出國報告（出國類別：開會）

參加第 15 屆 EPRW
歐洲農藥殘留研討會

服務機關：農業部農業藥物試驗所
姓名職稱：施念昊 助理研究員
派赴國家：瑞士 (蘇黎世)
出國期間：113 年 9 月 13 日至 113 年 9 月 24 日
報告日期：113 年 12 月 9 日

摘要

歐洲農藥殘留研討會（European Pesticide Residue Workshop, EPRW）是歐洲乃至全球最重要的農藥殘留分析與監測的專業會議之一，每兩年舉辦一次。該活動匯聚來自研究機構、政府監管機構、產業界及相關技術供應商的專家，為農藥殘留檢測和風險評估領域提供了一個國際化的交流平台，今年第十五屆研討會於2024 年 9 月 16 日至 20 日在瑞士蘇黎世舉行，會議主要議題聚焦於先進的分析技術和方法、高解析質譜的定性和定量方法、單一殘留方法、分析質量控制和驗證程序的指南、品質保證和實驗室認證要求、毒理學和風險評估、農藥註冊和使用的趨勢、監測計劃、法規問題、綠色分析化學、「新食品」分析等。特別值得關注的是，今年的主題日於 9 月 18 日（週三）舉行，聚焦“綠色分析化學、微型化與自動化”，專家分享此領域的多元觀點。此研討會促進國際間的合作與信息共享，還為標準制定與方法優化提供了科學依據，是農藥殘留檢測領域的重要風向標，共同推動農藥殘留分析領域的進步與發展。本所於研討會中發表「The application of Rapid Screening MassSpectrometry Mobile Detection Vehicles」壁報論文 1 篇。本報告將聚焦於今年主題日之重要內容及國際發展趨勢分享 6 篇口頭論文發表內容及 1 篇壁報展示內容，另外也分享亞洲國家日本及韓國壁報展示內容 4 篇，農藥參考物質壁報 1 篇，最後針對本年度得獎壁報 3 篇進行介紹。

目次

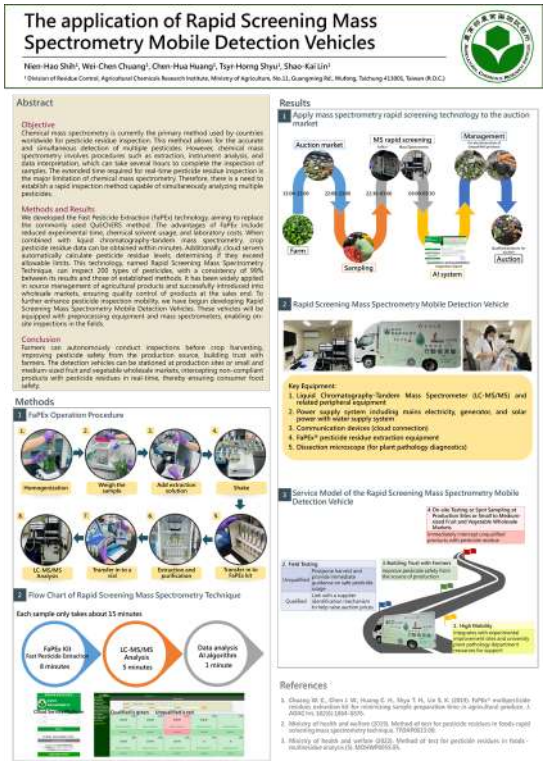
壹、目的

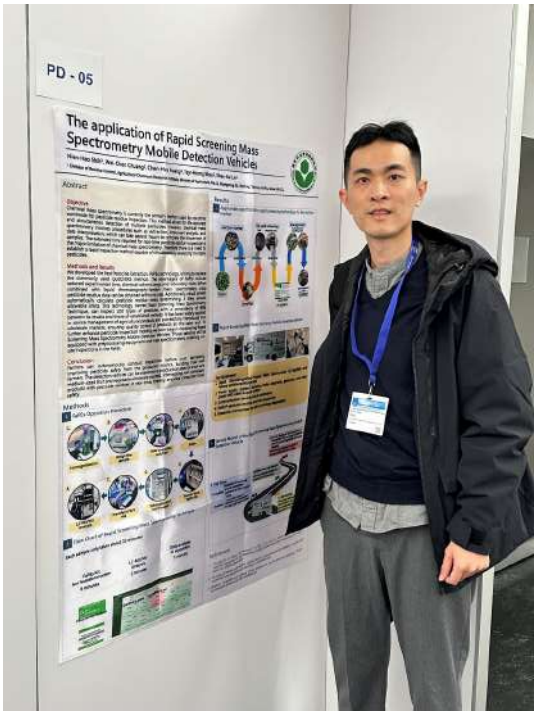
歐洲農藥殘留研討會（European Pesticide Residue Workshop, EPRW）是歐洲乃至全球最重要的農藥殘留分析與監測的專業會議之一，每兩年舉辦一次。該活動匯聚來自研究機構、政府監管機構、產業界及相關技術供應商的專家，為農藥殘留檢測和風險評估領域提供了一個國際化的交流平台，今年第十五屆研討會於2024 年 9 月 16 日至 20 日在瑞士蘇黎世舉行。此次研討會的核心議題涵蓋新型分析技術的開發與應用、多殘留分析方法的改進、檢測儀器的創新、數據質量與驗證標準的提升，以及法規與政策的最新動向。與會者將有機會參加專題演講、技術工作坊、口頭報告和學術壁報展示，全面瞭解行業進展。特別值得關注的是，今年的主題日於 9 月 18 日（週三）舉行，聚焦“綠色分析化學、微型化與自動化”，專家分享對這些日益重要領域的多元觀點。作為一項傳統，本屆研討會於 9 月 16 日（週一）下午啟動會前課程，由歐盟食品農藥殘留單一方法參考實驗室（European Union Reference Laboratory for Pesticide Residues in Food with Single Residue Methods）主講，深入探討單一殘留方法（SRM）化合物的最新進展。從週二到週五，科學日程將包括主旨報告、年輕科學家的口頭報告以及展示約 160 份壁報的專區，展現該領域充滿活力的研究社群。此外，展覽區和供應商專場將展示分析儀器和實驗室設備的最新創新技術，為儀器製造商和實驗室供應商提供展示其最新產品與服務的機會，推動新技術的市場化發展。該會議以促進科學研究與實際應用相結合為目標，幫助監管機構和產業界提高食品和農產品的安全性及合規性。隨著農業技術的進步和全球化的加速，農藥殘留問題已成為全球食品安全領域的關注焦點，EPRW 不僅促進了國際間的合作與信息共享，還為標準制定與方法優化提供了科學依據，是農藥殘留檢測領域的重要風向標，共同推動農藥殘留分析領域的進步與發展。

歷屆 EPRW 研討會手冊封面及舉辦地點(圖片摘錄自研討會提供手冊)

貳、過程

第 15 屆歐洲農藥殘留研討會於瑞士蘇黎世舉行，本次會議有 22 家廠商參展，29 位專家學者進行專題演講，展示壁報依主題分為分析方法的發展與應用、監管問題和監控、毒理學和攝取量評估、其他主題及廠商壁報 5 大類，共 156 份壁報。會議主要議題聚焦於先進的分析技術和方法、高解析質譜的定性和定量方法、單一殘留方法、分析質量控制和驗證程序的指南、品質保證和實驗室認證要求、毒理學和風險評估、農藥註冊和使用的趨勢、監測計劃、法規問題、綠色分析化學、「新食品」分析等。本所於研討會中發表「The application of Rapid Screening MassSpectrometry Mobile Detection Vehicles」壁報論文 1 篇。由於研討會議題廣泛，本次報告將聚焦於今年主題日“綠色分析化學、微型化與自動化”之重要內容及國際發展趨勢進行分享。



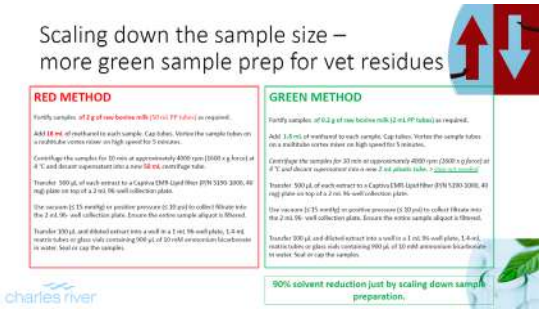


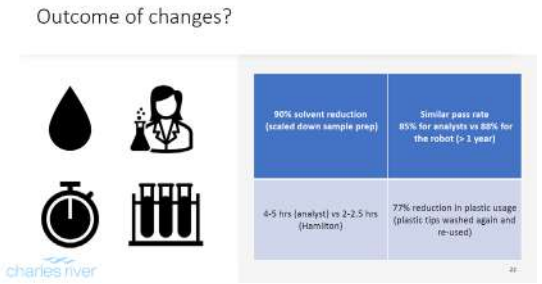
本所於研討會發表「質譜快檢行動檢測車之應用」之壁報論文。

一、口頭論文發表內容

主題一：殘留分析方法開發：從基本原理到現代效率(Residues method development: From first principles to modern efficiency)。由英國愛丁堡查理斯河實驗室(Charles River Laboratories) Pawel Markowicz 發表演說。

農藥的使用雖然提高了農業生產力，但也引發了對農藥殘留對健康和環境風險的擔憂，為保護人類、動物和環境健康，2020 年推出的歐盟「從農田到餐桌」戰略等嚴格的法規旨在限制有害物質的使用。由於農藥殘留的物理化學性質多樣及目標濃度極低，且需要對複雜基質進行樣品淨化，因此開發可靠的檢測方法具有挑戰性。準確且穩定方法需要高效的樣品製備和先進的檢測技術，方法開發對於全球分析實驗室來說是一個關鍵且耗時費力的過程，正確開發的方法是成功進行方法驗證和樣品分析的關鍵，以提供準確的數據用於監管提交。本報告將探討分析方法開發方面的策略，旨在提高效率、穩健性並縮短分析時間，概述結合基本原理和創新方法來優化傳統方法並開發新方法的策略，並利用現代設備和更綠色的實踐，強調瞭解化學原理在優化傳統方法中的重要性，通過整合先進技術和綠色溶劑，可以使方法更加穩健和環保，減少交叉污染風險並提高樣品處理量。重點將放在從傳統樣品製備技術轉向更現代化設備的更為友好的方法，將探討基本 pH 值層析分離在液相層析質譜儀分析中相對於酸性條件的優勢。此外，還將討論手性色譜技術，特別是對難以分離的手性分子使用超臨界流體色譜（SFC）的必要性，這種方法提高了分離對映異構體的分離度和效率，支持了製藥和農化行業的各種應用。

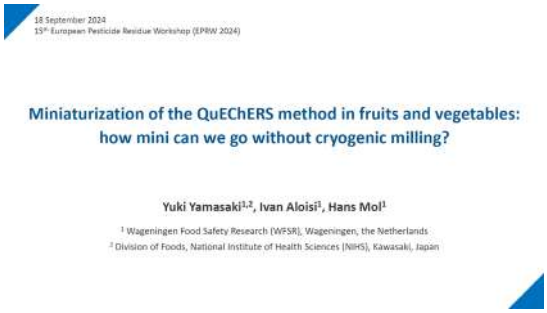


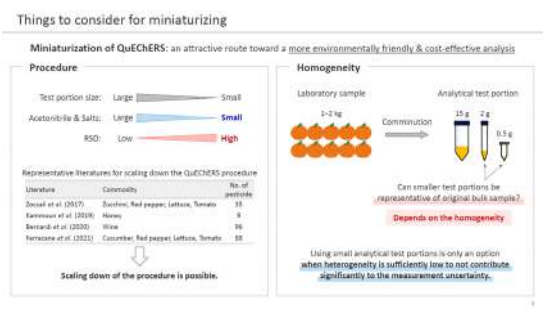


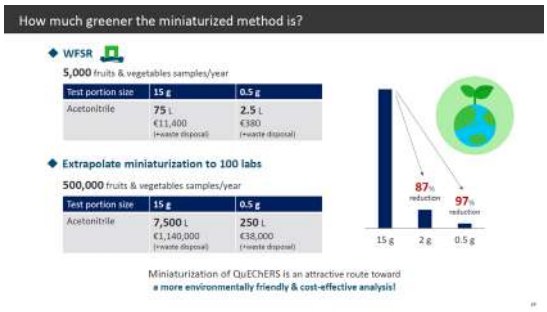
(Pawel Markowicz et al., 2024)

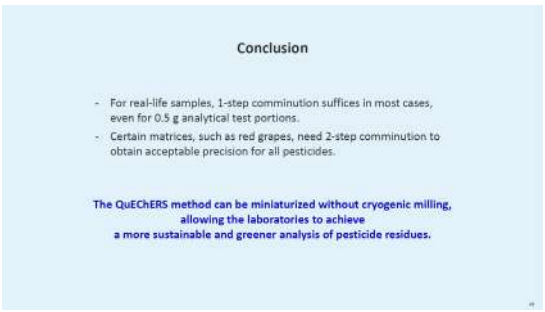
主題二：QuEChERS 方法在蔬果中的微型化：如不進行低溫研磨，我們能做到多小？(Miniaturization of the QuEChERS method in fruits and vegetables: How mini can we go without cryogenic milling?)。由荷蘭瓦赫寧根瓦赫寧根食品安全研究所 (Wageningen Food Safety Research) Yuki Yamasaki 發表演說。

QuEChERS 方法是一種常用的農藥殘留分析方法。然而，該方法通常需要較大量的溶劑和鹽，且需要較大的樣品量，這使得其不夠環保且成本較高。因此，研究者們一直致力於縮小該方法的規模，以實現更環保、更經濟的分析。本研究旨在探索 QuEChERS 方法的微型化潛力，即減少溶劑和鹽的用量，並縮小分析樣品的大小。研究者們特別關注如何通過標準食品加工設備（如 Stephan 混合器和 Turrax 均質器）對水果和蔬菜進行常溫研磨，以達到足夠的樣品均質性，從而實現小型分析樣品的使用。樣品均質性:對於菠菜和柑橘，1 步研磨就足以獲得足夠的樣品均質性，即使對於 0.5 g 的小型分析樣品也是如此。對於紅葡萄，2 步研磨是必要的，特別是對於小型分析樣品，才能獲得足夠高的精密度。農藥回收率：大多數農藥的濃度在不同大小的分析樣品之間是相似的。然而，極性農藥在小型分析樣品中的回收率較低，這可以通过使用回收因子進行校正。總體而言，本研究表明 QuEChERS 方法可以成功地微型化，而無需使用低溫研磨。這為實驗室實現更環保、更經濟的農藥殘留分析提供了新的途徑。





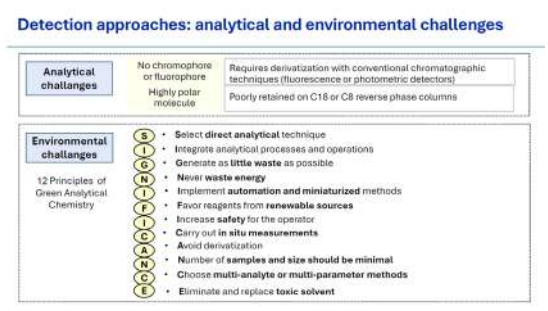


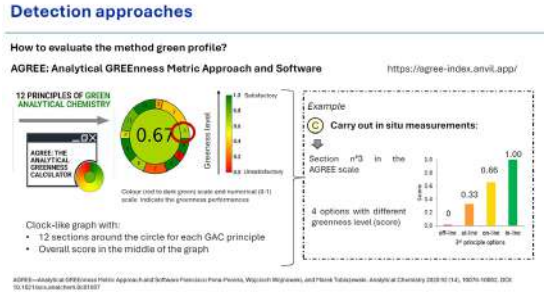


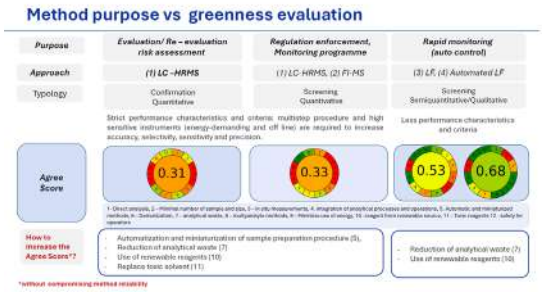
(Yuki Yamasaki et al., 2024)

主題三：食品中嘉磷塞的測定：質譜法和免疫層析法的性能評估與環境評估(Glyphosate determination in food: Performance evaluation, environmental assessment of mass spectrometric and immunochromatographic methods)。由義大利國家研究委員會食品生產科學研究(Institute of Sciences of Food Production, National Research Council of Italy) Biancamaria Ciasca 發表演說。

嘉磷塞受到國家和國際監管機構的定期評估，迄今為止，經提出了基於 LC-MS/MS 的方法來單獨或與其他極性農藥一起測定嘉磷塞，而流動注射-串聯質譜(FI-MS/MS)已被證明是一種有前途的快速檢測嘉磷塞的替代方法。此外，少數側流試紙(LFD)已被商業化，以經濟有效的方式快速篩選嘉磷塞。除了評估分析性能外，在選擇適合目的的分析方法時，還越來越需要評估所用方法的環境影響和操作員安全。本研究根據 SANTE/11312/2021 指南開發、驗證和比較三種不同的嘉磷塞測定方法，分別基於 LC-MS/MS、FI-MS/MS 和全自動免疫色譜測試，將基於 GAPI（綠色分析程序指數）工具評估所提出的分析方法的生態影響。具體來說，將使用 AGREE（分析綠色度度量方法和軟件）工具，該工具包含 10 個標準來評估導致整體環境影響的不同因素以評估綠色度。



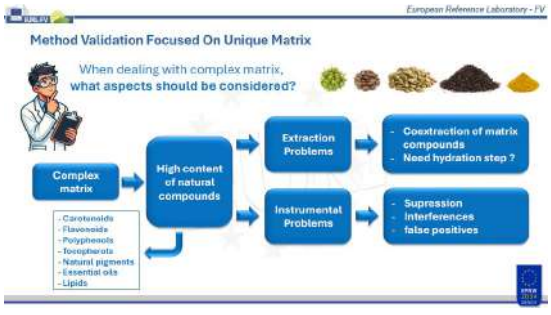


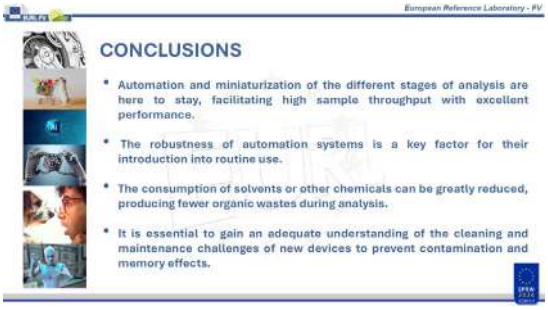


(Biancamaria Ciasca et al., 2024)

主題四：來自歐盟水果蔬菜參考實驗室的消息(Automation and Miniaturization for Enhancing Analytical Methods in Pesticide Residue Evaluation in Food)。由西班牙阿爾梅里亞-歐洲水果與蔬菜農藥殘留參考實驗室(European Reference Laboratory for Pesticide Residues in Fruit and Vegetables) Amadeo Fernandez Alba 發表演說。

