出國報告（出國類別：開會）

參加第12屆EPRW
歐洲農藥殘留研討會報告

服務機關：行政院農業委員會農業藥物毒物試驗所

姓名職稱：王熙宇 技佐

派赴國家：德國(慕尼黑)

出國期間：107 年 5 月 19 日至 107 年 5 月 29 日

報告日期：107 年 8 月 22 日

目次

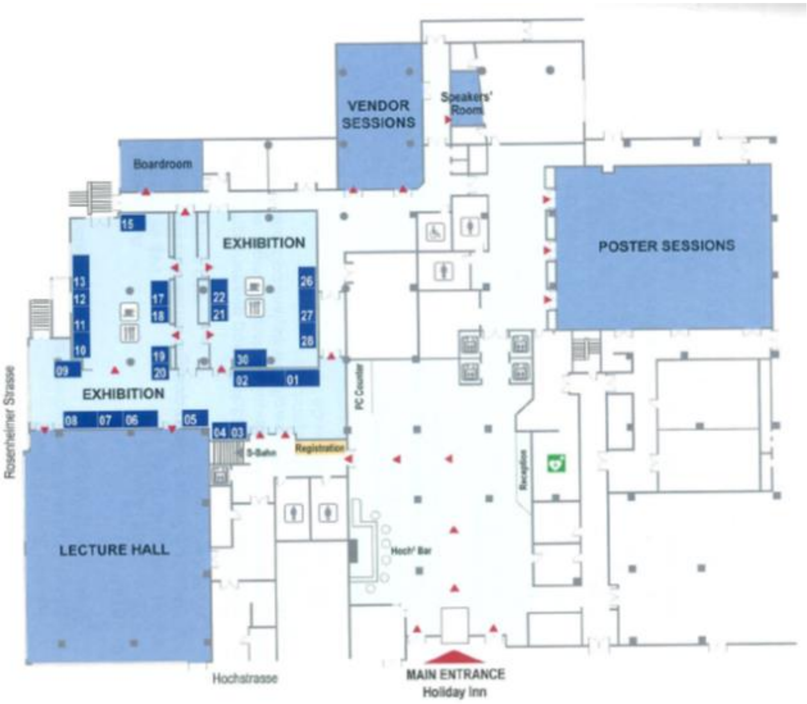
壹、目的

歐洲農藥殘留研討會（European Pesticide Residue Workshop, EPRW）每兩年由一個不同的歐洲成員國舉辦，介紹和討論食品和飲料中農藥殘留領域的最新概念和發展。本年舉辦之第十二屆研討會於德國慕尼黑舉行，其係由巴伐利亞健康和食品安全管理局（Bavarian Health and Food Safety Authority）主辦，與會人數計超過 500 人。主要討論之四大議題如下：（一）風險評估及溝通、（二）有機產品中的農藥殘留、（三）農藥殘留之監控、（四）農藥殘留之分析方法。本次研討會涵蓋近期關注之議題，並邀請歐洲及美加地區之風險評估及農藥殘留相關領域專家蒞臨演講，提供與會世界各地之政府單位、商業實驗室、監管機構、食品製造商及農藥製造商等單位代表交流研討之平台，內容包括風險評估之工具、累積暴露和風險、風險溝通及農藥對野生動物之毒害等。於分析方法方面，新型分析技術如：液相及氣相層析軌道阱質譜（LC and GC-Orbitrap）於蔬果中農藥殘留檢測之應用等議題，另亦針對不同樣品前處理流程或定量方法對農藥殘留檢驗之評估交流探討。其中主題日之議題為：有機產品中的農藥殘留，探討歐盟對有機生產之農藥殘留管制、有機農作物中農藥殘留分析所面臨的挑戰、荷蘭及瑞士的代表亦分享其國內對於有機產品之農藥殘留管制，共同針對農藥殘留檢驗在有機農業中之角色及問題進行討論。於農藥殘留之監控方面，提及去（106）年歐洲地區之芬普尼雞蛋事件，及其監控策略之後續等。並將演講及壁報投稿摘要集結成冊，提供與會人員參考。總計約有 160 篇之壁報發表，內容分為以下四個領域：（一）分析方法之開發及應用、（二）監管議題和監控、（三）毒理學及攝食量評估、（四）其他主題等。另有耗材或儀器供應商等舉辦新型儀器及分析技術之展示會，亦有研發技術相關之壁報論文發表計約 40 篇。本次參與研討會除瞭解歐洲地區近期於食品安全及農藥殘留領域關注之議題及相關分析技術之發展外，本所亦參與發表：承接衛福部委辦計畫成果之「開發利用氣相層析串聯質譜儀及液相層析串聯質譜儀於動物產品中分析多重農藥殘留方法」。由於研討會討論之議題與本所各領域業務甚為相關，且內容相當充實廣泛，於有限的時間內僅能就各重點主題節錄與本組業務較為相關之議題，建議若經費許可，未來可考慮擴大派員參與，以蒐集及瞭解更多國際間之新資訊及重要發展。

