.73) | 82.2 (6.49) | 84.8 (0.64) |
| 腈菌唑 | 0.22 | 0.67 | 83.0 (2.69) | 84.6 (1.36) | 85.2 (1.97) |
| 虫螨腈 | 1.99 | 5.97 | 87.4 (1.93) | 84.5 (7.30) | 88.5 (3.03) |
| 氟虫腈砷 | 0.26 | 0.78 | 85.8 (2.26) | 82.5 (1.35) | 85.2 (1.25) |
| 氟硅唑 | 0.63 | 1.89 | 85.2 (3.68) | 84.9 (2.99) | 85.6 (1.39) |
| 甲氧丙净 | 0.50 | 1.49 | 76.7 (4.39) | 74.6 (1.54) | 69.8 (2.14) |
| 噻呋酰胺 | 0.44 | 1.31 | 89.9 (1.17) | 90.2 (0.29) | 92.3 (1.56) |
| 除草醚 | 1.03 | 3.08 | 110.0 (2.17) | 98.6 (2.05) | 99.5 (0.79) |
| 2,4'-滴滴滴 | 0.15 | 0.46 | 84.6 (0.43) | 85.9 (0.66) | 92.7 (0.21) |
| 4,4'-滴滴滴 | 0.73 | 2.20 | 78.4 (2.15) | 62.5 (3.14) | 71.5 (7.60) |
| 噁霜灵 | 0.33 | 1.00 | 83.2 (3.20) | 72.1 (0.78) | 79.0 (3.72) |
| 2,4'-滴滴涕 | 0.06 | 0.17 | 78.4 (1.92) | 85.5 (0.66) | 95.4 (0.40) |
| 烯草酮 | 4.83 | 14.49 | 94.0 (5.03) | 72.1 (2.69) | 61.3 (2.74) |
| 三唑磷 | 0.70 | 2.10 | 88.2 (1.12) | 91.5 (1.52) | 97.4 (1.18) |
| 苯霜灵 | 1.71 | 5.14 | 80.8 (2.50) | 84.3 (1.11) | 92.9 (1.20) |
| 敌瘟磷 | 0.10 | 0.29 | 85.3 (1.25) | 92.5 (0.80) | 100.3 (1.48) |
| 脞菌酯 | 1.35 | 4.05 | 87.9 (1.00) | 90.8 (0.82) | 97.0 (1.00) |
| 丙环唑 | 0.57 | 1.71 | 91.5 (0.98) | 71.6 (0.79) | 85.9 (0.98) |
| 硫丹硫酸酯 | 0.11 | 0.33 | 84.5 (2.36) | 83.1 (0.17) | 82.8 (1.67) |
| 4,4'-滴滴涕 | 2.53 | 7.59 | 62.6 (0.23) | 71.0 (1.43) | 76.5 (10.79) |
| 戊唑醇 | 0.35 | 1.06 | 86.9 (1.44) | 85.9 (0.60) | 88.5 (1.66) |

表1(续)