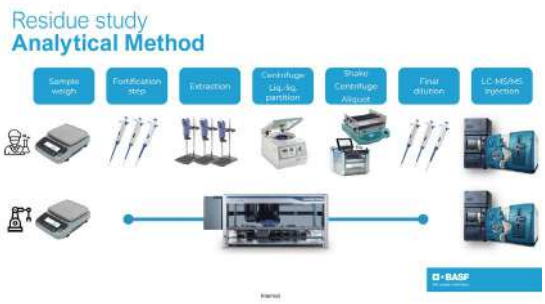
食物控制實驗室專門檢測農藥殘留，為了符合嚴格的食物安全法規，近年來透過先進質譜儀擴展分析範圍並降低定量極限(LOQ)而取得重大進展。然而，隨著新方法和分析物的引入，在不影響結果品質的前提下，加速分析程序變得至關重要。自動化和微型化無疑是支持這些新目標或擴展目標的重要議題，包括減少實驗室廢棄物。最近，開發了新設備來實現這些目標。同時，考慮可以解決這些實施問題的創新方法的差異以及在滿足食品控制實驗室日常應用實踐要求時可能出現的額外挑戰也至關重要。本研究探索和討論了一些新引入或即將實施的分析工具的進展。這些發展特別關注自動化和微型化。該研究強調分析方法的創新方向，強調它們向更高效和環保方法的演變。首先，重點關注樣品提取的自動化，使用 EDGE®或 Extreva®等分析工具，特別強調乾性樣品。接下來，討論以多殘留方法為重點的清潔程序，特別是微型固相萃取(Micro-SPE)。最後，深入研究層析法，特別是微流層析。對這些提案的評估，無論是新的還是相對成熟的，都可以提高樣品處理量，減少實驗室廢物，並根據 ISO 17025 維持必要的性能。

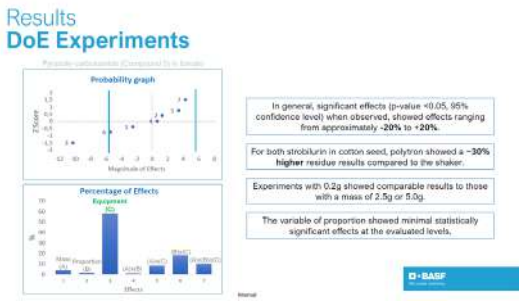


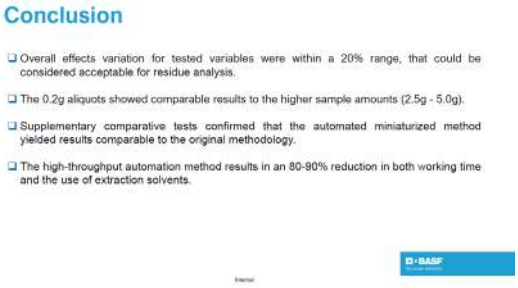


(Amadeo Fernandez Alba et al., 2024)

主題五：食品農藥殘留分析中樣品大小和萃取設備影響的全面評估(Comprehensive evaluation on the impact of sample size and extraction equipment in pesticide residue analysis in food)。由巴斯夫公司(BASF S.A) Wesley Jose 發表演說。正確的樣品採樣和處理對於獲得準確的農藥殘留分析結果一直至關重要。然而，隨著行業和實驗室開始使用高通量自動化分析方法分析約 100 mg 的測試樣品，這個問題變得更加重要。減少分析測試樣品的大小通常可以提高樣品處理量、減少勞動力並實施自動化方法。然而，必須確保測試樣品準確代表原始大批量樣品，以滿足分析要求。為了確定最適合的樣品大小並評估提取設備的潛在差異，選擇來自不同代表性的 4 種基質進行了徹底分析，這些基質含有來自多種不同分析物的殘留。首先採用實驗設計(DOE)方法，特別是利用全因子設計(2^3，這些分析系統地評估殘留分析萃取步驟中不同因素的影響，例如樣品大小、萃取設備和樣品量/萃取體積比例比，以實現高通量自動化程序在我們的分析實驗室中的實施。考慮縮小樣品大小以適用於多種分析方法，這項額外評估有助於確認先前的發現，並提供有關最佳樣品大小和萃取設備要求的更多見解。本研究旨在分享綜合研究的結果，為適當的農藥殘留分析樣品處理技術提供寶貴的見解，這些發現不僅有利於農化產業，還有利於監管機構、實驗室和涉及確保食品安全和環境保護的利益相關者。



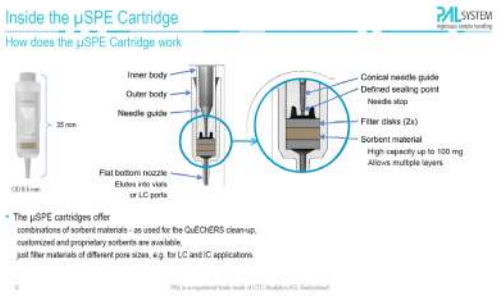


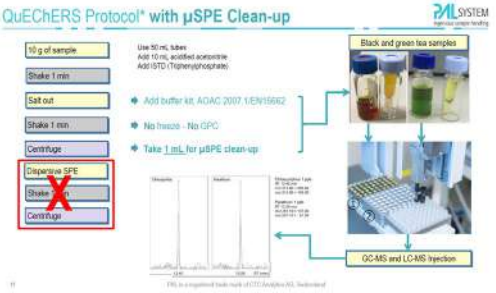


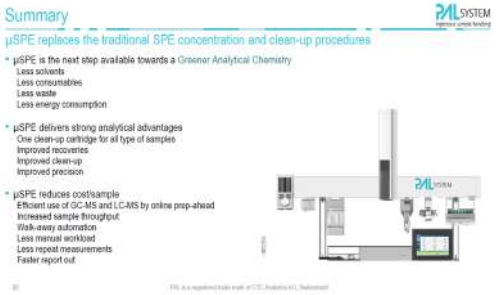
(Wesley Jose et al., 2024)

主題六：全新 μSPE 用於自動化農藥萃取與淨化(The New PAL Micro-SPE Cartridge for Automated Pesticides Extraction and Clean-up)。由瑞士思特斯分析儀器有限公司(CTC Analytics AG) Hans-Joachim Hübschmann 發表演說。

一種新的 μSPE 柱被引入，用於自動處理農藥分析的原始提取物，以便進行 GC-MS 或 LC-MS 分析。本文討論新型 PAL μSPE 的設計標準以及與傳統 SPE 的比較。μSPE 柱的新格式允許在 PAL RTC 機器人採樣系統上可靠地自動化，用於獨立和在線 GC-MS 以及 LC-MS 分析。此外，只需過濾樣品即可進行自動 LC 或 IC 分析。μSPE 的使用結合了許多對實驗室物流和數據質量的優勢，吸附劑材料的選擇大大簡化，適用於所有食品商品，甚至高脂肪含量樣品。省去了耗時的洗脫液蒸發步驟。所有樣品可以在同一時間線上進行製備和分析，以實現最佳的再現性。當然，自動化系統不僅可以解放人力，還可以騰出時間進行數據評估和報告。自動化 μSPE 清潔工作流程的多功能性體現在農藥分析中，包括使用乙腈或乙酸乙酯的 QuEChERS 萃取，或使用甲醇進行 QuPPe 萃取以獲得高極性化合物。本文介紹常規實驗室中實踐的幾個應用範例。





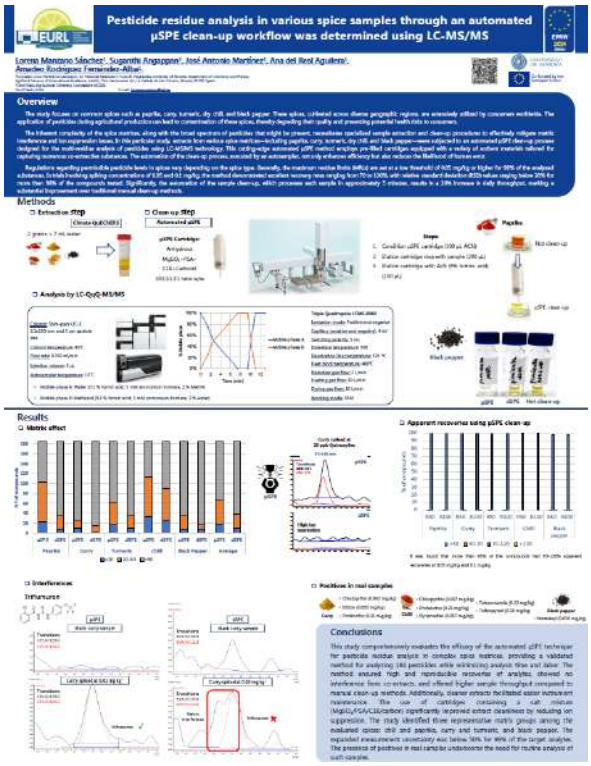


(Hans-Joachim Hübschmann., 2024)

二、壁報展示內容

壁報一：以自動化 μSPE 淨化流程及 LC-MS/MS 進行各種香料樣品農藥殘留分析 (Pesticide residue analysis in various spice samples through an automated μSPE clean-up workflow was determined using LC-MS/MS)。由阿爾梅里亞大學-歐洲水果與蔬菜農藥殘留參考實驗室 José Antonio Martínez 等人發表。

由於香料基質的複雜性以及可能存在的農藥種類繁多，因此需要採用專業化的樣品提取和淨化流程，以有效減少基質干擾和離子抑制問題。在本研究中，不同香料基質（包括辣椒粉、咖喱、薑黃、幹辣椒和黑胡椒）的提取物被應用自動化的 μSPE 淨化，旨在使用 LC-MS/MS 技術進行農藥的多殘留分析。這種先進的自動化 μSPE 方法使用預填充的柱筒，其中裝有多種吸附材料，專門用於捕獲多種共提取物質。淨化過程由自動進樣器執行自動化操作，不僅提高了效率，還降低了人為誤差的可能性。不同香料的 MRLs 因香料種類而異。通常情況下，99%分析物質的 MRLs 設定在 0.05 mg/kg 或更高。在 0.05 和 0.1 mg/kg 的回收試驗中，該方法顯示出優異的回收率（70%至 120%），並且超過 98%的化合物的 RSD 值低於 20%。值得注意的是，樣品淨化的自動化處理每個樣品僅需約 5 分鐘，相較于傳統的手動淨化方法，日處理量提高了 20%，顯著提升了工作效率。

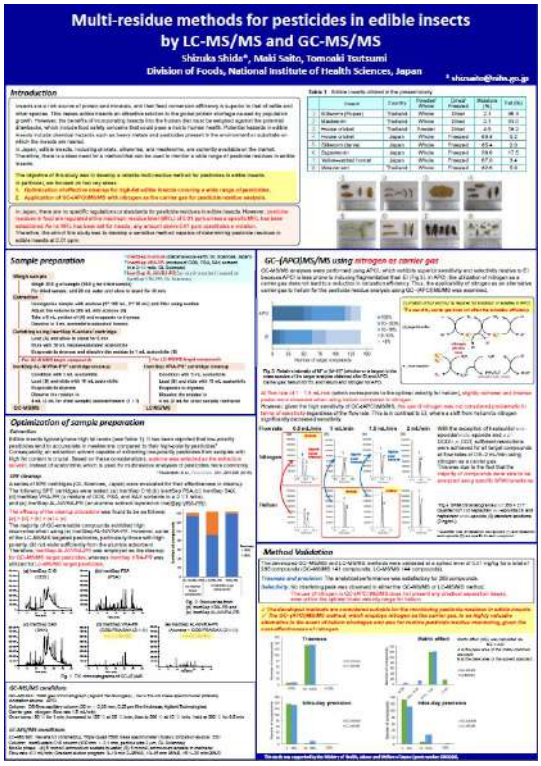


(José Antonio Martínez1 et al., 2024)

本研討會亞洲國家日本及韓國也有派員參加，以下將介紹 2 篇日本及 2 篇韓國壁報內容：

壁報二：LC-MS/MS 和 GC-MS/MS 檢測食用昆蟲中的農藥殘留(Multi-residue methods for pesticides in edible insects by LC-MS/MS and GC-MS/MS)。由日本國立保健科學研究所食品部(Division of Foods, National Institute of Health Sciences, Japan) Shizuka Shida 等人發表。

昆蟲富含蛋白質和礦物質，其飼料轉換效率高於牛和其他物種。這使得食用昆蟲成為解決人口增長導致全球蛋白質短缺具吸引力的解決方案。然而，使用食物和農業廢物作為昆蟲飼料存在風險，尤其是農藥污染。在日本，蟋蟀、蠶和黃粉蟲等食用昆蟲已經上市。因此，開發一種監測食用昆蟲中廣泛農藥殘留的方法至關重要。本研究開發的方法使用 LC-MS/MS 或 GC-MS/MS 對 285 種化合物進行 0.01 mg/kg 的確效。269 種化合物取得了令人滿意的分析性能，準確度範圍為 70%至 120%，精密度小於 20%。此方法被認為適用於監測食用昆蟲中的農藥殘留，已獲得日本厚生勞動省認可（grant number 23K1010）。

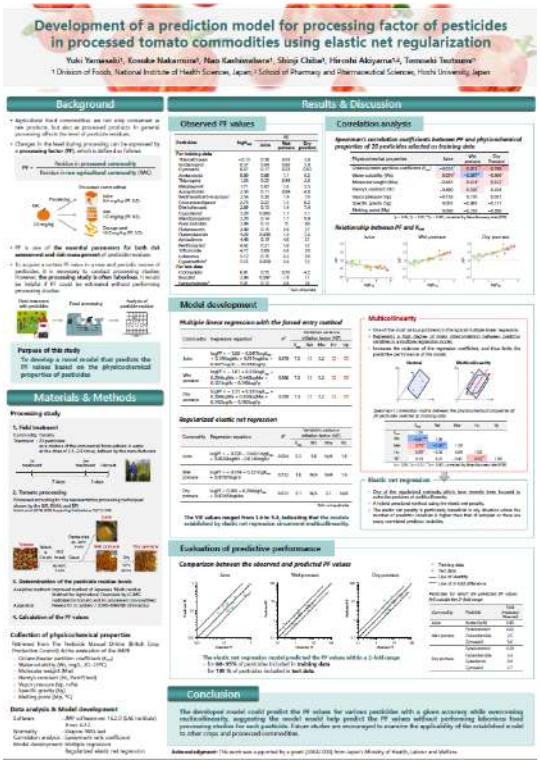


(Shizuka Shida et al., 2022)

壁報三：使用彈性網路迴歸開發加工番茄商品中農藥處理因子的預測模型(Development of a prediction model for processing factor of pesticides in processed tomato commodities using elastic net regularization)。由日本國立保健科學研究所食品部 Yuki Yamasaki 等人發表。

加工因子(PF)是評估加工食品中農藥殘留風險的重要參數，代表著食品加工過程中農藥殘留水平的變化。PF 值是透過加工研究的結果計算得出的實際數值，但此類研究通常需要繁瑣的程序，例如種植作物、田間噴灑農藥、食品加工以及分析農藥殘留量等。若能不進行加工研究就能估算 PF 值，將會非常便利。因此，

本研究開發了一個新型模型，可以根據農藥的理化特性來預測 PF 值。研究人員選用了 23 種具有廣泛理化特性的農藥，在番茄田裡進行了兩次施藥。採收後兩天，番茄加工成汁液、濕渣和乾渣。利用 LC-MS/MS 分析了生鮮番茄和加工番茄製品中的農藥殘留物。在數據分析中，將選定的 23 種農藥分為訓練數據(20 種)和測試數據(3 種)，並利用訓練數據開發模型。斯皮爾曼等級相關係數顯示，PF 值與農藥的理化特性(例如分子量、辛醇/水分配系数、水溶性等)呈正向或負向相關。

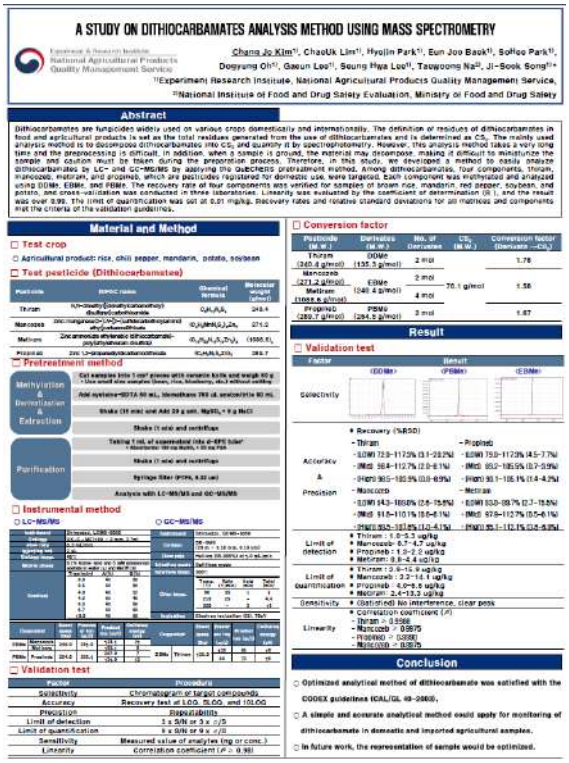


(Yuki Yamasaki et al., 2024)

壁報四：二硫代胺基甲酸鹽類質譜分析方法之研究(A STUDY ON DITHIOCARBAMATES ANALYSIS METHOD USING MASS SPECTROMETRY)。由韓國國家農產品品質管理局實驗研究所(Experiment Research Institute, National Agricultural Products Quality Management Service) Chang Jo Kim 等人發表。

目前主要使用的分析方法是將二硫代胺基甲酸鹽類分解為 CS_2，並透過分光光度法對其進行定量。然而，這種分析方法需要很長時間，而且預處理較困難。此外，研磨樣品可能會導致物質分解，使得樣品微型化變得困難，且在製備過程中需格外小心。因此，本研究開發了一種利用 QuEChERS 前處理方法，以 LC-MS/MS 和 GC-MS/MS 輕鬆分析二硫代氨基甲酸酯的方法。在二硫代氨基甲酸酯中，針對了四種國內登記使用的農藥成分：得恩地、鋅錳乃浦、免得爛和甲基鋅乃浦。使用 DDMe、EBMe 和 PBMe 對進行甲基化和分析。 對糙米、橘子、紅辣椒、大豆和馬鈴薯樣品確效了四種成分的回收率，並在三個實驗室進行了交叉確效。通過決定係數（R^2）評估線性，結果大於 0.99。定量極限為 0.01 mg/kg。所有基質和

成分的回收率和相對標準偏差均符合驗證指南的。



A STUDY ON DITHIOCARBAMATES ANALYSIS METHOD USING MASS SPECTROMETRY

Chang Jo Kim[1], ChaoUk Lim[1], Hyojin Park[1], Eun Joo Baek[1], Soohee Park[1], Dooyung Oh[1], Gaeun Lee[1], Seung Hwa Lee[2], Taeyoong Na[2], Ji-Sook Song[2]*

[1]Experiment Research Institute, National Agricultural Products Quality Management Service,
[2]National Institute of Food and Drug Safety Evaluation, Ministry of Food and Drug Safety