貳、過程

此次 EPRW 研討會於德國慕尼黑之慕尼黑市中心假日酒店(Holiday Inn Munich City Centre)舉行，研討會每日皆開放現場註冊，另有全程參與之報名註冊方式可選擇(官方網站上有提供全程參與之早鳥優惠)。參加研討會期間需配戴識別名牌，否則將被禁止入場。官方語言為英文，不另外提供翻譯服務，且全程禁止錄音錄影，會後若經講者及壁報論文之作者同意，大會即可提供投影片及壁報論文之電子檔給每一位參與者。壁報論文之開放時間僅每日約 45 分鐘，因此在研討

會期間仍需於有限的時間內針對重點議題進行蒐集與紀錄，但仍稍有遺漏。由於大會議題廣泛，涵蓋風險評估、農藥殘留監控、有機農產品農藥殘留檢驗及農藥殘留分析方法開發等，謹就各重點議題節錄與本組業務較為相關之重要內容及國際發展趨勢進行分享。



研討會於慕尼黑市中心假日酒店內之使用空間配置(圖片摘錄自大會提供手冊)

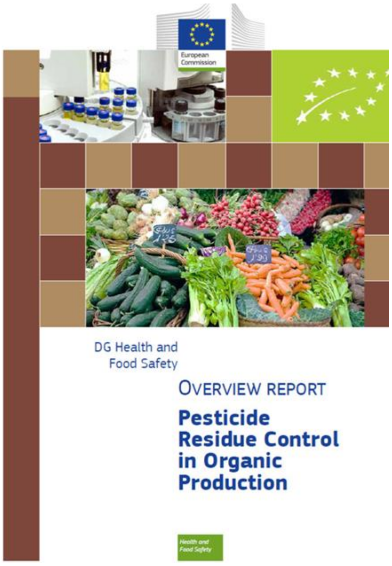
一.重要演講內容

主題一：風險評估及溝通：以農藥殘留為重點的風險溝通。由 Department Pesticide Safety German Federal Institute for Risk Assessment (BfR)的 Roland Solecki 發表演說。風險溝通的總體目標為採取措施以縮小專家(“客觀”的風險評估)與目標群體(人們對健康風險的“直覺”)之間的差距，所謂客觀的風險評估係基於以科學可衡量的風險標準進行評估，而直覺則為主觀的風險認知，與社會文化因素有關。有效的風險溝通需要瞭解和理解目標群體的看法。在對食品和健康的風險認知上，人們通常傾向於低估自然產生的風險(如黴菌產生會導致肝癌的黃麴毒素)，而高估人為來源(如種植農作物時施用農藥)造成的風險。可用於評估主觀風險認知的方法有：德爾菲研究、消費者討論會議、群體調查、重點小組討論會議，媒體分析和社群媒體分析等。其中媒體對於大眾風險認知的影響甚鉅，最近在 BfR 關於農藥殘留的媒體分析顯示，大多數關於農藥殘留的文章都提到了健康風險。僅在少數關於農藥殘留的文章中提到了效益，而絕大多數的文章沒有提到任何效益。而一方面，大眾對食品中的農藥殘留有高度的認知；但在另一方面，對與農藥殘留相關的食品消費行為影響卻很小。2016 年於德國有關植物保護產品的代表性群體調查顯示：在過去的兩年裡，有七成的消費者在