| 化合物 | LODs ($\mu\text{g}/\text{kg}$) | LOQs ($\mu\text{g}/\text{kg}$) | 回收率(RSDs)/% | | |
|--------|-------------------------------------|-------------------------------------|--------------|--------------|--------------|
| | | | 0.01 mg/kg | 0.02 mg/kg | 0.10 mg/kg |
| 炔螨特 | 5.07 | 15.21 | 94.6 (8.44) | 90.6 (2.95) | 101.3 (0.36) |
| 增效醚 | 0.42 | 1.27 | 105.5 (0.15) | 102.9 (1.12) | 105.6 (0.61) |
| 磷酸三苯酯 | 0.21 | 0.62 | 86.8 (2.91) | 83.9 (0.75) | 88.0 (0.41) |
| 生物苯唑菊酯 | 5.86 | 17.58 | 112.6 (3.14) | 103.3 (0.61) | 93.6 (0.50) |
| 新燕灵 | 0.29 | 0.86 | 87.3 (1.87) | 85.3 (2.90) | 89.7 (1.59) |
| 异菌脲 | 1.17 | 3.51 | 68.0 (6.14) | 78.9 (3.13) | 93.5 (2.76) |
| 啶虫脒 | 5.32 | 15.97 | 66.8 (9.53) | 74.3 (10.03) | 67.7 (2.27) |
| 谷硫磷 | 0.14 | 0.42 | 93.6 (0.30) | 90.2 (0.79) | 91.9 (1.72) |
| 亚胺硫磷 | 0.21 | 0.63 | 93.6 (0.31) | 90.2 (0.80) | 91.9 (1.72) |
| 联苯菊酯 | 0.34 | 1.03 | 85.4 (0.28) | 86.7 (1.88) | 93.3 (0.84) |
| 溴螨酯 | 1.62 | 4.85 | 90.0 (3.61) | 88.5 (1.98) | 94.2 (1.29) |
| 联苯肼酯 | 4.90 | 14.70 | 94.9 (5.46) | 88.1 (6.05) | 95.6 (0.43) |
| 甲氧菊酯 | 1.42 | 4.26 | 89.2 (0.33) | 90.4 (1.58) | 97.0 (1.05) |
| 吡螨胺 | 0.07 | 0.22 | 90.2 (0.69) | 85.6 (2.61) | 89.1 (0.57) |
| 啶螨醚 | 1.13 | 3.39 | 81.3 (1.77) | 84.1 (0.60) | 89.9 (0.86) |
| 伏杀硫磷 | 0.51 | 1.52 | 84.1 (1.85) | 82.7 (1.12) | 89.1 (0.85) |
| 吡丙醚 | 0.39 | 1.17 | 84.5 (5.75) | 91.6 (6.15) | 94.5 (1.09) |
| 氯氟菊酯 | 2.18 | 6.53 | 95.2 (2.66) | 88.9 (0.48) | 94.5 (0.67) |
| 灭蚊灵 | 0.04 | 0.11 | 66.7 (5.88) | 70.2 (1.25) | 72.5 (2.17) |
| 吡啶醚菊酯 | 0.34 | 1.01 | 81.0 (1.62) | 76.7 (1.85) | 86.7 (0.29) |
| 氯菊酯 | 10.91 | 32.72 | 91.7 (0.81) | 90.6 (1.06) | 97.0 (1.08) |
| 氯氟菊酯 | 0.54 | 1.62 | 89.2 (0.89) | 90.0 (1.28) | 86.2 (0.97) |
| 啶螨灵 | 0.24 | 0.73 | 95.2 (2.21) | 93.6 (1.57) | 98.3 (0.53) |
| 蝇毒磷 | 1.24 | 3.73 | 95.1 (0.40) | 95.7 (3.42) | 97.0 (0.67) |
| 对氧磷 | 2.03 | 6.10 | 100.5 (1.03) | 90.9 (0.41) | 77.0 (3.22) |
| 咪鲜胺 | 0.14 | 0.42 | 95.3 (2.04) | 93.0 (1.76) | 98.2 (0.50) |
| 螺螨酯 | 6.52 | 19.56 | 99.6 (7.01) | 79.8 (7.68) | 76.6 (0.65) |
| 腈苯唑 | 0.59 | 1.76 | 83.5 (2.33) | 86.6 (1.89) | 87.6 (1.21) |

表1(续)

| 化合物 | LODs ($\mu\text{g}/\text{kg}$) | LOQs ($\mu\text{g}/\text{kg}$) | 回收率(RSDs)/% | | |
|-------|-------------------------------------|-------------------------------------|--------------|--------------|--------------|
| | | | 0.01 mg/kg | 0.02 mg/kg | 0.10 mg/kg |
| 啶酰菌胺 | 0.30 | 0.90 | 88.2 (0.96) | 86.6 (0.96) | 84.4 (2.34) |
| 噻乐灵 | 5.45 | 16.35 | 102.1 (4.96) | 92.1 (0.62) | 96.6 (0.46) |
| 氟戊菊酯 | 3.32 | 9.97 | 104.4 (8.28) | 93.7 (1.84) | 95.9 (0.76) |
| 醚菊酯 | 2.12 | 6.36 | 104.3 (5.49) | 92.4 (0.72) | 96.4 (0.31) |
| 氯氟菊酯 | 0.25 | 0.74 | 86.5 (1.31) | 89.2 (0.98) | 97.6 (0.49) |
| 氟戊菊酯 | 4.00 | 12.01 | 110.0 (3.77) | 94.7 (1.02) | 97.6 (0.31) |
| 氟胺菊酯 | 0.23 | 0.70 | 85.5 (4.91) | 104.5 (0.70) | 119.3 (0.17) |
| 苯醚甲环唑 | 0.24 | 0.72 | 87.6 (2.24) | 87.0 (0.31) | 90.9 (0.76) |
| 溴氧菊酯 | 4.79 | 14.37 | 114.3 (3.50) | 99.6 (2.64) | 101.6 (0.92) |
| 啉菌酯 | 0.63 | 1.89 | 83.9 (2.88) | 84.4 (3.68) | 82.1 (2.75) |
| 烯酰吗啉 | 0.60 | 1.79 | 89.0 (1.60) | 86.3 (1.78) | 83.9 (2.26) |