Abstract

Material and Method

Result

Conclusion

(Chang Jo Kim et al., 2024)

壁報五：農產品、有機資材及農業環境中 463 種農藥殘留物分析方法開發 (DEVELOPMENT OF ANALYSIS METHODS FOR 463 TYPES OF PESTICIDE RESIDUES IN AGRICULTURAL PRODUCTS, ORGANIC FARMING MATERIALS, AND AGRICULTURAL ENVIRONMENTS)。由韓國國家農產品品質管理局實驗研究所 Chang Jo Kim 等人發表。

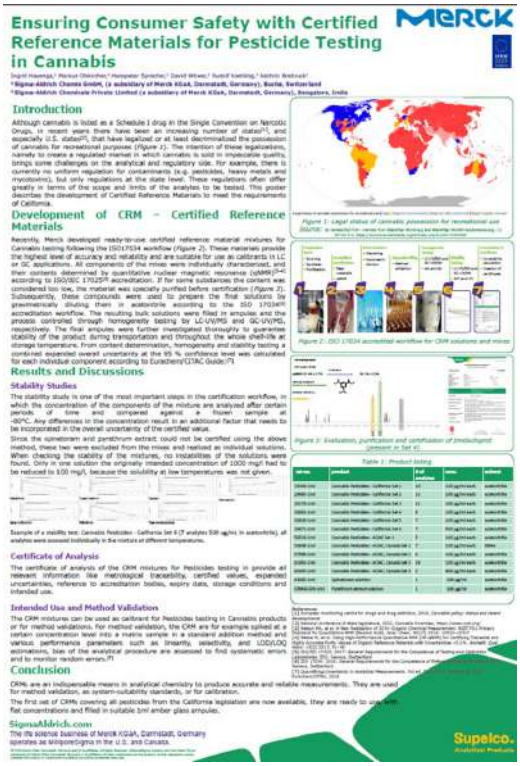
總共開發了三種分析方法：農產品分析方法、有機資材分析方法和農業材料（蘑菇培養基、果袋）、土壤和水分析方法。總共選定了 463 種農藥，包括國內分佈和使用量較高的農藥，以及在農業環境殘留調查中檢測到的成分。測試的農藥相同，但分析方法根據每個樣品的特徵進行了修改。前處理方法是 QuEChERS 方法的改良版，使用的分析儀器是 LC-MS/MS 和 GC-MS/MS。之後，對分析方法進行確效。該分析方法由三個實驗室進行了交叉確效。結果定量極限低於 0.01 mg/kg，決定係數大於 0.98。大多數基質和成分的回收率和相對標準偏差符合驗證指南的標準。

(Chang Jo Kim et al., 2024)

本次研討會也展示少數農藥參考物質之研究：

壁報六：確保消費者安全：大麻農藥檢測中認證參考物質的重要性(Ensuring Consumer Safety with Certified Reference Materials for Pesticide Testing in Cannabis)。由 Sigma-Aldrich 公司 Ingrid Hayenga 等人發表。

近年來，越來越多州將娛樂用大麻合法化，這導致了對監管的需求。認證參考物質有助於實施這些法規並確保合規。該壁報描述了專門用於測試大麻產品的農藥溶液的開發過程。這包括起始材料的認證、溶液的重量分析製備、穩定性監測和可追溯性測量。

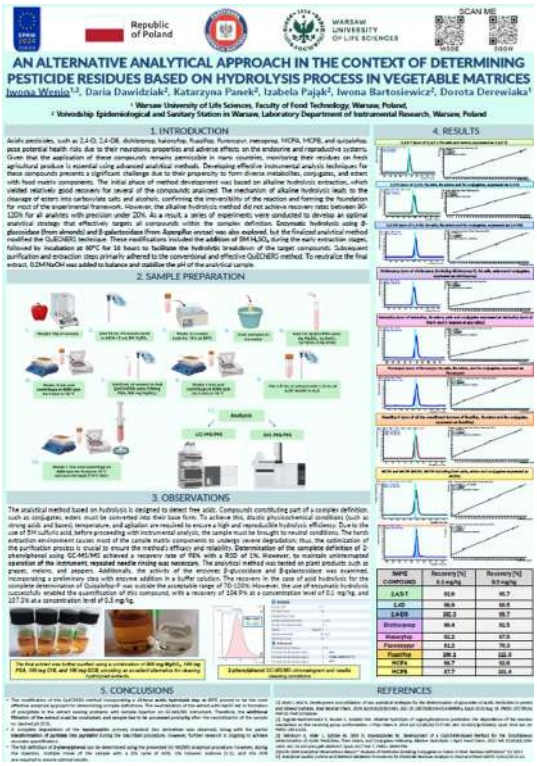


(Ingrid Hayenga et al., 2024)

本次研討會有 3 篇得獎壁報，壁報獎評選標準為科學內容與品質、原創性對日常應用的相關性、設計/佈局/清晰度/自解釋性及個人展示（回答問題），以下將介紹得獎壁報：

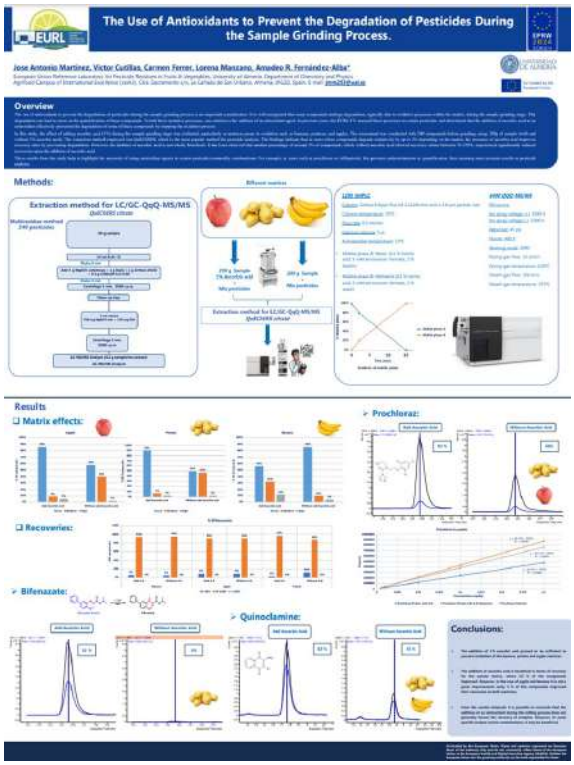
壁報七：一種將蔬菜基質水解的農藥殘留分析替代方法(AN ALTERNATIVE ANALYTICAL APPROACH IN THE CONTEXT OF DETERMINING PESTICIDE RESIDUES BASED ON HYDROLYSIS PROCESS IN VEGETABLE MATRICES)。由華沙生命科學大學食品技術學院(Warsaw University of Life Sciences, Faculty of Food Technology) Iwona Wenio 等人發表。

酸性農藥廣泛應用於農業，但其反應性官能團（羧基、酚基、氨基等）常導致與基質成分形成各種結合物，使總殘留量測定變得困難。因此，在樣品製備過程中加入水解步驟以分解結合物和酯類，生成易於定量為游離酸的明確化合物至關重要。修改後的 QuEChERS 方法，加入了在 60°C 進行 16 小時的酸性水解步驟，被證明是測定複雜化合物組成的最有效分析方法。然而，用 NaOH 中和提取液時，提取液中會產生沉澱，導致 GC-MS/MS 儀器進樣困難。因此，必須對提取液進行額外的過濾，並且在將樣品中和至所需 pH 值（5.5）後，應立即處理樣品。



(Iwona Wenio et al., 2024)

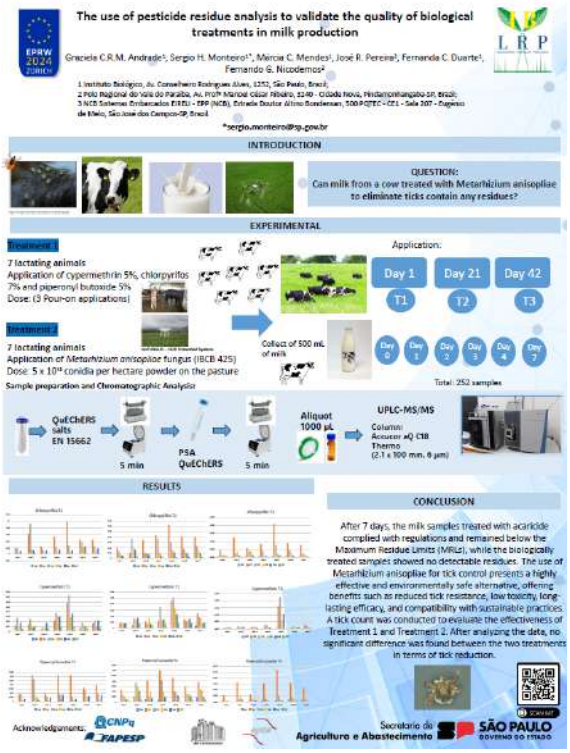
壁報八：抗氧化劑在樣品研磨過程中防止農藥降解的應用(The Use of Antioxidants to Prevent the Degradation of Pesticides During the Sample Grinding Process)。由阿爾梅里亞大學-歐洲水果與蔬菜農藥殘留參考實驗室 Jose Antonio Martínez 等人發表。抗氧化劑可用於防止農藥在樣品研磨過程中降解。眾所周知，某些化合物在研磨過程中會因基質中的氧化過程而降解，這可能導致定量結果的誤差。為了阻止這些氧化過程，一種解決方案是添加抗氧化劑。在過去幾年裡，歐洲聯盟參考實驗室（EURL-FV）對某些農藥進行了評估，並確定添加抗壞血酸（維生素 C）作為抗氧化劑可以有效防止某些化合物的降解，阻止氧化過程。本研究評估樣品研磨過程中添加 1% 抗壞血酸的效果，特別是在易於氧化的基質如香蕉、馬鈴薯和蘋果中。使用 200 克樣品（添加和未添加 1% 抗壞血酸）對 240 種化合物進行了研磨前的評估。提取方法採用 QuEChERS。結果顯示，根據基質不同而氧化降解 3% 的化合物，添加抗壞血酸防止降解提高了回收率。然而，添加抗壞血酸並非完全有益，觀察到另外約 3% 的化合物，在不添加抗壞血酸的情況下回收率在 70-120% 之間，但在添加抗壞血酸後回收率顯著降低。研究結果突顯了在某些農藥/商品組合中使用抗氧化劑的必要性。例如，在撲克拉或賽福座的情況下，這可以防止定量低估，從而確保農藥分析結果更準確。



(Jose Antonio Martínez et al., 2024)

壁報九：利用農藥殘留分析驗證牛奶生產中生物處理的品質(The use of pesticide residue analysis to validate the quality of biological treatments in milk production)。由巴西聖保羅生物研究所(Instituto Biológico, São Paulo, Brazil;) Graziela C.R.M. Andrade 等人發表。

蜱蟲是畜牧業常見的問題，如果不加以控制，可能會影響牛奶的品質。巴西生物研究所一直在研究利用無人機在牧場中施用真菌來控制牛蜱（Rhipicephalus microplus）。本研究旨在評估使用陶斯松、賽滅寧和協力精等殺蟲劑處理奶牛（CC 組）和使用綠僵菌（Metarhizium anisopliae, IBCB 425）處理奶牛（CB 組）的牛奶樣品中的農藥殘留。實驗在巴西聖保羅州進行，持續 63 天。兩組都進行了三次處理，間隔 21 天。採用 QuEChERS 進樣品製備，使用 EN15662 乙酸緩衝液和 UPLC-MS/MS（MRM 模式）檢測，並根據歐盟指南（SANTE/11312/2021）進行驗證。結果 CC 組：在處理後第 1 天和第 7 天檢測到陶斯松、賽滅寧和協力精的殘留。CB 組：未檢測到任何農藥殘留物。結論真菌處理是一種高效且環境友好的蜱蟲控制替代方案。與化學殺蟲劑相比，真菌處理具有減少蜱蟲抗藥性、低毒性、持久功效和與可持續使用等優點。真菌處理可顯著降低動物產品中農藥殘留風險，促進更安全、更可持續的蜱蟲控制方法。



(Graziela C.R.M. Andrade et al., 2024)

參、心得

歐洲農藥殘留研討會是歐洲乃至全球最具影響力的農藥殘留分析與監測領域專業會議之一。本次研討會吸引了來自全球的科學家、監管機構代表、研究人員及相關產業專家，共同探討最新的科學技術、監管政策及市場趨勢。會議主題涵蓋範圍廣泛包括：1.農藥殘留檢測技術的最新進展：如 LC-MS/MS、GC-MS/MS 及快速檢測技術等。2.毒理學與風險評估：關注農藥殘留對人類健康及環境的長期影響，評估殘留物質在不同暴露條件下的風險。3.農藥註冊與使用趨勢：包括新農藥分子研發方向、綠色農藥的應用，以及各國對於不同農藥的法規要求。4.監管政策及國際標準化：討論如何推動國際間的合作，例如歐盟、日本、韓國等主要市場的法規標準協調，並與國際食品法典委員會（Codex Alimentarius）的標準接軌。本次會議的主題日活動更是重點突出，針對以下議題進行了深入探討：1.新興污染物與多重殘留分析方法：隨著新型農藥及化學物質的出現，傳統方法難以完全覆蓋，研究者提出了多通量及高靈敏度的檢測技術應對挑戰。2.氣候變遷對農藥殘留的影響：氣候條件的變化可能改變作物病蟲害特性，從而影響農藥使用及殘留模式。3.數據驅動的監測與管理系統：利用大數據及人工智慧技術，提高農藥殘留監測的效率與準確性。雖然研討會內容豐富，但由於經費有限形成的人員限制，故難以全面詳細吸收所有議題，日本與韓國等鄰近國家均派遣 2 人以上的團隊參與，顯示其對農藥殘留議題的高度重視。相比之下，本次會議台灣僅能派遣 1 人參與，難以全面涵蓋包括毒理學、法規、註冊管理等非個人核心

業務範疇，僅能聚焦於主題日內容及與業務相關的國際發展趨勢進行報告和資料蒐集。

四、建議

一、目前，歐洲在農藥殘留分析方法的開發上，正朝著更高效率、更穩定性以及更短分析時間的目標邁進。這些策略包括引入現代化設備及綠色實踐，例如減少溶劑使用量和萃取鹽類的用量，同時縮小分析樣品大小，減少環境負擔。這些措施不僅符合節能減碳的國際趨勢，也呼應了國內在降低碳排放的政策方向。此外，隨著未來勞動力減少和人力成本提升，分析實驗室自動化的推行變得尤為重要。實現高效且環保的分析技術，將為實驗室運作帶來長期效益，並提高國際市場的競爭力。

二、歐洲農藥殘留研討會的議題範圍廣泛，涵蓋了前沿的分析技術和方法，如高解析質譜（HRMS）的定性和定量方法、針對單一農藥殘留的分析方法、多重殘留檢測技術等。此外，會議還深入探討了分析質量控制及驗證程序的指南、品質保證與實驗室認證要求等。對於環保與健康的重視，毒理學及風險評估仍是討論重點，而農藥註冊及使用的趨勢、監測計劃、國際法規的協調也為監管部門提供了重要參考。特別是「綠色分析化學」和「新食品」分析，代表了未來農藥殘留分析的新興方向。儘管會議內容豐富且具有前瞻性，但以 1 人之力難以全面吸收與涵蓋所有重要議題。建議在未來如第 16 屆 EPRW 於荷蘭鹿特丹舉行時，可派遣至少 2 位以上不同專業背景的代表參與。一方面可進一步深化對技術趨勢的學習，另一方面藉由團隊內部的討論和協作，能夠更全面地蒐集與分析資訊，進一步將國際經驗與新知識轉化為本地應用的具體策略。

附錄一：研討會議程表 (摘錄自研討會手冊)

MONDAY, 16TH SEPTEMBER

13:00 - 20:00 Registration Open

14:00 - 18:00 **Pre-Workshop Course**
Developments in Single Residue Methods
Michelangelo Anastassiades, Eric Eichhorn & Ann-Kathrin Schäfer
EURL SRM – European Union Reference Laboratory for Pesticide Residues in Food with Single Residue Methods, CVUA-Stuttgart, Fellbach - Germany

18:00 - 20:30 Welcome Cocktail Reception

TUESDAY, 17TH SEPTEMBER

08:30 - 18:00 Registration Open

Chairpersons: Andreas Schürmann and André de Kok

09:00 – 09:30 Welcome – Opening Speech

09:35 – 10:05 ***Keynote lecture 1: HRMS selectivity and sensitivity: where are we now?***
O-1 **Anton Kaufmann**
Official food control authority of the Canton of Zurich, Zurich - Switzerland

10:05 – 10:35 ***Keynote lecture 2: Managing pesticides: an industry perspective***
O-2 **Till Goldmann**
Nestlé Institute of Food Safety & Analytical Sciences - Switzerland

10:35 – 11:40 Refreshment Break
Exhibition & Posters

10:50 – 11:15 ***Americas Chemical Society – AGRO Division Ambassador: Are the pesticides compliance policies harmonized?***
Carmen Tiu
American Chemical Society, Indianapolis - United States

Chairpersons: Patrizia Pelosi and Carmen Ferrer

11:40 – 12:00 ***The 2022 EU Report on pesticide residues in food: latest figures***
O-3 **Luis Carrasco Cabrera**
European Food Safety Authority (EFSA), Parma – Italy

12:05 – 12:25 ***How much data is needed to prove an acceptable level of safety for a pesticidal active substance?***
O-4 **Minako Allen**
Exponent International Limited, Harrogate - United Kingdom

12:30 – 12:50 ***News from EURL-AO***
O-5 **Bjoern Hardebusch**
EURL AO – European Reference Laboratory for Pesticide Residues of Food of Animal Origin and Commodities with High Fat Content, CVUA, Freiburg - Germany

12:50 – 13:05 Questions and Discussion

13:05 – 14:50 Lunch break / Exhibition

V-2 **Vendor Session 2** (13:20 – 13:55)
Advanced mass spec techniques for pesticide analysis
Jianru Stahl-Zeng
Senior Technical Marketing Manager, SCIEX, Darmstadt - Germany

V-3 **Vendor Session 3** (14:10 – 14:45)
ChemisTwin™ Portal for Automated Structure Verification and Quantification of Pesticides by NMR
Albert Farre Perez
Merck KGaA, Buchs - Switzerland

Chairpersons: Despo Louca Christodoulou and Magnus Jezussek

14:50 – 15:10 ***Prioritisation of pesticides and target organ system for dietary cumulative risk assessment based on 2019-2021 monitoring cycle***
O-6 **Efisio Solazzo**
European Food Safety Authority (EFSA), Parma - Italy

15:15 – 15:35 ***Monitoring and dietary risk assessment of pesticide residues in polished, parbolized, and brown rice collected from Rio Grande do Sul State in Brazil***
O-7 **Ionara Pizzutti**
UFSM – Federal University of Santa Maria, Santa Maria - Brazil

15:40 – 15:50 ***Development of targeted and suspected screening approaches for the determination of biocidal substances of concern in food of animal origin by LC-HRMS***
O-8 **Gael Touchais**
French Agency for Food Environmental and Occupational Health Safety (ANSES), Fougeres - France