媒體上接收到有關農藥殘留的報導;三分之二的人們認為食品中的農藥殘留普遍受到禁止(即食品中不允許有農藥殘留)；十分之三的人們曾關注有關嘉磷塞(Glyphosate)的報導。講者於農藥殘留領域的風險溝通挑戰中舉了四個案例作探討，分別為：1.食物中的農藥殘留：母乳中的嘉磷塞、2.食物中的農藥殘留：啤酒中的嘉磷塞、3.食物中的農藥殘留：暴露於多重農藥殘留下(雞尾酒效應)、4.風險評估程序的整合協調，這四個案例的討論結論分別為：1. 在母乳中沒有檢測到嘉磷塞殘留(以定量極限為 1 ng / mL 或更低之兩種方法分析至少 100 份母乳樣品)、2.啤酒中的嘉磷塞沒有健康風險(只發現了微量的嘉磷塞殘留，若要攝取會對健康造成危害的嘉磷塞的量，成年人必須在一天內喝大約 1000 公升的啤酒)、3.累積風險評估的方法已被制定並且已在使用中，且在對累積殘留量的監測數據的評估中，尚未發現從前未被認知到的健康風險、4. 國際間主管機關和組織間的整合協調與透明化的程序是必要的。總結提到近期風險溝通的挑戰有：應妥善處理影響風險認知的因素、改進評估風險認知的方法、納入風險認知研究及為不同的目標群體選擇溝通工具，並與公眾展開更有效的風險溝通。而人類健康風險評估的創新挑戰有：納入國際間研究的結果、改進國際間公認的指導和指引、整合協調累積風險評估的方法、考慮設定容許量(MRL)的適當混合效應、加強科學合作和能力養成、根據匯入資料建立最新數據庫、評估程序更加透明和一致性、保持並改進高水準的科學專業知識、防止人類的健康受到農藥有害的影響及實現消費者的選擇自由。

主題二：歐盟對有機生產中農藥殘留控制之審視。由 European Commission DG Health and Food Safety 的 Jan Von Kietzell 發表演說。講者來自歐洲委員會衛生和食品安全總司(European Commission’s Directorate-General for Health and Food Safety) ，該機構之主管範圍包含食品、動物健康、動物福祉、有機生產、農藥殘留，污染物等。並針對有機生產中的農藥殘留檢測執行一項計畫，該計畫之執行背景為: 1.農藥殘留檢測為有機生產中的一個控制方式、2.自 2014 年起，法規要求需查驗 5%的有機經營者 3.幫助歐盟會員國實施有機生產中農藥殘留檢測的有效控制。該機構於 2014 年 12 月時向所有會員國發送問卷，調查有機生產中的農藥殘留檢測情況，隨後在 2015 年和 2016 年間針對 5 個會員國(英國、波蘭、德國、西班牙及芬蘭)進行了一系列的審視。調查結果顯示：農藥殘留檢驗的取樣對象包括：食品、飼料、葉子 、土壤及水；樣品取樣之階段包括：生產、加工、零售及進口。雖然有關於採樣程序的官方指導文件，但在生產階段的採樣通常沒有明確的程序（例如樹葉、土壤和水)，且官方採樣程序不適用於識別鄰田農藥飄散。主管當局估計，含有農藥殘留的樣品中有三分之一與飄散有關，其可能來自採樣人員實施錯誤的採樣程序，導致檢驗結果的解釋可能會受到不適合其目的的採樣程序影響。在參與檢驗的實驗室及分析方法部分，缺乏分析方法(如分析的品項範圍及其定量極限等)的官方標準會對控制系統產生負面影響。關於調查門檻(行動值，action level)的設定：某些驗證機構在決