注: 相对标准偏差(relative standard deviation, RSD)。

2.5 实际样品测定

采用本研究建立的方法对猪肉、牛肉、羊肉、鸡肉、鱼肉和鸡蛋各10批样品进行检测。结果显示,1批鸡肉中检出啶酰菌胺(1.80 $\mu\text{g}/\text{kg}$),2批鸡蛋中检测出氟虫腈(1.74 $\mu\text{g}/\text{kg}$ 、1.90 $\mu\text{g}/\text{kg}$),5批鱼肉中均检出4,4-滴滴伊(1.80~2.18 $\mu\text{g}/\text{kg}$),其含量均远低于GB 2763—2021《食品安全国家标准 食品中农药最大残留限量》的限量要求,色谱图详见图5。此外,5批鱼肉中有其他农药检出,包括氟铃脲、二甲戊灵、噻唑酰胺、氟戊菊酯,测定含量均高于LOQ,但其在GB 2763—2021中均未规定限量要求,按照日本《食品中残留农业化学品肯定列表制度》^[31]规定的“一律

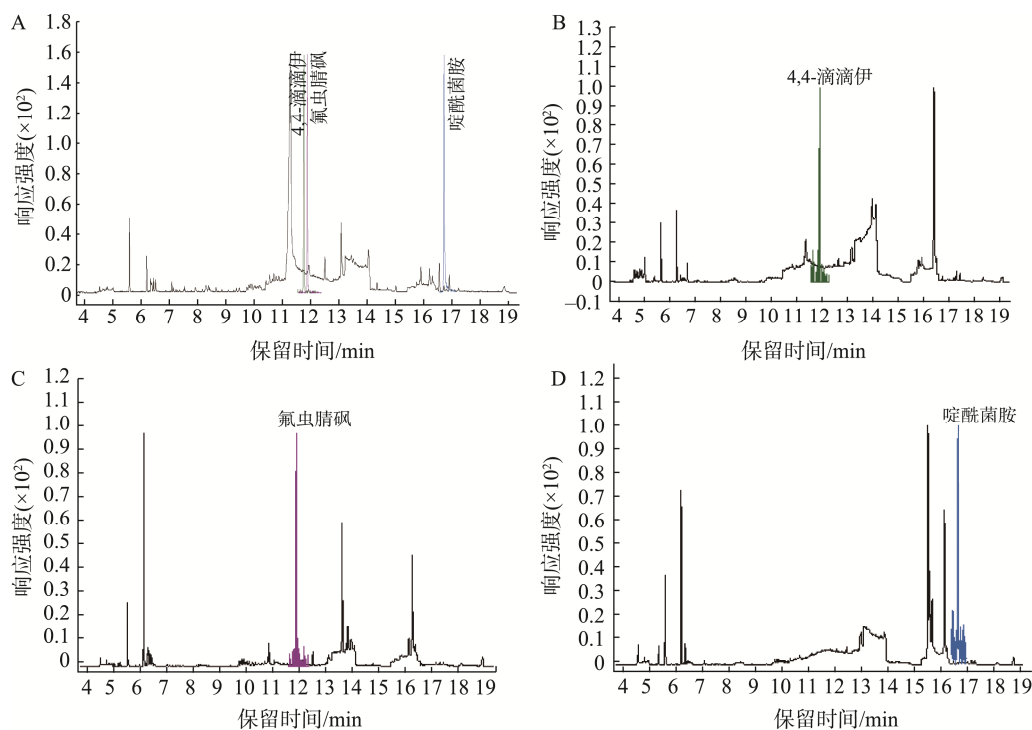


图5 标准溶液(A)和阳性样品(B 鱼肉, C 鸡蛋, D 鸡肉)的色谱图

Fig.5 Chromatograms of standard solution (A) and positive samples (B fish, C egg, D chicken)

标准”限量值为 10 $\mu\text{g}/\text{kg}$, 有 3 批鱼肉中的氟铃脲高于此限量要求, 其他样品均未检出农药残留。可见, 鱼肉中农药残留的风险值得关注。

3 结 论

本研究以 dSPE EMR-Lipid 净化技术为前处理的去脂手段, 结合 GC-MS/MS 建立一种快速、准确测定动物性食品中 146 种农药残留的定性定量分析方法。该前处理方法操作简便, 净化效果好, 可有效降低基质中的杂质干扰, 选择性和准确度高, 适用于动物性食品中多种农药残留的同时测定分析, 可为动物性食品中多农药残留的日常监测和监管提供技术支撑, 也可为后续标准的制修订提供参考。

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