15:50 – 16:05 Questions and Discussion

16:05 – 17:00 Refreshment Break
Exhibition & Posters

V-4 **Vendor Session 4** (16:25 - 16:50)
Sampleprep - Improved Analysis of Organic Pollutants in Food Products (Pesticide Residues) Sample Preparation by Optimising Bulk Sample Comminution Alongside Automated Residue Extraction Equipment
Paul Lynch
Cole-Parmer, London - United Kingdom

17:00 – 18:00 **Poster Session I (Even numbers, authors present)**

WEDNESDAY, 18TH SEPTEMBER

THEMED DAY "Green Analytical Chemistry, Miniaturization and Automation"

08:30 – 18:00 Registration Open

09:00 – 09:10 Announcements

Chairpersons: Susanne Ekroth and Hans Mol

09:10 – 09:40 ***Green Chemistry Opportunities for Pesticide Analysis, Remediation and Replacements***
O-9 **John C. Warner**
Technology Greenhouse, LLV, Woburn, MA - United States

09:45 – 10:25 ***Facilitating high throughput food determinations with chemical biopsy probe***
O-10 **Janusz Pawliszyn**
Department of Chemistry, University of Waterloo Ontario Canada

10:25 – 10:40 Questions and Discussion

10:40 – 11:40 Refreshment Break
Exhibition & Posters

V-5 **Vendor Session 5** (10:50 – 11:15)
Comparison of automated vs. centrifugal μ-SPE for the analysis of pesticides and other contaminants in a variety of foods
Steven J. Lehotay & Nicolas Michlig
USDA Agricultural Research Service Eastern Regional Research Center, Wyndmoor - USA

Chairpersons:	Susanne Ekroth and Hans Mol
11:40 – 12:00	***Residues method development: From first principles to modern efficiency***
O-11	**Pawel Markowicz** *Charles River Laboratories, Edinburgh - United Kingdom*
12:05 – 12:25	***Miniaturization of the QuEChERS method in fruits and vegetables: How mini can we go without cryogenic milling?***
O-12	**Yuki Yamasaki** *Wageningen Food Safety Research (WFSR), Wageningen - Netherlands*
12:30 – 12:50	***Glyphosate determination in food. Performance evaluation, environmental assessment of mass spectrometric and immunochromatographic methods***
O-13	**Biancamaria Ciasca** *Institute of Sciences of Food Production, National Research Council of Italy, Bari - Italy*
12:50 – 13:05	**Questions and Discussion**
13:05 – 14:50	**Lunch break / Exhibition**
V-6	**Vendor Session 6** (13:20 – 13:55) ***New developments in high resolution LC-MS/MS QTOF pesticide analysis from screening to quantitation with DIA and HR-MRM workflows*** **Alan Barnes[1] & Steve Williams[2] & Stéphane Moreau[3] & Neil Loftus[3]** *[1] Shimadzu Corporation, Manchester – United Kingdom* *[2] 2SGS Cambridge Limited, Cambridge – United Kingdom* *[3] Shimadzu Europa GmbH, Duisburg – Germany*
V-7	**Vendor Session 7** (14:10 – 14:45) ***The New PAL Micro-SPE Cartridge for Automated Pesticides Extraction and Clean-up*** **Hans-Joachim Hübschmann** *CTC Analytics AG, Zwingen – Switzerland*

Chairpersons:	Susanne Ekroth and Hans Mol
14:50 – 15:10	***Pitfalls and challenges in automation and miniaturization***
O-14	**Friederike Habedank** *State Office for Agriculture, Food Safety and Fisheries – MV, Rostock – Germany*
15:15 – 15:25	***Improvements in automation of sample preparation for residue analysis in food of animal origin***
O-15	**Anna Buettner** *Technical University Dresden, Dresden – Germany*
15:30 – 15:50	***High-Throughput, Miniaturized, Automated, and "Green" Analysis of a Wide Scope of Pesticides and Other Residues in Fatty and Non-Fatty Foods***
O-16	**Steven Lehotay** *USDA Agricultural Research Service, Wyndmoor - USA*
15:50 – 16:05	**Questions and Discussion**
16:05 – 17:00	**Refreshment Break** **Exhibition & Posters**
V-8	**Vendor Session 8** (16:25 – 16:50) ***Automation of relevant workflows for residue analysis*** **Mikko Hofsommer[1] & Steffen Rothmeier[2]** *[1] Gfl, Gesellschaft für Lebensmittel-Forschung mbH, Berlin - Germany* *[2] Institut Kirchhoff Berlin, Berlin- Germany*
17:00 – 18:00	**Poster Session II (Odd numbers, authors present)**
19:00	**Gala Dinner at "Zunfthaus zur Meisen" (tickets required)**

THURSDAY, 19TH SEPTEMBER

08:30 – 18:00	**Registration Open**
09:00 – 09:10	**Announcements**

Chairpersons:	Antonio Valverde and Ionara Pizzutti
09:10 – 09:30	***Automation and Miniaturization for Enhancing Analytical Methods in Pesticide Residue Evaluation in Food***
O-17	**Amadeo Fernandez Alba** *EURL-FV – European Reference Laboratory for Pesticide Residues in Fruit and Vegetables, University of Almería, Almería - Spain*
09:35 – 09:55	***Multiclass methods for the global chemical safety evaluation of foods and the role of pesticide residue laboratories***
O-18	**Horacio Heinzen** *Universidad de la República/ Facultad de Química, Montevideo - Uruguay*
10:00 – 10:20	***Comprehensive evaluation on the impact of sample size and extraction equipment in pesticide residue analysis in food***
O-19	**Wesley Jose** *BASF S.A., Guaratinguetá - Brazil*
10:20 – 10:35	**Questions and Discussion**
10:35 – 11:40	**Refreshment Break** **Exhibition & Posters**
V-9	**Vendor Session 9** (10:50 – 11:15) ***Is an Inert LC-Column Hardware Beneficial for Pesticide Analysis? -Innovative Liquid Chromatography Techniques and Columns-*** **Diego Lopez** *Restek Corporation, Bellafonte/PA - USA*

Chairpersons:	Hermann Unterluggauer and Steven Lehotay
11:40 – 12:00	***An update on the determination of highly polar anionic pesticides in food and feed by HILIC-MS/MS***
O-20	**Jonatan Dias** *Wageningen Food Safety Research (WFSR), Wageningen – Netherlands*
12:05 – 12:25	***Analysis of cationic pesticide residues in food samples by ICMS***
O-21	**Anatte Margalit** *Food Chemistry Division Backweston, Celbridge, Co. Kildare - Ireland*
12:30 – 12:50	***Stereoisomers of pesticides: Differences in biological activity, metabolism in crops, environmental fate, and toxicity***
O-22	**Ignaz Buerge** *Agroscope, Wädenswil - Switzerland*
12:50 – 13:05	**Questions and Discussion**
13:05 – 14:50	**Lunch break / Exhibition**
V-10	**Vendor Session 10** (13:20 – 13:55) ***New and classic approaches for pesticide testing - how to save costs & time and reduce the CO2-footprint of your lab without compromising excellent performance!*** **Stuart Adams & David Gould** *Waters Corp. – United Kingdom*
V-11	**Vendor Session 11** (14:10 – 14:45) ***Maximizing sample throughput and scope of pesticide residue coverage using high resolution and nominal mass spectrometry techniques.*** **Jonathan Spencer[1] & Teresa Klink[2]** *[1] Agilent Technologies, Cheadle – United Kingdom* *[2] Agilent Technologies, Waldbronn - Germany*

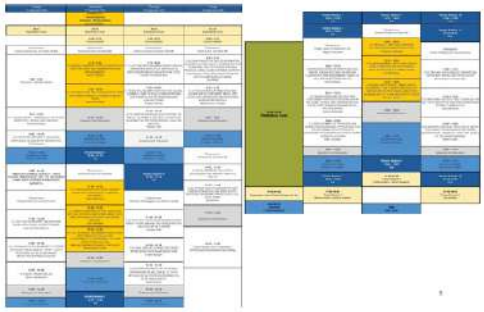
Chairpersons:	Finbarr O'Regan and Veronica Cesio
14:50 – 15:10	*Dealing with Residue Definitions Entailing Esters and Conjugates*
O-23	**Michelangelo Anastassiades** *CVUA-Stuttgart, Fellbach - Germany*
15:15 – 15:35	*Brushing up OECD Test Guideline 506 on the stability of pesticide residues in stored commodities*
O-24	**Britta Michalski** *German Federal Institute for Risk Assessment, Berlin – Germany*
15:40 – 16:00	*Mapping pesticide profiles in beers: Exploring consequences between geographical origin of hops and levels of pesticide residues*
O-25	**Martin Dusek** *Research Institute of Brewing and Malting, Prague - Czech Republic*
16:00 – 16:15	Questions and Discussion
16:15 – 17:10	Refreshment Break Exhibition & Posters
V-12	**Vendor Session 12** (16:35 – 17:00) *One Analyzer, Multiple Solutions: From MOSH, MOAH, Pesticides, and Beyond* **Dmitrii Rakov** *LECO EATC, Berlin - Germany*
17:00 – 18:00	**Poster Session III** (All posters, authors present)

FRIDAY, 20TH SEPTEMBER

08:30 – 13:30	Registration Open
09:00 – 09:10	Announcements
Chairpersons:	André de Kok and Hans Mol
09:10 – 09:30	*Non-target data acquisition for target analysis (NDATA) workflow for screening 1087 pesticides in fresh produce using liquid chromatography-high resolution mass spectrometry with a compound database*
O-26	**Jon Wong** *U.S. Food and Drug Administration College Park, Maryland - United States*
09:35 – 09:55	*Evaluation, optimisation, and validation of different micro-SPE clean-up cartridges for pesticide residues in cereals*
O-27	**Mette Erecius Poulsen** *Technical University of Denmark, Lyngby - Denmark*
09:55 – 10:10	Questions and Discussion
10:10 – 11:00	Refreshment Break Exhibition & Posters
Chairpersons:	André de Kok and Hans Mol
11:00 – 11:20	*Chili peppers: Analytical challenges and market insights*
O-28	**Leos Uttl** *University of Chemistry and Technology, Prague - Czech Republic*
11:25 – 11:45	*Application of concentration prediction in routine wide scope pesticide screening based on LC-full scan HRMS*
O-29	**Paul Zomer** *Wageningen Food Safety Research, part of Wageningen University & Research, Wageningen - Netherlands*

附錄二：心得分享簡報內容

主題日
綠色分析



22家廠商參展

演講 29場

壁報
PD development and application of analytical methods
分析方法的發展與應用
數量:65

PM regulatory issues and monitoring
監管問題和監控
數量:25

PT toxicology and intake assessment
毒理學和攝取量評估
數量:4

PO other topics
其他主題
數量:37

PV vendor posters
廠商壁報
數量:25

EPRW 2024 將聚焦於以下主要議題

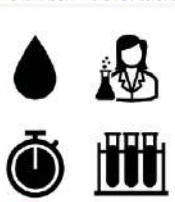
- 先進的分析技術和方法
- 高解析質譜的定性和定量方法
- 單一殘留方法
- 分析質量控制和驗證程序的指南
- 品質保證和實驗室認證要求
- 毒理學和風險評估
- 農藥註冊和使用的趨勢
- 監測計劃
- 法規問題
- 綠色分析化學
- 「新食品」分析

本次報告內容

- 主題日「綠色分析化學」分享6篇口頭及1篇
- 另外也分享亞洲國家日本及韓國4篇
- 農藥參考物質1篇
- 最後針對本年度得獎3篇進行介紹

O-11

Method development: more modern approach
方法開發：更現代的方法



charles river

How can we do this?
我們該怎麼做？

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Scaling down the sample size – more green sample prep for vet residues

RED METHOD

GREEN METHOD

基體越多比例縮小樣品即可減少 90% 的溶劑
90% solvent reduction just by scaling down sample preparation.

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Scope for scaling down?

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Acetonitrile – is it green enough?

- 毒性：可引起例如對呼吸道的刺激
- **Toxicity:** can cause e.g. irritation of the respiratory track
- **Environmental impacts** not easily biodegradable ● 環境影響：不易生物降解
- **Highly flammable**
  ● 高度易燃

Possible alternatives:

- ethanol, methanol, ethyl lactate, 2-methyl tetrahydrofuran

可能的替代方案：
● 乙醇、甲醇、乳酸乙酯、2-甲基四氫呋喃

STAR and STARlet Hamilton robots

Sample preparation 樣品製備

Stocks and intermediate stocks dilutions
儲備液和中間儲備液稀釋液

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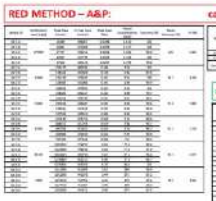
RED METHOD – results for linearity prep by analyst

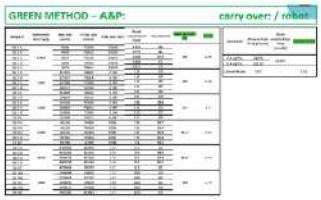
GREEN METHOD – results for linearity / robot

"Johnnie":
22 years of experience as analytical chemist

RED METHOD – A&P: carry over: /analyst

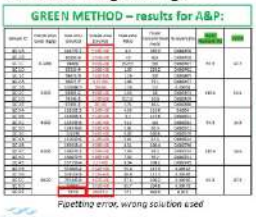


GREEN METHOD – A&P: carry over: / robot



Scaling down the sample size – difficult beginnings

GREEN METHOD – results for A&P:



Pipetting error, wrong solution used

Long term testing (> 1 year) 85% pass rate by lab analysts vs 88% robot.

長期測試（＞1 年）：人工的通過率為 85%，而機器人的通過率為 88%。

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Scaling down the sample size – less plastic

RED METHOD

ca. 1.3 kg of plastic used:

- 50 mL polypropylene tubes;
- pipette tips;
- packaging (e.g. pipette containers, foils);
- 2 plastic filtration plates (contamination).

GREEN METHOD

300 grams of plastic used:

- plastic tubes of smaller size;
- pipette tips consumption reduced by using Hamilton CO-Re II tips (washed/re-used up to 20 times) - 95% reduction of plastic tips consumption.

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Tip Novus Mini

Objectives:

- The TipNovus Mini® is a bench top tip washer device that is capable of washing and sanitizing contaminated tips for reuse.
- As a modular and fully customizable model, the TipNovus Mini™ has the ability to wash various tip brands and sizes.
- Capacity: One tip rack wash, one tip rack dry.
- Throughput: 6-8 tip racks per hour.

是一款Tip清洗器設備，能將清洗和消毒受污染的Tip以供重複使用

Requirements:

- Electrical: 220V, 10amp.
- 90 PSI Gas supply.
- Water supply: either bottle or filtered input.
- Waste supply: to either bottle or drain.

Performance:

- Tips are washed up to 20 times to allow for a 95% reduction in tip usage.

Tip最多可清洗 20 次，以減少 95% 的塑膠用量。

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Outcome of changes?
改變的結果？

90% solvent reduction (scaled down sample prep) 溶劑減少 90%（縮小樣品製備規模）	Similar pass rate 85% for analysts vs 88% for the robot (> 1 year) 操作者成效，人工為85%，機器為88%（>1年）
4-5 hrs (analyst) vs 2-2.5 hrs (Hamilton) 4–5 小時（人工）與 2–2.5 小時（機器）	77% reduction in plastic usage (plastic tips washed again and re-used) 塑膠使用量減少 77%（清洗塑膠Tip並重複使用）

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Thanks to:

- Iain Love
- Daniel Gorman
- Sean Gaffney

Contact:
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Method development team leader
Charles River Labs (Edinburgh, Scotland)
Chemistry Department/Residues analysis

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18 September 2024
15th European Pesticide Residue Workshop (EPRW 2024)

Miniaturization of the QuEChERS method in fruits and vegetables: how mini can we go without cryogenic milling?

QuEChERS 方法在蔬果中的微型化：如不進行低溫研磨，我們能做到多小？

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[1] Wageningen Food Safety Research (WFSR), Wageningen, the Netherlands
[2] Division of Foods, National Institute of Health Sciences (NIHS), Kawasaki, Japan

O-12

Things to consider for miniaturizing

微型化QuEChERS：最著要環保和成本效益更高的分析選擇

Miniaturization of QuEChERS: an attractive route toward a more environmentally friendly & cost-effective analysis

Procedure

Test portion size:	Large	Small
Acetonitrile & Salts:	Large	Small
RSD:	Low	High

Representative literatures for scaling down the QuEChERS procedure

Literature	Commodity	No. of pesticide
Zoccali et al. (2017)	Zucchini, Red pepper, Lettuce, Tomato	43
Kawamura et al. (2018)	Honey	6
Bertand et al. (2021)	Wine	33
Fernández et al. (2021)	Cucumber, Red pepper, Lettuce, Tomato	88

Scaling down of the procedure is possible.

Homogeneity

Laboratory sample 1~3 kg → Comminution → Analytical test portion 15 g, 7 g, 0.5 g

Can smaller test portions be representative of original bulk sample?

Depends on the homogeneity

取決於均勻性

Using small analytical test portions is only an option when heterogeneity is sufficiently low to not contribute significantly to the measurement uncertainty.

使用小樣品分析只是一種選擇
當異質性足夠低，不會對測量不確定度產生重大影響。

Cryogenic milling?

低溫研磨：獲得高度均勻性的黃金標準

Cryogenic milling: the gold standard for obtaining a high degree of homogeneity

- Need pre-freezing
- Need volatilization of remaining dry ice
- More problematic for larger size laboratory samples

- 需要預凍
- 需要揮發剩餘的乾冰
- 對大尺寸樣品更具問題

often laborious and impractical for routine analysis

對於常規分析來說費力且不切實際

Purpose of this study

Examine to what extent the QuEChERS method can be miniaturized for representative fruits and vegetables comminuted under ambient conditions with standard food processing equipment

評估QuEChERS方法在蔬果樣品中的微型化程度

Commodity & Comminution

Commodity	Difficulty	Minimum size of laboratory samples*
Spinach	Easy	1 kg
Orange	Normal	2 kg (at least 10 units)
Red grape	Hard	2 kg (at least 5 units)

*COMMISSION DIRECTIVE 2002/63/EC

Comminution

1-step : Stephan mixer
2-step : Stephan mixer → Ultra-turrax

1st comminution → 2nd comminution

Comminution: 1-step, 2-step

Spinach, Orange, Red grape

All procedures were performed under ambient conditions.

Sample preparation

	Test portion size: 15 g	Test portion size: 2 g	Test portion size: 0.5 g
Sampling	15 ± 0.1 g in 50 mL tube	2000 ± 13.3 mg in 15 mL tube	400 ± 3.3 mg in 5 mL tube
Extraction	15 mL of ACN with 1 % acetic acid Shaking (5 min) by shaker	2 mL 5 min by shaker	0.5 mL 1 min by vortex
Salting out	6 g of $MgSO_4$ & 1.5 g of NaOAc Shaking (5 min) by shaker Freeze-out (−80°C, 10 min) Centrifugation (4000 rpm, 4 min)	0.8 g & 0.2 g 5 min by shaker	0.2 g & 0.05 g 1 min by vortex
	Supernatant (ACN layer)		
Analysis	Dilution (4 times with MeOH) LC-MS/MS analysis Injection volume: 2 µL		

Targeted pesticides

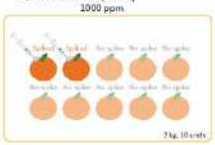
Pesticide	Chemical group	Retention time (min)	Log K_{ow}	Polarity
Omethoate	Organophosphate	2.0	−0.74	Neutral
Propamocarb	Carbamate	2.2	0.84	Potentially cationic
Acetamiprid	Neonicotinoid	4.2	0.80	Neutral
Metoxuron	Urea	5.2	1.6	Neutral
Haloxyfop	Aryloxyphenoxy propionate	8.1	4.3	Potentially anionic
Azoxystrobin	Strobilurin	8.2	2.5	Neutral
Cyprodinil	Anilinopyrimidine	9.5	4.0	Neutral
Tebuconazole	Triazole	9.6	3.7	Neutral
Chlorpyriphos	Organophosphate	10.5	5.2	Neutral
Spinosyn A	Macrocyclic lactone	10.5	3.5	Potentially cationic
Spinosyn D	Macrocyclic lactone	11.3	4.3	Potentially cationic
Deltamethrin	Pyrethroid	11.6	4.6	Neutral

How to spike pesticides on commodities?

Spiking by syringe

- Spike the pesticides at 100 ppb by syringe
- Spike 200 µL of 1 mg/mL mixed solution to 20% of commodities (2 units)

1000 ppm



Analyzed value in 15 g test portion

Replicate	Residue (ppb)
1	102.8
2	93.2
3	94.8
4	101.0
5	151.0
6	104.6

Hot spot was observed even in 15 g test portion!

This spiking procedure is too extreme to mimic incurred commodities.
此加藥方式過於極端，無法模擬為商品

How to spike pesticides on commodities?

Spiking by spray

- Spike the pesticides at 150 ppb by spray
- Add 10 mL of 30 µg/mL mixed solution to 50% of commodities (5 units)

30 ppm

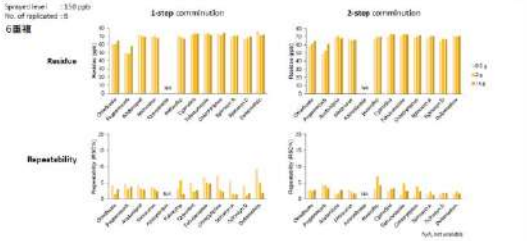
農藥僅分佈在表層
→ 仍然預期是不均勻的

- ✓ Spiked pesticides distribute only on the skin.
  → Still expected to be inhomogeneous.
- ✓ The absolute residue is NOT specified as 150 ppb.
  → Homogeneity can be evaluated by repeatability.

絕對殘留量非指定值150 ppb
→均勻性可以總體可重複性來評估

Residues in orange – spray before comminution

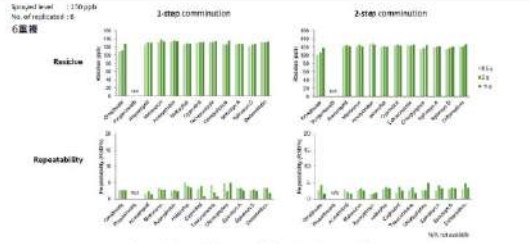
橘子



Repeatability was < 10 RSD% even in 0.5 g test portion prepared by 1-step comminution.
重複性RSD < 10 %，即便採用1次法粉碎法製備的 0.5 g 測試件也是如此

Residues in spinach – spray before comminution

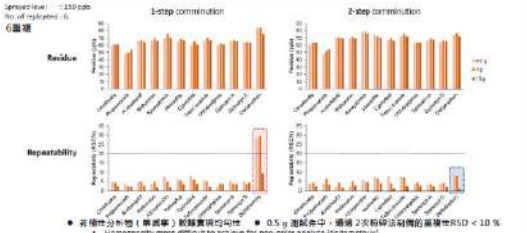
菠菜



Repeatability was < 6 RSD% even in 0.5 g test portion prepared by 1-step comminution.
重複性RSD < 6 %，即便採用1次粉碎法製備的 0.5 g 測試件也是如此

Residues in red grape – spray before comminution

紅葡萄



- 若極性分析物（單農藥）較難實現均勻性 ■ 0.5 g 測試件中，通過 2次粉碎法製備的重複性RSD < 10 %
  - Homogeneity more difficult to achieve for non-polar analyte (acts mostly).
  - Repeatability was < 10 RSD% in 0.5 g test portion prepared by 2-step comminution.
  - → 2-step comminution is essential for red grape, but 0.5 g test portion is acceptable!

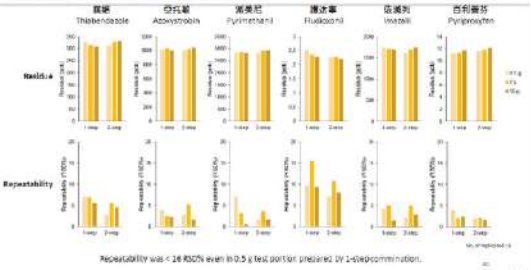
In real-life sample?

Simulated situation	Actual situation
Pesticides that exhibit a broad range of physicochemical properties can be included.	
• In laboratory bench • With small sprayer • As standard solution prepared in organic solvent	• On the field • With industrial sprayer • As formulation ex. emulsifiable concentrate (EC) wettable powder (WP) etc.

Comparable?

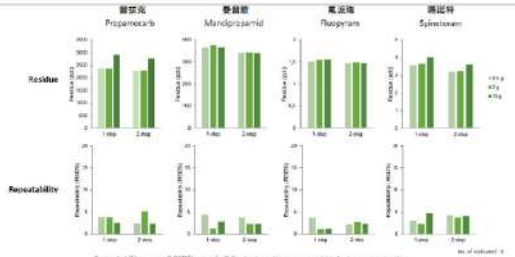
Residues in orange – incurred pesticides

橘子



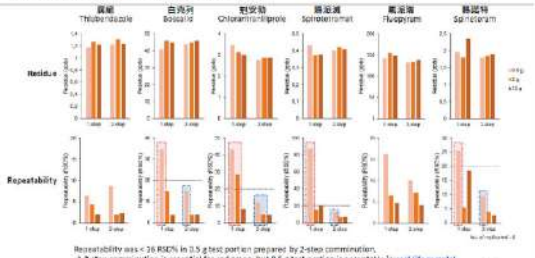
Repeatability was < 20 RSD% even in 0.5 g test portion prepared by 1-step comminution.

Residues in spinach – incurred pesticides



Repeatability was < 6 RSD% even in 0.5 g test portion prepared by 1-step comminution.

Residues in red grape – incurred pesticides



Repeatability was < 16 RSD% in 0.5 g test portion prepared by 2-step comminution.
→ 2-step comminution is essential for red grape, but 0.5 g test portion is acceptable in real-life sample.

Can spraying mimic 'incurred' situation?

Commodity : Red grape
No. of replicates : 6

Sprayed (sprayed level: 150 ppb)

Pesticide	Log K_{ow}	Repeatability (RSD%) 1-step	2-step
Omethoate	-0.74	4.5	3.5
Propamocarb	0.84	3.4	3.9
Acetamiprid	0.80	4.4	2.1
Metalaxyl	1.6	3.3	2.1
Azoxystrobin	4.3	7.8	5.5
Haloxyfop	2.5	6.1	2.4
Cyprodinil	4.0	8.1	7.5
Tebuconazole	3.7	5.6	7.7
Chlorpyrifos	5.2	1.8	3.9
Spinosyn A	3.9	5.4	5.2
Spinosyn D	4.3	4.7	3.7
Deltamethrin	4.6	28	9.0

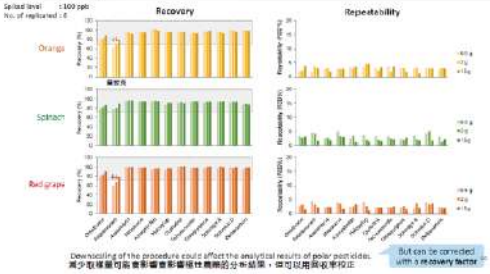
Incurred

Pesticide	Log K_{ow}	Repeatability (RSD%) 1-step	2-step
Thiabendazole	2.4	6.3	8.7
Boscalid	3.0	34	15
Chlorantraniliprole	2.8	43	12
Spirotetramat	2.5	47	13
Fluopyrm	3.3	36	10
Spirotetram	4.1	25	9.5

No. of pesticides whose repeatability was > 20 RSD% Sprayed (1/12) < Incurred (4/6)

Incurred commodity seems to be more inhomogeneous than sprayed one.
實際商品似乎比實驗室噴施更不均勻。

Recovery test – spike after comminution



Downscaling of the procedure could affect the analytical results of polar pesticides.
減少取樣量可能會影響會影響極性農藥的分析結果，但可以用回收率校正

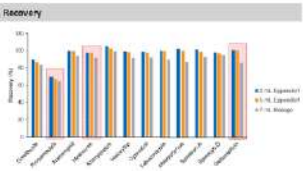
But can be corrected with a recovery factor

Recovery in different extraction procedure

Recovery test for 0.5 g test portion

Commodity : Red grape
Spiked level : 100 ppb
No. of replicates : 6

Recovery



- Recovery: 2 mL, Bontage < 2 mL & 5 mL, Eppendorf
- Low recovery can be explained by the difference in matrix effect for some pesticides but not for others.
其他農藥回收率較低可用基質效應來解釋

Extraction procedure for 0.5 g test portion could affect pesticide's recovery.
0.5 g取樣方式可能會影響農藥回收率

Conclusion

對於真實樣品，在大多數情況下，1次粉碎就足夠了，即使是 0.5 g 的分析測試已是如此。

- For real-life samples, 1-step comminution suffices in most cases, even for 0.5 g analytical test portions.
- Certain matrices, such as red grapes, need 2-step comminution to obtain acceptable precision for all pesticides.
某些基質（如紅葡萄）需要2次粉碎所有農藥才能獲得可接受的精密度。

The QuEChERS method can be miniaturized without cryogenic milling, allowing the laboratories to achieve a more sustainable and greener analysis of pesticide residues.

QuEChERS 方法可以微型化，無需低溫研磨，使實驗室能夠實現更永續、更環保的農藥殘留分析。

How much greener the miniaturized method is?

◆ **WFSR**

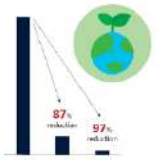
5,000 fruits & vegetables samples/year

Test portion size	15 g	0.5 g
Acetonitrile	75 L €13,400 (+waste disposal)	2.5 L €380 (+waste disposal)

◆ **Extrapolate miniaturization to 100 labs**

500,000 fruits & vegetables samples/year

Test portion size	15 g	0.5 g
Acetonitrile	7,500 L €1,140,000 (+waste disposal)	250 L €38,000 (+waste disposal)



Miniaturization of QuEChERS is an attractive route toward **a more environmentally friendly & cost-effective analysis!**

Acknowledgement

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Dr. Hans Mol
Dr. Ivan Alolsi
Agnieszka, Arnoud, Basia, Dennis, Federico, Helmoed, Jermaine, Jonatan, Ling, Mounir, Nick, Paul, Renée, Susann, Theo,
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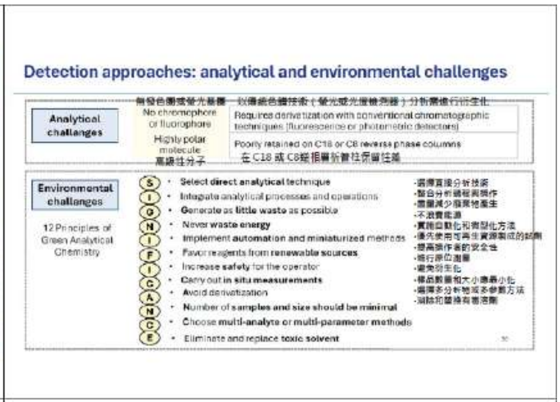
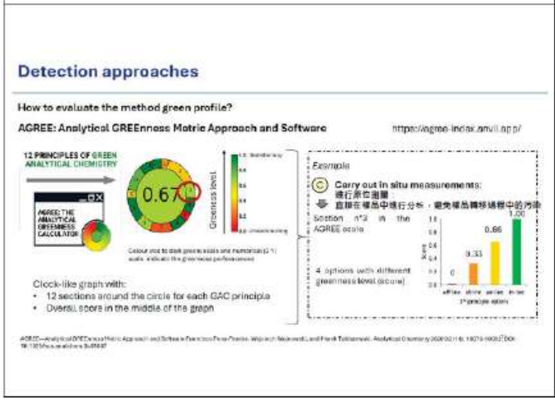
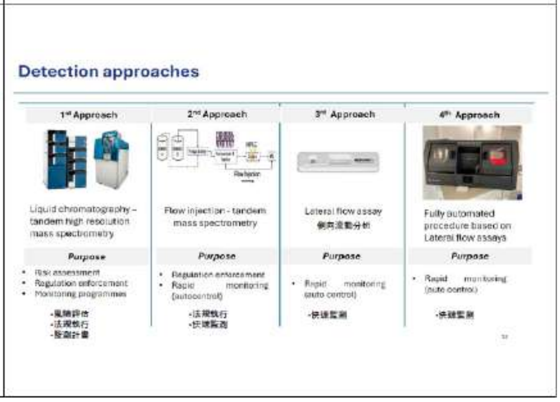
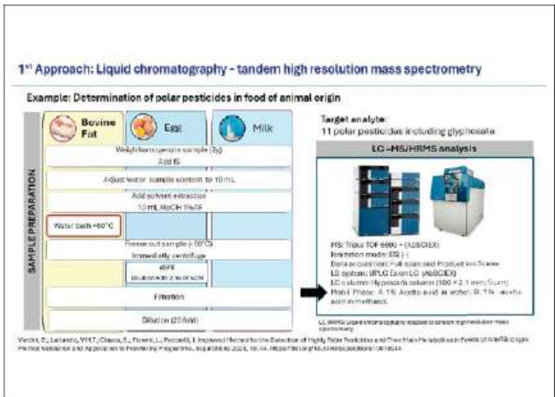
The Uehara Memorial Foundation

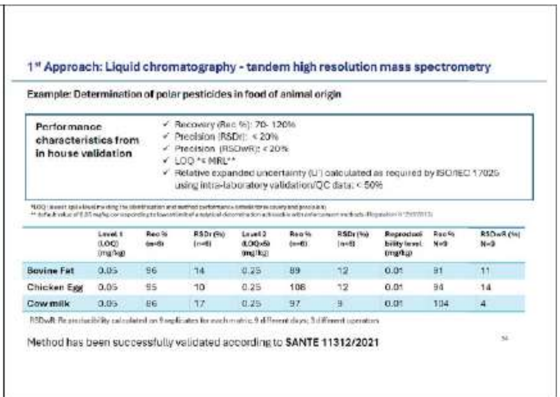

EPRW 2024 ZÜRICH
EU Food Safety Platform
ISPA
Glyphosate determination in food: Performance evaluation, environmental assessment of mass spectrometric and immunochromatographic methods
食品中嘉磷塞的測定：質譜法和免疫層析法的性能評估與環境評估
O-13

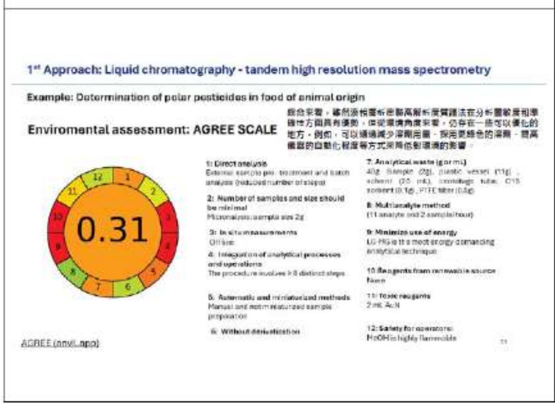

Detection approaches: analytical and environmental challenges
Analytical challanges
No chromophore or fluorophore
Requires derivatization with conventional chromatographic techniques (fluorescence or photometric detectors)
Highly polar molecule
Poorly retained on C18 or C8 reverse phase columns
在 C18 或 C8
Environmental challanges
12 Principles of Green Analytical Chemistry
S I G N I F I C A N C E
Select direct analytical technique
Integrate analytical processes and operations
Generate as little waste as possible
Never waste energy
Implement automation and miniaturized methods
Favor reagents from renewable sources
Increase safety for the operator
Carry out in situ measurements
Avoid derivatization
Number of samples and size should be minimal
Choose multi-analyte or multi-parameter methods
Eliminate and replace toxic solvent

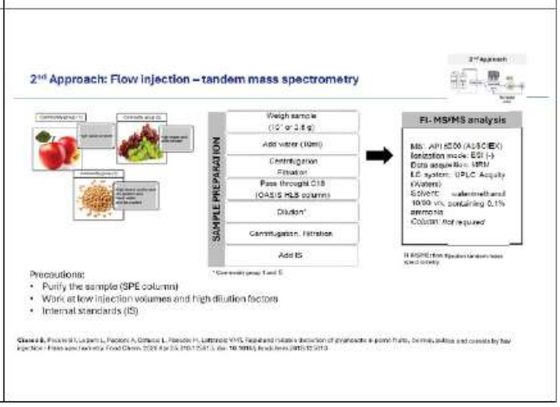

Detection approaches
How to evaluate the method green profile?
AGREE: Analytical GREEnness Metric Approach and Software
https://agree-index.anvil.app/
12 PRINCIPLES OF GREEN ANALYTICAL CHEMISTRY
AGREE: THE ANALYTICAL GREENNESS CALCULATOR
0.67
Greenness level
Example
Carry out in situ measurements:
Section n°3 in the AGREE scale
4 options with different greenness level (score)
1.00
0.66
0.33
0
Clock-like graph with:
12 sections around the circle for each GAC principle
Overall score in the middle of the graph


Detection approaches
1st Approach
Liquid chromatography – tandem high resolution mass spectrometry
Purpose
Risk assessment
Regulation enforcement
Monitoring programmes
2nd Approach
Flow injection – tandem mass spectrometry
Purpose
Regulation enforcement
Rapid monitoring (autocontrol)
3rd Approach
Lateral flow assay
Purpose
Rapid monitoring (auto control)
4th Approach
Fully automated procedure based on Lateral flow assays
Purpose
Rapid monitoring (auto control)


1st Approach: Liquid chromatography - tandem high resolution mass spectrometry
Example: Determination of polar pesticides in food of animal origin
Bovine Fat
Egg
Milk
SAMPLE PREPARATION
Add IS
Adjust water sample content to 10 mL
Add solvent extraction
Water bath +40°C
Filtration
Dilution (20 fold)
Target analyte:
11 polar pesticides including glyphosate
LC-MS/HRMS analysis


1st Approach: Liquid chromatography - tandem high resolution mass spectrometry
Example: Determination of polar pesticides in food of animal origin
Performance characteristics from in house validation
Recovery (Rec %): 70- 120%
Precision (RSDr): < 20%
Precision (RSDwR): < 20%
LOQ * ≤ MRL**
Relative expanded uncertainty (U') calculated as required by ISO/IEC 17025 using intra-laboratory validation/QC data: < 50%
Bovine Fat 0.05 96 14 0.25 89 12 0.01 91 11
Chicken Egg 0.05 95 10 0.25 108 12 0.01 94 14
Cow milk 0.05 86 17 0.25 97 9 0.01 104 4
Method has been successfully validated according to SANTE 11312/2021


1st Approach: Liquid chromatography - tandem high resolution mass spectrometry
Example: Determination of polar pesticides in food of animal origin
Enviromental assessment: AGREE SCALE
0.31
1: Direct analysis
2: Number of samples and size should be minimal
3: In situ measurements
4: Integration of analytical processes and operations
5: Automatic and miniaturized methods
6: Without derivatization
7: Analytical waste (g or mL)
8: Multianalyte method
9: Minimize use of energy
10 Reagents from renewable source
11: Toxic reagents
12: Safety for operators:
AGREE (anvil.app)


2nd Approach: Flow injection – tandem mass spectrometry
SAMPLE PREPARATION
Weigh sample
Add water (10ml)
Centrifugation Filtration
Pass through C18 (OASIS HLB column)
Dilution
Centrifugation, Filtration
Add IS
FI-MS/MS analysis
Precautions:
Purify the sample (SPE column)
Work at low injection volumes and high dilution factors
Internal standards (IS)

2nd Approach: Flow injection – tandem mass spectrometry

Performance characteristics from in house validation (according to SANTE 11312/2021)

- ✓ **Recovery** (Rec %): 70- 120%
- ✓ **Precision** (RSDr): < 20%
- ✓ **Precision** (RSDwR) < 20%
- ✓ **LOQ ≤ MRL** (for commodity group 2 and 5)

Commodity groups	MRL (mg/kg)	Spiking level (mg/kg)	Recovery (%)	RSDr (%)	RSDwR (%)
1: High water content (Apples)	0.1*	0.5 (MRL)	78	17	17
		0.5 (level)	84	8.2	8.5
		0.3 (LOQ)	82	9.3	–
2: High acid content and high water content (Grapes)	0.5	50 (MRL)	89	13	13
		5.0 (level)	89	19	19
		3.0 (LOQ)	88	18	–
5: High starch and/or protein content (cereals, maize and rice) content (Cereals)	10	100 (MRL)	111	9.0	9.8
		10 (level)	97	7.5	9.8
		6.0 (LOQ)	92	19	–

*lowest limit of analytical determination

- ✓ **Trueness:** comparison of data from incurred contaminated samples obtained by the EI- HSIRMS method and the QuPPE reference method → Agreement between the results obtained with the 2 methods
- ✓ **Identification requirements:** ion ratio should be within ± 30% to that obtained from the average of calibration standards from the same sequence

Sample		FEPS/HRMS	FEPS/HRMS Identification ratio	QuPPE
Chickpea	A	15.6 ± 2.4	0.4%	21.5 ± 0.3
	B	28.0 ± 4.8	0.2%	17.7 ± 7.5
Commodity group (n)	C	29.0 ± 5.6	-0.1%	15.5 ± 8.1
	D	25.7 ± 5.1	-0.0%	15.2 ± 6.7
	E	34.4 ± 6.7	0.4%	43.7 ± 7.9
Wheat Commodity group (5)	1	1.5 ± 0.5	0.4%	1.4 ± 0.4
	2	1.5 ± 0.3	0.0%	1.5 ± 0.5
	3	1.6 ± 0.5	0.9%	1.3 ± 0.4
	4	1.2 ± 0.3	0.0%	2.3 ± 0.8
	5	1.5 ± 0.5	0.9%	1.7 ± 0.5
	6	0.9 ± 2.1	–	0.3 ± 0.1

2nd Approach: Flow injection – tandem mass spectrometry

Enviromental assessment: AGREE SCALE

1: Direct analysis
External sample pre- and treatment and batch analysis (reduced number of steps)

2: Minimal number of samples and size
Microanalytic sample size 2.5g/10g

3: In situ measurements
Off line

4: Integration of analytical processes and operations
The procedure involves 2-5 distinct steps

5: Automatic and miniaturized methods
Manual and not miniaturized sample preparation

6: Derivatization
None

7: Analytical waste (g or mL)
Sample (10g), solvent (2 mL)

8: Multianalyte method
1 analyte and 12 samples/hour)

9: Minimize use of energy
LC- US is the most energy-demanding analytical technique

10: Reagents from renewable source
None

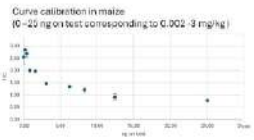
11: Toxic reagents
None

12: Safety for operators:
MeOH is a flammable solvent

3rd approach: Lateral flow assay

- Assay at **room temperature**
- **Solvent free** extraction and analysis
- Matrix specific calibration curve uploaded into the reader as QR code

Curve calibration in maize
(0 – 20 ng on test corresponding to 0.002 - 3 mg/kg)



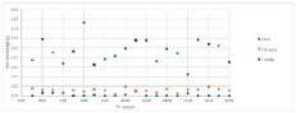
3rd Approach: Lateral flow assay

Evaluation of performance characteristics according to SANTE 11312/2021

For qualitative/semiquantitative methods:

Screening detection limit (SDL): the lowest concentration for which it has been demonstrated that a certain analyte can be detected in at least 95% of the samples (i.e. false negative rate of 5% is accepted)
- SDL: 1 mg/kg
- SDL: 0.2 mg/kg (evaluation in progress)

MRL: 1 mg/kg for maize, 10 mg/kg for wheat



For quantitative methods:
- ✓ **Trueness:** average recovery after additions of known amounts of the analyte to a blank matrix should be 70- 120%
- ✓ **Precision:** < 20%

	Maize			Wheat		
	Mean response (mg/g)	Recovery (%)	RSD (%)	Mean response (mg/kg)	Recovery (%)	RSD (%)
Blank	0.02	-	155	0.6	-	142
Level 1: 0.1 mg/kg	0.12	120	30	0.1	100	54
Level 2: 1 mg/kg	0.9	90	27	1.1	110	37

3rd approach: Lateral flow assay

Enviromental assesment

Manual

1: Direct analysis
In field sampling and on line analysis

2: Minimal number of samples and size
Microanalysis: sample size 3g

3: In situ measurements
At line

4: Integration of analytical processes and operations
The procedure involves 7 distinct steps

5: Automatic and miniaturized methods
Manual and not miniaturized sample preparation

6: Derivatization
None

7: Analytical waste (g or mL)
Sample (3g), lateral flow device (5g), pipette tips (1g), reagents (0.2 mL)

8: Multianalyte method
(1 analyte and 4 samples/hour)

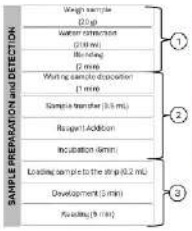
9: Minimize use of energy
Immunoassay

10: Reagents from renewable source
None

11: Toxic reagents
None

12: Safety for operators:
No risk for operators

4th Approach: Automated lateral flow

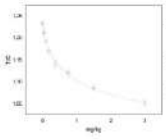


Automated LF

Device currently used for mycotoxin analysis
- Easy to use for non-expert users
- Lectures at the same time: up to 6

4th Approach: Fully automated procedure based on lateral flow assay

Preliminary evaluation



	Wheat (Manual)			Wheat (automatized procedure)		
	Mean response (mg/kg)	Recovery (%)	RSD (%)	Mean response (mg/kg)	Recovery (%)	RSD (%)
Blank	n.d	-	155	n.d	-	-
Level (1 mg/kg)	0.9	90	27	1.13	100	15

Working in progress

Optimization of storage conditions of reagents in the automatic device
Optimization of the mechanical part and microfluidics to increase precision and reduce sample volume

優化自動設備中試劑的儲存條件
優化機械部件和微流體，以提高精度並減少樣品量

4th Approach: Fully automated procedure based on lateral flow assay

Enviromental assessment

Automatic

1: Direct analysis
In field sampling and on line analysis

2: Minimal number of samples and size
Microanalytic sample size 20g

3: In situ measurements
At line

4: Integration of analytical processes and operations
The procedure involves 1 step

5: Automatic and miniaturized methods
Automatic and not miniaturized procedure

6: Derivatization
None

7: Analytical waste (g or mL)
Samples (10g), lateral flow devices (5g), pipette tips (1g)

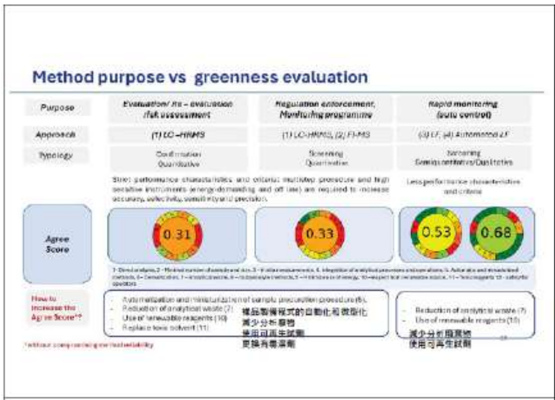
8: Multianalyte method
(1 analyte and 8 samples/hour)

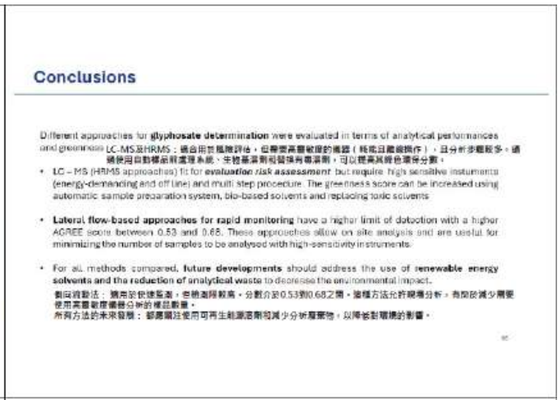
9: Minimize use of energy
Immunoassay

10: Reagents from renewable source
None

11: Toxic reagents
No toxic reagents

12: Safety for operators:
No risk for operators

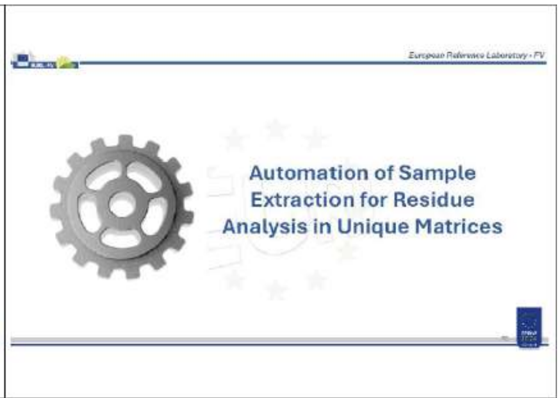

Method purpose vs greenness evaluation
Purpose
Approach
Typology
Agree Score
0.31
0.33
0.53
0.68
樣品製備程式的自動化和微型化
減少分析廢物
使用可再生試劑
更換有毒溶劑
減少分析廢棄物
使用可再生試劑


Conclusions
Different approaches for glyphosate determination were evaluated in terms of analytical performances and greenness
LC – MS (HRMS approaches) fit for evaluation risk assessment but require high sensitive instuments (energy-demanding and off line) and multi step procedure. The greenness score can be increased using automatic sample preparation system, bio-based solvents and replacing toxic solvents
Lateral flow-based approaches for rapid monitoring have a higher limit of detection with a higher AGREE score between 0.53 and 0.68. These approaches allow on site analysis and are useful for minimizing the number of samples to be analysed with high-sensitivity instruments.
For all methods compared, future developments should address the use of renewable energy solvents and the reduction of analytical waste to decrease the environmental impact.


15th European Pesticide Residue Workshop
16 – 20 September 2024 | Zürich, Switzerland
THANK YOU
for
YOUR ATTENTION
Acknowledgments
Dr. Ivan Pecorelli
Emanuela Verdini
Matteo Luppi
Andrea Dell'Erta
EU Food Safety Platform
Veronica
Lattanzio


15th European Pesticide Residue Workshop
16 – 20 September 2024 | Zürich, Switzerland
News from the EURL for Fruit and Vegetables
來自歐盟水果蔬菜參考實驗室的消息
EURL-FV
Amadeo Rodríguez Fernández-Alba and Carmen Ferrer
6-17


European Reference Laboratory - FV
AUTO-MATION
加快分析時間
Speed up the analysis time
減少實驗室浪費
Reduce laboratory waste.
避免將繁瑣和重複的任務分配給人員（處理步驟）
Avoid assigning tedious and repetitive tasks to the personnel (steps of handling)
提高結果的品質
Improve the quality of the results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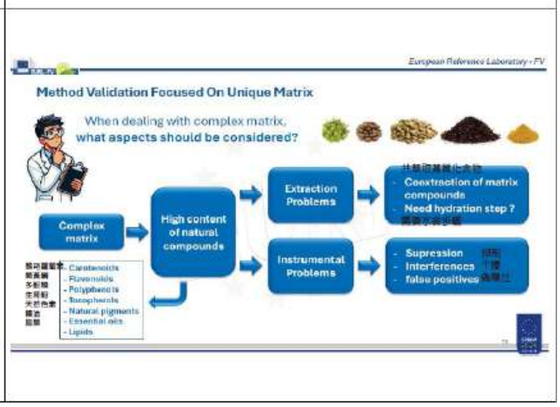
Automation of Sample Extraction for Residue Analysis in Unique Matrices


European Reference Laboratory - FV
Method Validation Focused On Unique Matrix
Annex A. Commodity groups and representative commodities
Difficult or unique matrix
EURL
SANTE/11312/2021(V2)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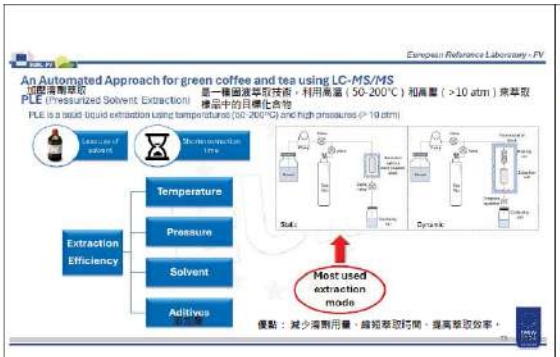
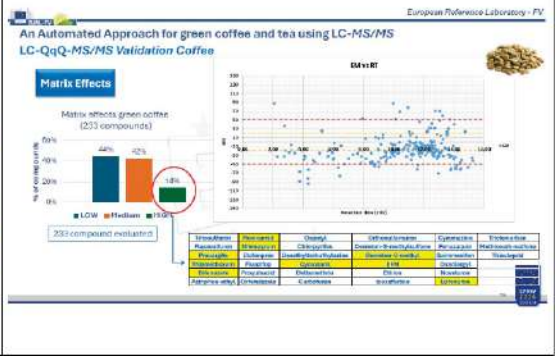
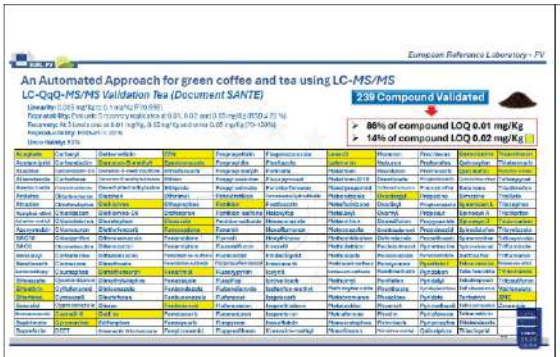
Method Validation Focused On Unique Matrix
When dealing with complex matrix, what aspects should be considered?
Complex matrix
High content of natural compounds
Extraction Problems
Coextraction of matrix compounds
Need hydration step ?
Instrumental Problems
Supression
Interferences
false positives
Carotenoids
Flavonoids
Polyphenols
Tocopherols
Natural pigments
Essential oils
Lipids


European Reference Laboratory - FV
An Automated Approach for green coffee and tea using LC-MS/MS
PLE (Pressurized Solvent Extraction)
PLE is a solid-liquid extraction using temperatures (50-200 °C) and high pressures (> 10 atm)
Temperature
Pressure
Solvent
Additives
Extraction Efficiency
Most used extraction mode
優點：減少溶劑用量、縮短萃取時間、提高萃取效率，


European Reference Laboratory - FV
An Automated Approach for green coffee and tea using LC-MS/MS
EXTREVA ASE
3g of sample hydrated with 3mL of water
Mix 3g of hydrated sample with 3g of DE
Volume collected: 10 mL
filters
Mix sample and DE
225 mg MgSO4
filters


European Reference Laboratory - FV
An Automated Approach for green coffee and tea using LC-MS/MS
LC-QqQ-MS/MS Validation Coffee (Document SANTE)
239 Compound Validated
89% of compound LOQ 0.01 mg/Kg
11% of compound LOQ 0.02 mg/Kg


European Reference Laboratory - FV
An Automated Approach for green coffee and tea using LC-MS/MS
LC-QqQ-MS/MS Validation Coffee
Matrix Effects
Matrix effects green coffee (233 compounds)
LOW
Medium
HIGH
233 compound evaluated


European Reference Laboratory - FV
An Automated Approach for green coffee and tea using LC-MS/MS
LC-QqQ-MS/MS Validation Tea (Document SANTE)
239 Compound Validated
86% of compound LOQ 0.01 mg/Kg
14% of compound LOQ 0.02 mg/Kg


European Reference Laboratory - FV
An Automated Approach for green coffee and tea using LC-MS/MS
LC-QqQ-MS/MS Analysis of EUPT-FV-SC07
加水與不加水對農藥殘留檢測結果的影響
With Water
Without water
Robust mean
Adding water causes more caffeine to be extracted and therefore more superposition
Adding water is necessary to extract the more polar pesticides
The developed method has obtained good z-score values


European Reference Laboratory - FV
QuEChERS citrate
Sample amount: 5g
Hydration volume:10 mL H2O
Solvent: 10 mL AcN
Salts: 6.5 g QuEChERS salts
Clean-up: 125 mg PSA and 750 mg MgSO4
Freezing-out: Yes/No
Time extraction
Stages of handling: 6 steps
PLE
Sample amount: 3g
Hydration volume: 3mL H2O
Solvent: 20 mL AcN/MeOH
Salts: 225 mg MgSO4
DE: 3 g 矽藻土
Clean-up: Not use
Freezing-out: Yes/No
Time extraction (X4) similar
Stages of handling: 3 steps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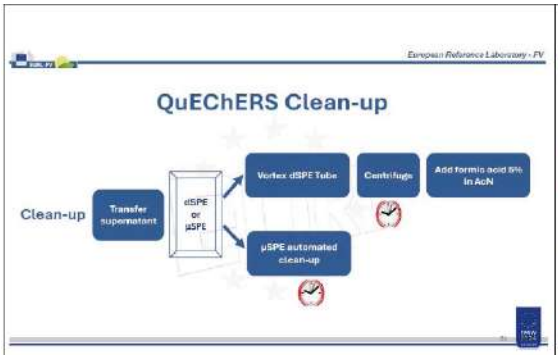
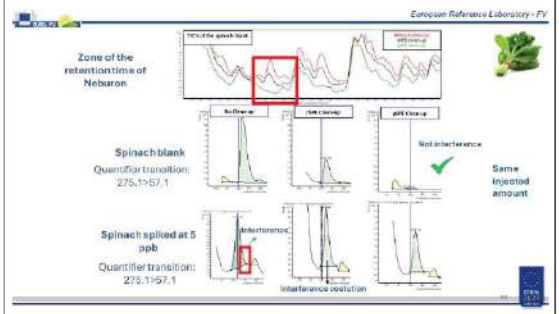
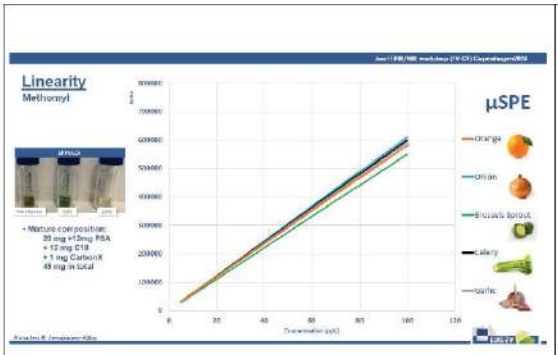
Automation and miniaturization of the cleanup step following QuEChERs extraction via microSPE

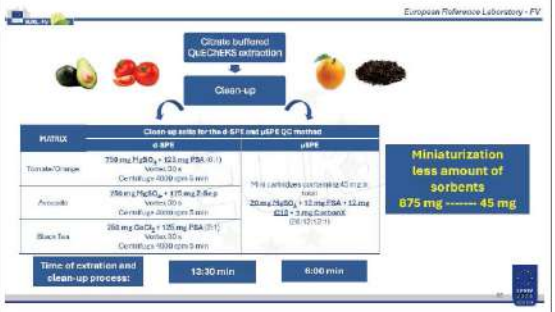

European Reference Laboratory - FV
QuEChERS Clean-up
Clean-up
Transfer supernatant
dSPE or µSPE
Vortex dSPE Tube
Centrifuge
Add formic acid 5% in AcN
µSPE automated clean-up

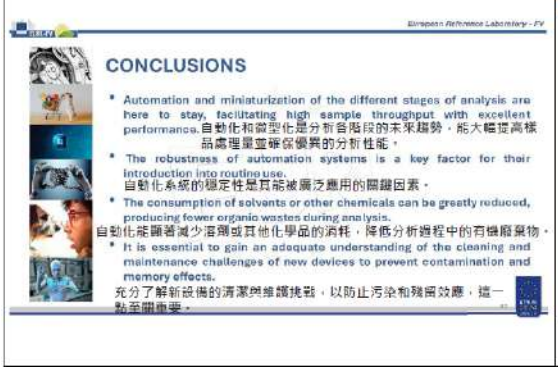

European Reference Laboratory - FV
Clean up Step
Manual dSPE
Automated µSPE
Elution Solvent
µSPE Cartridge:
20 mg Anhydrous MgSO4 +
12mg PSA +
12 mg C18 +
1 mg CarbonX
Total injected amount: 1 mg
Injection volume 2.5 µL
Total injected amount: 0.25 mg
Injection volume 2.5 µL


European Reference Laboratory - FV
Zone of the retention time of Neburon
Spinach blank
Quantifier transition:
275.1>57.1
Not interference
Same injected amount
Spinach spiked at 5 ppb
Quantifier transition:
275.1>57.1
Interference
Interference solution


European Reference Laboratory - FV
Optimization of PAL µSPE QuEChERS clean-up workflow
Tomato blank extract spiked at 10 ppb
Haloxyfop
Quizalofop
Fluazifop
Without elution step
With elution step


Linearity
Methomyl
µSPE
orange
onion
broccoli sprout
celery
garlic

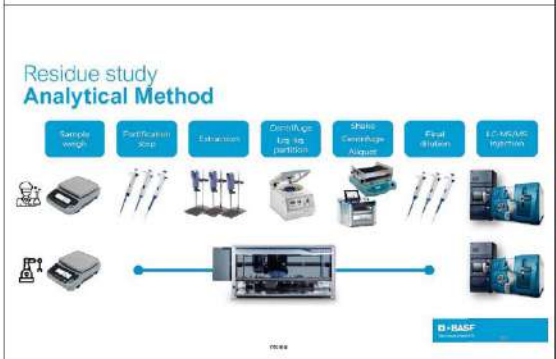

European Reference Laboratory - FV
Citrate buffered QuEChERS extraction
Clean-up
MATRIX
Clean-up salts for the d-SPE and µSPE QC method
d-SPE
µSPE
Tomato/Orange
Avocado
Black Tea
Miniaturization less amount of sorbents
875 mg ------- 45 mg
Time of extration and clean-up process:
13:30 min
6:00 min


European Reference Laboratory - FV
CONCLUSIONS
Automation and miniaturization of the different stages of analysis are here to stay, facilitating high sample throughput with excellent performance.自動化和微型化是分析各階段的未來趨勢，能大幅提高樣品處理量並確保優異的分析性能。
The robustness of automation systems is a key factor for their introduction into routine use.
自動化系統的穩定性是其能被廣泛應用的關鍵因素。
The consumption of solvents or other chemicals can be greatly reduced, producing fewer organic wastes during analysis.
自動化能顯著減少溶劑或其他化學品的消耗，降低分析過程中的有機廢棄物。
It is essential to gain an adequate understanding of the cleaning and maintenance challenges of new devices to prevent contamination and memory effects.
充分了解新設備的清潔與維護挑戰，以防止污染和殘留效應，這一點至關重要。


Thank You for Your Attention
EURL-FV

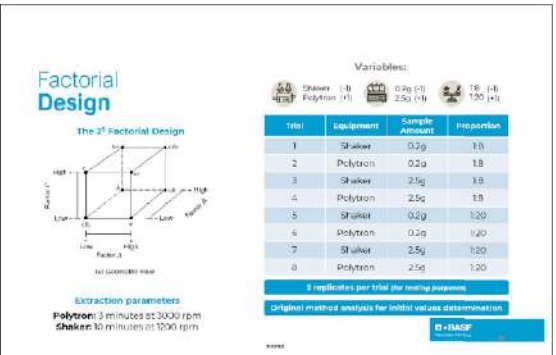

BASF
EPRW 2024
Comprehensive evaluation on the impact of sample size and extraction equipment in pesticide residue analysis in food
食品農藥殘留分析中樣品大小和萃取設備影響的全面評估
O-19


Our
Goal 將分析方法縮小規模，使其能夠與自動化設備兼容
Demonstrate the feasibility of scaling-down analytical methods to make them compatible with automation:
Extraction equipment
Sample amount
2.5 – 5.0g
0.10 – 0.25g


Residue study
Analytical Method
Sample weigh
Purification step
Extraction
Centrifuge Log kow partition
Shake Centrifuge Aliquot
Final dilution
LC-MS/MS Injection


Sample
Homogenization

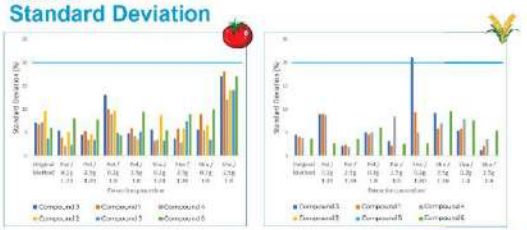

Particle Size
Measurement
粒子大小分析儀
Mean particle size µm
D(0.5) µm
347 211
265 116
285 189
318 136
446 353
577 504
423 342
199 146
448 377
517 478
Overall mean particle size
199 – 517 µm
研究評估了不同穀物（水稻、小麥、大麥、燕麥）的粒徑對萃取效率的影響，發現當穀物粒徑大於40目（約425微米）時，萃取效果較好


Factorial
Design
The 2³ Factorial Design
Extraction parameters
Polytron: 3 minutes at 3000 rpm
Shaker: 30 minutes at 1200 rpm
Variables:
Shaker (-1) Polytron (+1)
0.2g (-1) 2.5g (+1)
1:8 (-1) 1:20 (+1)
Trial | Equipment | Sample Amount | Proportion
1 | Shaker | 0.2g | 1:8
2 | Polytron | 0.2g | 1:8
3 | Shaker | 2.5g | 1:8
4 | Polytron | 2.5g | 1:8
5 | Shaker | 0.2g | 1:20
6 | Polytron | 0.2g | 1:20
7 | Shaker | 2.5g | 1:20
8 | Polytron | 2.5g | 1:20
3 replicates per trial for testing purposes
Original method analysis for initial values determination

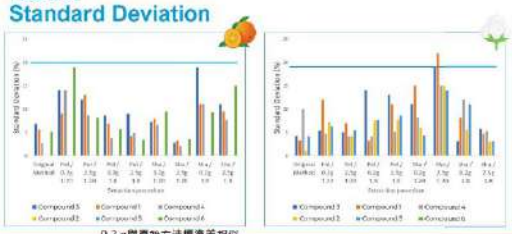

Field
Samples
Matrices
Tomato (fruit)
Citrus (fruit)
Rice (grain)
Cotton (seed)
Analytes
Fungicides
Insecticides
嗎酸酯類殺菌劑 Strobilurin (Compound 1)
苯甲醯尿素類 Benzoylurea (Compound 6)*
Strobilurin (Compound 2)
三唑類 Triazol (Compound 3)
Pyrazole-carboxamide (Compound 4)
Pyrazole-carboxamide (Compound 5)*
Over 1500 individual data


Results: Triazol (Compound 3) in tomato
Trial | Equip. | Sample Amount | Proportion | Residues (mg/kg) | Mean | SRD | Normalized Results (%) | % of Mean Residue
Ctrl.p. | Polytron | 2g | 1:20, 100 mL | 0.22 0.23 0.23 0.25 0.19 | 0.23 | 7.0 | 104 108 99 99 90 | 100
1 | Shaker | 0.2 g | 1:8, 1.6 mL | 0.18 0.20 0.20 0.19 0.19 | 0.19 | 4.5 | 87 96 96 87 88 | 90
2 | Polytron | 0.2 g | 1:8, 1.6 mL | 0.21 0.19 0.20 0.20 0.26 | 0.21 | 17 | 99 89 95 95 124 | 97
3 | Shaker | 2.5 g | 1:8, 20 mL | 0.19 0.21 0.21 0.21 | 0.20 | 5.4 | 88 98 92 98 | 95
4 | Polytron | 2.5 g | 1:8, 20 mL | 0.22 0.21 0.22 0.25 0.20 | 0.21 | 4.8 | 105 98 103 98 93 | 100
5 | Shaker | 0.2 g | 1:20, 4 mL | 0.22 0.21 0.21 0.23 0.24 | 0.22 | 5.4 | 106 99 103 106 114 | 105
6 | Polytron | 0.2 g | 1:20, 4 mL | 0.20 0.18 0.19 0.21 0.19 | 0.19 | 5.6 | 92 82 91 97 86 | 90
7 | Shaker | 2.5 g | 1:20, 50 mL | 0.20 0.21 0.22 0.20 | 0.21 | 3.7 | 96 99 102 94 | 97
8 | Polytron | 2.5 g | 1:20, 50 mL | 0.19 0.23 0.22 0.21 0.22 | 0.20 | 7.5 | 91 106 105 101 105 | 99

Results
Standard Deviation



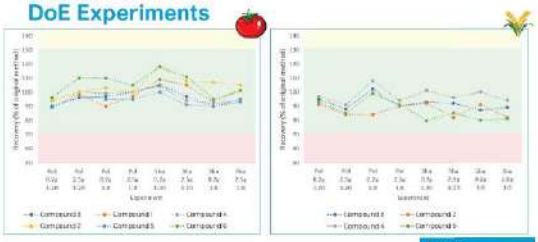
Results
Standard Deviation



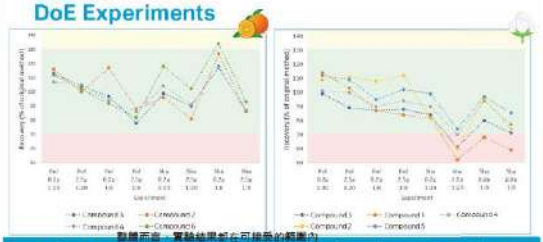
0.2 g與原始方法標準差相似

Experiments using 0.2g showed consistent standard deviations compared to the original method

Results
DoE Experiments



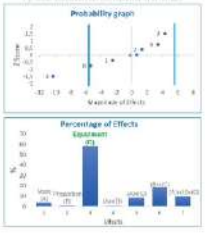
Results
DoE Experiments



整體而言，實驗結果都在可接受的範圍內

Overall, results are within acceptable range, without significant differences between a.is.

Results
DoE Experiments



顯著影響的範圍大致在-20%到+20%之間，檢查跟著不同的實驗條件可能會導致回收率有20%左右的變化。

在標籤樣品中，使用Polytron設備的回收率比使用Shaker設備的回收率高約30%。

使用0.2g樣品的回收率與使用2.5g或5.0g樣品的回收率相當。

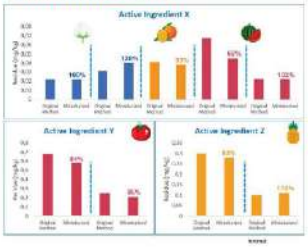
In general, significant effects (p-value <0.05, 95% confidence level) when observed, showed effects ranging from approximately **-20%** to **+20%**.

For both strobilurin in cotton seed, polytron showed a ~**30%** **higher** residue results compared to the shaker.

Experiments with 0.2g showed comparable results to those with a mass of 2.5g or 5.0g

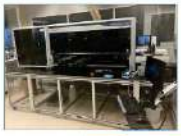
The variable of proportion showed minimal statistically significant effects at the evaluated levels.

Results
Miniaturization



Automated method:

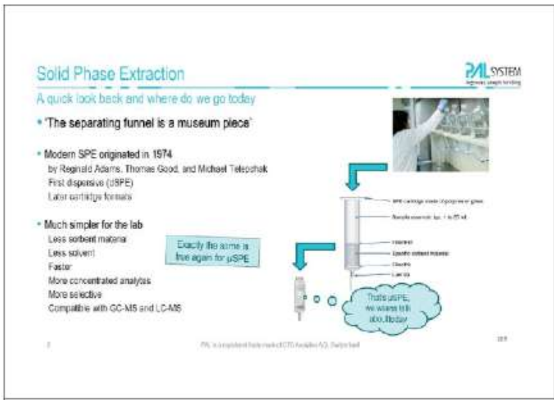
- Hamilton Microlab STAR LHS for extraction and maintained same proportion mass/volume.
- Sample weigh was reduced from 2.5 – 5g to 0.20 – 0.25g.

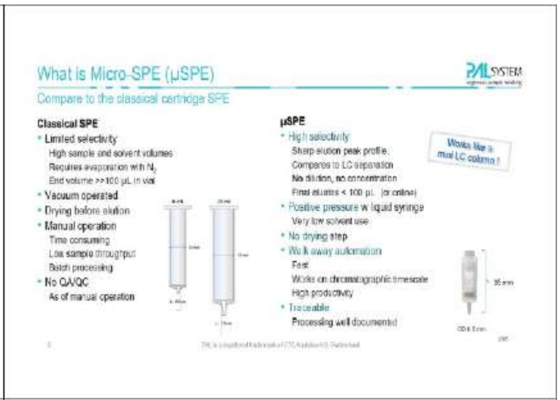


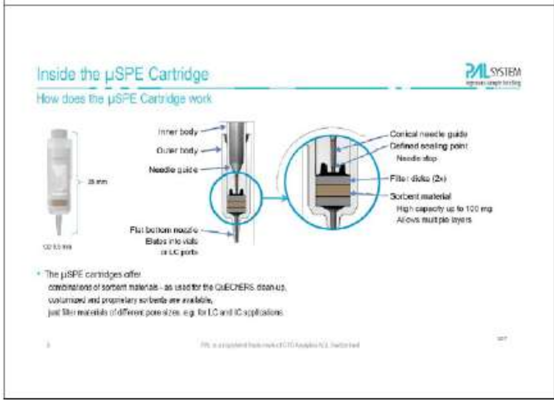
Conclusion

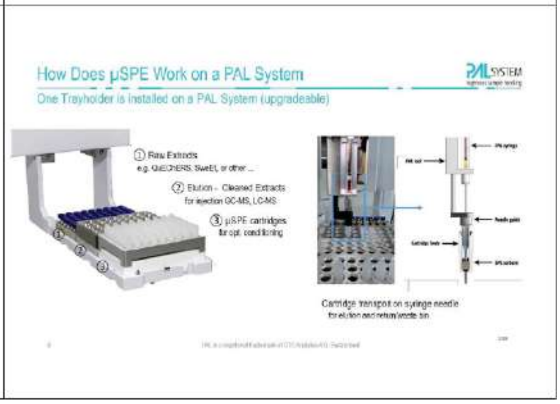
- Overall effects variation for tested variables were within a 20% range, that could be considered acceptable for residue analysis.
- The 0.2g aliquots showed comparable results to the higher sample amounts (2.5g - 5.0g).
- Supplementary comparative tests confirmed that the automated miniaturized method yielded results comparable to the original methodology.
- The high-throughput automation method results in an 80-90% reduction in both working time and the use of extraction solvents.

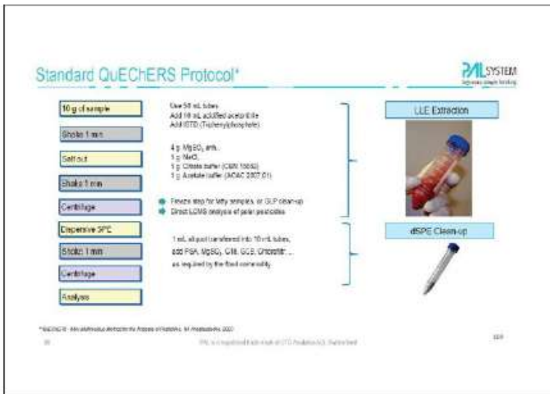
•在測試的變量中，整體影響的變化控制在20%以內，這對於殘留分析來說是可以接受的。
•使用0.2g的樣品得到的結果與使用較大量樣品（2.5-5.0g）的結果相當。
•自動化微型化方法產生的結果與原始方法的結果相當。
•高通量自動化方法使得工作時間和萃取溶劑的使用量減少了80-90%。

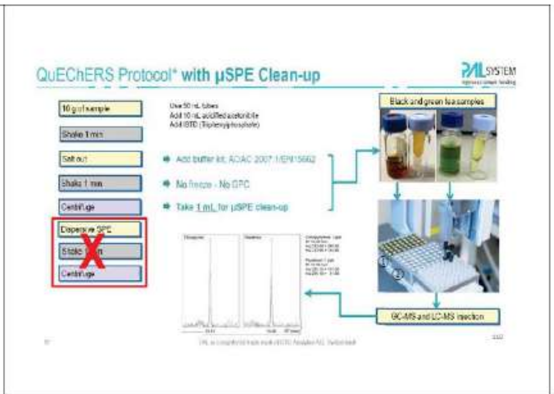

Solid Phase Extraction
A quick look back and where do we go today
'The separating funnel is a museum piece'
Modern SPE originated in 1974
by Reginald Adams, Thomas Good, and Michael Telepchak
First dispersive (dSPE)
Later cartridge formats
Much simpler for the lab
Less sorbent material
Less solvent
Faster
More concentrated analytes
More selective
Compatible with GC-MS and LC-MS
Exactly the same is true again for µSPE
Thats µSPE, we wana talk abo…today

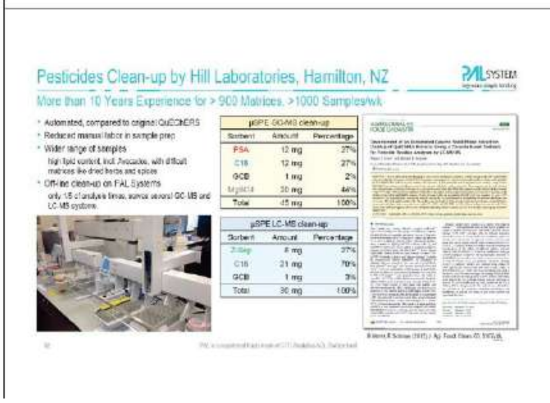

What is Micro-SPE (µSPE)
Compare to the classical cartridge SPE
Classical SPE
Limited selectivity
High sample and solvent volumes
Requires evaporation with N2
End volume >>100 µL in vial
Vacuum operated
Drying before elution
Manual operation
Time consuming
Low sample throughput
Batch processing
No QA/QC
As of manual operation
µSPE
High selectivity
Sharp elution peak profile
Compares to LC separation
No dilution, no concentration
Final eluates < 100 µL (or online)
Positive pressure w liquid syringe
Very low solvent use
No drying step
Walk away automation
Fast
Works on chromatographic timescale
High productivity
Traceable
Processing well documented
Works like a real LC column !
35 mm

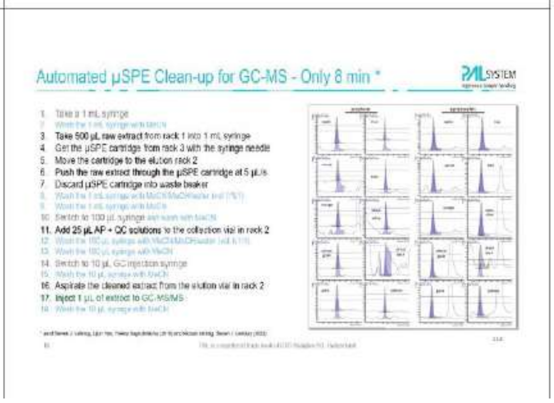

Inside the µSPE Cartridge
How does the µSPE Cartridge work
Inner body
Outer body
Needle guide
Flat bottom needle
Elutes into vials or LC ports
Conical needle guide
Defined sealing point
Needle stop
Filter disks (2x)
Sorbent material
High capacity up to 100 mg
Allows multiple layers
The µSPE cartridges offer
combinations of sorbent materials - as used for the QuEChERS clean-up,
customized and proprietary sorbents are available,
just filter materials of different pore sizes, e.g. for LC and IC applications


How Does µSPE Work on a PAL System
One Trayholder is installed on a PAL System (upgradeable)
① Raw Extracts
e.g. QuEChERS, SweEt, or other …
② Elution - Cleaned Extracts
for injection GC-MS, LC-MS
③ µSPE cartridges
for opt. conditioning
Cartridge transport on syringe needle
for elution and return/waste bin


Standard QuEChERS Protocol*
10 g of sample
Shake 1 min
Salt out
Shake 1 min
Centrifuge
Dispersive SPE
Shake 1 min
Centrifuge
Analysis
LLE Extraction
dSPE Clean-up


QuEChERS Protocol* with µSPE Clean-up
10 g of sample
Shake 1 min
Salt out
Shake 1 min
Centrifuge
Dispersive SPE
Centrifuge
No freeze - No GPC
Take 1 mL for µSPE clean-up
Black and green tea samples
GC-MS and LC-MS injection

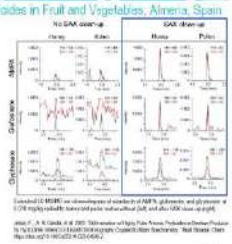

Pesticides Clean-up by Hill Laboratories, Hamilton, NZ
More than 10 Years Experience for > 900 Matrices, >1000 Samples/wk
Automated, compared to original QuEChERS
Reduced manual labor in sample prep
Wider range of samples
Off-line clean-up on PAL Systems
µSPE GC-MS clean-up
Sorbent | Amount | Percentage
PSA | 12 mg | 27%
C18 | 12 mg | 27%
GCB | 1 mg | 2%
Total | 45 mg | 100%
µSPE LC-MS clean-up
Sorbent | Amount | Percentage
C18 | 21 mg | 70%
GCB | 1 mg | 3%
Total | 30 mg | 100%


Automated µSPE Clean-up for GC-MS - Only 8 min *
1. Take a 1 mL syringe
3. Take 500 µL raw extract from rack 1 into 1 mL syringe
4. Get the µSPE cartridge from rack 3 with the syringe needle
5. Move the cartridge to the elution rack 2
6. Push the raw extract through the µSPE cartridge at 5 µL/s
7. Discard µSPE cartridge into waste beaker
10. Switch to 100 µL syringe
11. Add 25 µL AP + QC solutions to the collection vial in rack 2
14. Switch to 10 µL GC injection syringe
16. Aspirate the cleaned extract from the elution vial in rack 2
17. Inject 1 µL of extract to GC-MS/MS

Highly Polar Pesticides in Complex Matrices (QuPPe)

Glyphosate, AMPA, Glufosinate, ... EURL for Pesticides in Fruit and Vegetables, Almeria, Spain

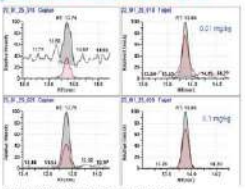
- Matrix:honey, pollen, coffee beans
- Acidified methanol extraction
- Automated µSPE clean-up
  50 mg SAX (strong ion exchange)
- Clean-up procedure
  1000 µL methanolic raw extract
  Load at 5 µL/s
  Matrix washed with 600 µL methanol
  Analytes elute with 400 µL methanol/HCl (9:1)
- Inject 10 µL to LC-MS/MS
- Cost saving: 500 mg → 50 mg SAX material
- Time saving: manual → automated 10:1
- Analytical: Improved recoveries up from avg. 70 → 86%



Ethylacetate Extraction of Pesticides from Foods (aka SweEt)

Big time savings and reduced manual effort for high fat matrices – Cantonal Lab, Zurich, CH

- EtOAc extracts wider range of polar pesticides
- But, also extract high amounts of matrix
- GPC or extract freezing was used as clean-up
- Clean-up using µSPE
  45 mg of PSA, C18, GCB, $MgSO_4$
  Load 200 µL raw EtOAc extract: 2 µL/s
  Blow-out: 1 mL air
- Injection 3 µL cleaned extract to GC-MS/MS
- Significant improvements:
  Difficult and fatty samples e.g. dried spices, egg, avocado, or liver are successfully processed.
  Captan and Folpet with good recoveries.
  One µSPE cartridge for all food matrices
  No time consuming freeze-out or GPC required anymore.

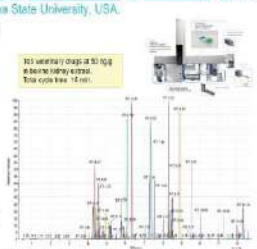


Captan and folpet in raspberry samples after µSPE clean-up

Veterinary Drug Screening by online µSPE – LC-MS/MS

From the Veterinary Diagnostic Laboratory, Iowa State University, USA.

- Veterinary drugs are legally controlled in large number of samples in difficult matrix.
- QuEChERS extraction (LLE with MeCN)
  from 5 g muscle, or kidney
- Automated µSPE clean-up
  on Thermo Scientific™ TriPlus™ RSH sampler,
  µSPE cartridge with 15 mg of endcapped C18,
  300 µL of supernatant at 2 µL/s,
  the eluate diluted 3+1 with mobile phase,
  injected into a 2 µL loop on the injection valve.
  Clean-up takes only 8.5 min to complete
- Cost saving on C18: 500 mg → 15 mg (30x less)
- Time saving: 80 min/15 samples → Zero, online prep
- No additional consumables



Automated QuEChERS Extraction and µSPE Clean-up

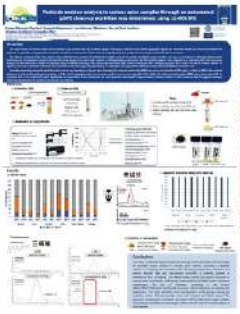
Application for homogeneous samples like beverages

- Why not automate all steps? The QuEChERSs extraction with SPE clean-up?
- Homogeneous samples
  Do not need much manual treatment
  Can be pipetted into 2 mL vials (also automatically!)
- QuEChERS extraction is automated in 2 mL vials with buffer salts previously added.
  Then added acidified MeCN,
  sat. NaCl solution.
- µSPE clean-up
  45 mg of PSA, C18, GCB, $MgSO_4$
  Load 250 µL raw extract: 2 µL/s
- Injection 3 µL cleaned extract to GC-MS/MS
- Combines all benefits
  from QuEChERS, µSPE clean-up, and prep-ahead automation

Summary

µSPE replaces the traditional SPE concentration and clean-up procedures

- µSPE is the next step available towards a Greener Analytical Chemistry
  Less solvents
  Less consumables
  Less waste
  Less energy consumption
- µSPE delivers strong analytical advantages
  One clean-up cartridge for all type of samples
  Improved recoveries
  Improved clean-up
  Improved precision
- µSPE reduces cost/sample
  Efficient use of GC-MS and LC-MS by online prep-ahead
  Increased sample throughput
  Walk-away automation
  Less manual work-load
  Less repeat measurements
  Faster report out



以自動化µSPE淨化流程及LC-MS/MS進行各種香料樣品農藥殘留分析

由於香料基質的複雜性以及可能存在的農藥種類眾多，因此需要採用專為化合物樣品提取和淨化流程，以有效減少基質干擾和離子抑制問題。在本研究中，不同香料基質（包括辣椒粉、咖喱、薑黃、幹辣椒和黑胡椒）的提取物或應用自動化的µSPE淨化，旨在使用LC-MS/MS技術進行農藥的多殘留分析。這種先進的自動化µSPE方法使用填充的柱箱，其中裝有多種呼附材料，專門用於捕獲多種共提取物質。淨化過程由自動進樣器執行自動化操作，不僅提高了效率，還降低了人為誤差的可能性。不同香料的MRLs因香料種類而異，通常情況下，99%分析物質的MRLs設定在0.05 mg/kg或更高，並0.05和0.1 mg/kg的回收試驗中，該方法顯示出優異的回收率（70%至120%），並且超過98%的化合物的RSD值低於20%。值得注意的是，樣品淨化的自動化處理每個樣品僅需約5分鐘，相較于傳統的手動淨化方法，日處理量提高了20%，顯著提升了工作效率。

PD-01

LC-MS/MS和GC-MS/MS檢測食用昆蟲中的農藥殘留

昆蟲富含蛋白質和礦物質，其飼料轉換效率高於牛和豬等傳統禽畜，使得食用昆蟲成為解決人口增長導致全球蛋白質短缺問題的解決方案。然而，使用食物和農藥殘留物評估昆蟲飼料存在風險，尤其是農藥污染，在日本，螺蛳、蠶和黃粉蟲等食用昆蟲已經上市。因此，開發一種能測食用昆蟲中廣泛農藥殘留的方法至關重要。

本研究開發的方法使用LC-MS/MS或GC-MS/MS對285種化合物進行0.01 mg/kg的篩查，269種化合物取得了令人滿意的分析性能，準確度範圍為70%至120%，精密度小於20%。此方法被認為適用於檢測食用昆蟲中的農藥殘留。本研究獲得日本厚生勞動省認可（grant number 23K1010）。

PD-14

使用彈性網路迴歸開發加工番茄醬產品中農藥處理因子的預測模型

加工因子（PF）是評估加工食品中農藥殘留風險的重要參數，代表著食品加工過程中農藥殘留水平的變化。PF 值是透過加工研究的結果計算得出的實驗數值，但此類研究通常需要複雜的程序，例如種植作物、田間噴灑農藥、食品加工以及分析農藥殘留量等，若能不進行加工研究就能估算 PF 值，將會非常便利。因此，本研究開發了一個新型模型，可以根據農藥的理化特性來預測 PF 值。

研究人員應用了 23 種具有廣泛理化特性的農藥，在番茄田種植進行了兩次施肥、採收後兩天，番茄加工成汁液、濃縮和乾燥，利用LC-MS/MS分析了生鮮番茄和加工番茄醬產品中的農藥殘留物。在數據分析中，將穩定的 23 種農藥分為訓練數據（20 種）和測試數據（3 種），並利用訓練數據開發模型。斯皮爾曼等級相關係數顯示，PF 值與農藥的理化特性（例如分子量、辛醇/水分配係數、水溶性等）呈正向或負向相關。

PO-07

二硫代胺基甲酸鹽類殘留分析方法之研究

目前主要使用的分析方法是將二硫代胺基甲酸鹽類分解為CS_2，並透過分光光度法對其進行定量，然而，這種分析方法需要很長時間，而且預處理影響極大，此外，研磨樣品可能會導致物質分解，使得樣品問題化變得困難，目在製備過程中需格外小心，，因此，本研究開發了一種利用QuEChERS萃取處理方法，以LC-MS/MS和GC-MS/MS質譜分析二硫代氨基甲酸鹽的方法，在二硫代氨基甲酸酯中，針對了四種國內登記使用的農藥成分：福美雙、錳鋅乃浦、免賴得和甲基鋅乃浦，使用DDMP、EBMeP和PBMeP對進行甲基化和分析，製備洋、橘子、紅辣椒、大豆和馬鈴薯樣品驗效了四種成分的回收率，並在三個實驗室進行了交叉驗證，通過決定係數（R^2）評估線性，結果大於0.99，定量極限為0.01 mg/kg，所有基質和成分的回收率和相對標準偏差均符合驗證指南的。

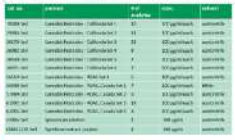
PD-24

農產品、有機資材及農業環境中463種農藥殘留物分析方法開發

建共開發了三種分析方法：農產品分析方法、有機資材分析方法和農業材料（酪酸培養基、果樹）、土壤和水分析方法，總共鑑定了463種農藥，包括國內分析和使用量較高的農藥，以及在農業環境殘留調查中檢測到的成分，測試的農藥相同，但分析方法根據每個樣品的特徵進行了修改。前處理方法是QuEChERS方法的改良版，使用的分析儀器是LC-MS/MS和GC-MS/MS，之後，對分析方法進行驗證，該分析方法由三個實驗室進行了交叉驗證。結果定量極限低於0.01 mg/kg，決定係數大於0.98，大多數基質和成分的回收率和相對標準偏差符合驗證指南的標準。

PD-27

確保消費者安全：大麻農藥檢測中認證參考物質的重要性



得獎

獎評選標準

- 科學內容與品質
- 原創性
- 對日常應用的相關性
- 設計/佈局/清晰度/目解釋性
- 個人展示（回答問題）

一種兼顧葉基質水解的農藥殘留分析替代方法

- 酸性農藥適合應用於農藥，但其反應性官能團（羧基、胺基、氨基等）常螯合基質成分形成各種結合物，使總殘留量測定變得困難。因此，在樣品製備過程中加入水解步驟以分解結合物和鹽類，生成易於定量為游離酸的阿維化合物至關重要。
- 經修改後的QuEChERS方法，加入了在60°C進行16小時的酸性水解步驟，被證明是測定糧穀化合物組成的最有效分析方法。然而，用NaOH中和提取液時，提取液中會產生沉澱，導致GC-MS/MS儀器堵塞問題。因此，必須對提取液進行額外的過濾，並且在將樣品的中和至所需pH值（5.5）後，應立即處理樣品。

PD-21

抗氧化劑在樣品研磨過程中防止農藥降解的應用

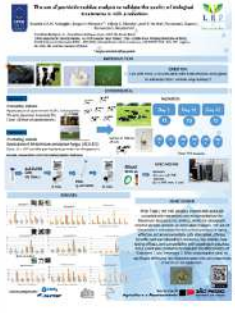
抗氧化劑可用於防止農藥在樣品研磨過程中降解，眾所周知，某些化合物在研磨過程中會因基質中的氧化過程而降解，這可能導致定量結果的誤差。為了阻止這些氧化過程，一種解決方案是添加抗氧化劑。

在過去幾年裡，歐洲聯盟參考實驗室（EURL-FV）對某些農藥進行了評估，並確定添加抗壞血酸（維生素C）作為抗氧化劑可以有效防止某些化合物的降解，阻止氧化過程。

本研究評估樣品研磨過程中添加 1% 抗壞血酸的效果，特別是在易於氧化的基質的番茄，馬鈴薯和蘋果中，使用 200 克樣品（添加和未添加 1% 抗壞血酸）對 240 種化合物進行了研磨前的評估，提取方法採用 QuEChERS。結果顯示，根據基質不同而氧化降解 3% 的化合物，添加抗壞血酸防止降解超過了60%效率，然而，添加抗壞血酸並非完全有益，觀察到另外約 3% 的化合物，在不添加抗壞血酸的情況下回收率在 70-120% 之間，但在添加抗壞血酸後回收率顯著降低。

研究結果突顯了在某些農藥/商品組合中使用抗氧化劑的必要性，例如，在嚴重氧化或質疑的情況下，能可以防止定量低估，從而確保農藥分析結果更準確。

PD-56



利用農藥殘留分析篩選牛奶生產中生物處理的品質

蜱蟲是畜牧業常見的問題，如果不加以控制，可能會影響牛奶的品質，巴西生物研究所一直在研究利用無人機在牧場中施用真菌來控制牛蜱（Rhipicephalus microplus）。

本研究旨在評估使用梅斯松、賽滅寧和環刀螨等殺蟲劑處理奶牛（CE組）和使用綠僵菌（Metarhizium anisopliae, IBCB 425）處理奶牛（CB組）的牛奶樣品中的農藥殘留。

實驗在巴西聖保羅州進行，時長63天，兩組都進行了三次處理，間隔21天，採用QuEChERS進樣品製備，使用EN15662乙酸緩衝液和UPLC-MS/MS（MRM模式）檢測，並根據歐盟指南（SANTE/11312/2021）進行驗證。

結果

•CE組：在處理後第1天和第7天檢測到胸斯松、賽滅寧和殺力靈的殘留。

•CB組：未檢測到任何農藥殘留物。

結論

•真菌處理是一種高效且環境友好的蜱蟲控制替代方案。

•與化學殺蟲劑相比，真菌處理具有減少蜱蟲抗藥性、低毒性、持久功效和適可持續使用等優點。

•真菌處理可顯著降低動物產品中農藥殘留風險，促進更安全、更可持續的蜱蟲控制方法。

PO-28


Save the date
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Workshop of the 4 EURLs for pesticides residues
Freiburg, Germany
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從1923年開始，賈科梅蒂花了兩年的時間繪製這些壁畫和屋頂畫，創造出一個生動的獨特空間，因為花形圖案眾多，當地人稱這裡為 "Blümlihalle"（花廳），現為警察局的大廳。


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創立於1855年，有「歐陸第一名校」的美譽，亦是愛因斯坦的母校。至今蘇黎世聯邦理工學院已產生超過 30 位諾貝爾獎得主。


感謝聆聽，敬請指正