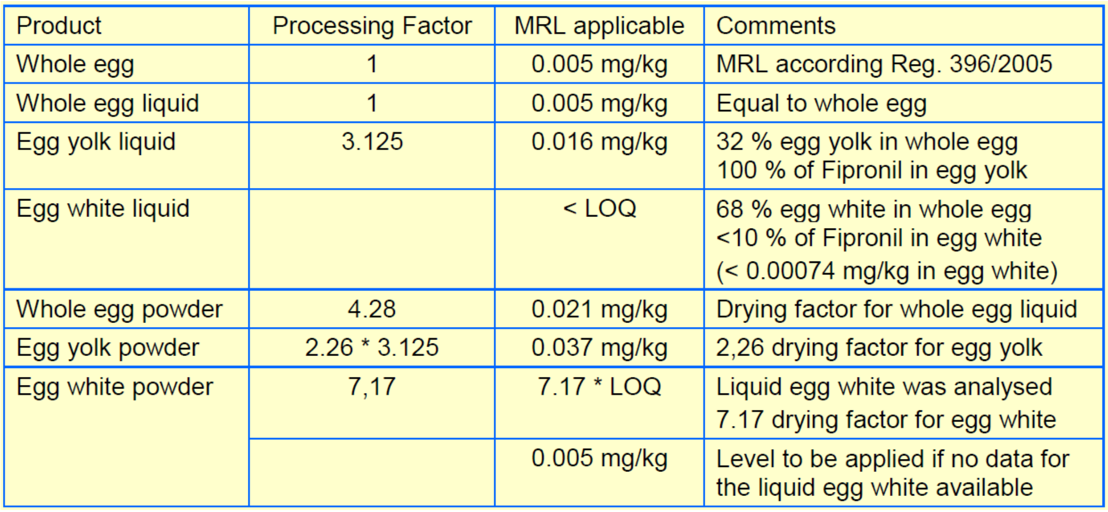
定是否啟動調查之前會納入加工因子作為考量(例如香料的加工因子最高可到10) ，講者特別提到將量測不確定度與定量極限聯繫起來在技術上是不正確的，任何等於或高於定量極限的結果都可以被量化。在調查的程序部分：在正式調查過程中，有機農產品會被封鎖且認定為未經認證（低農藥殘留的情況例外）。各個驗證機構啟動調查的程度和性質各不相同，某些驗證機構在檢出低農藥殘留的情況下（例如 0.01-0.02 mg / kg）會向有機生產者發出信函，通知他們結果，並要求解釋。在葉子上經常檢測到農藥殘留，一些驗證機構會應用數學模型來確定農藥殘留是否來自使用未推薦農藥而沒有至現場調查。如果有機生產者已採取足夠的預防措施，則認為鄰田飄散和其他污染原因是可以接受的，同時並沒有官方標準來決定預防措施的充分性，採用逐案判斷，不適用一致的規則。某些會員國會進行系統性的現場調查，逐案跟進、並訪問鄰近的慣行農場，取得樣本、檢查這些鄰近慣行農場的用藥記錄等。關於執法和結果回報方面，在 5 個會員國中的 2 個國家，所有檢測到定量極限以上的農藥殘留都導致了執法行動和裁罰。5 個會員國中沒有一個具有固定的行動值，超過該行動值將採取執法行動，並且都有定期通知主管當局的程序。關於執法的結論：有機生產中的農藥殘留檢測是確定與農藥殘留有關的問題的合適工具、歐盟之指引提供了充分的資訊，可用以逐案調查農藥殘留檢測、農藥殘留檢測的結果解釋和後續行動的官方標準差異阻礙了對於合乎規定的處理的一致性，特別是在低濃度的農藥殘留檢測結果下尤其明顯。各會員國的主管機構應考慮：在生產過程中對農藥殘留分析的採樣程序實施明確的指示、在適當的情況下，採樣程序應適用於識別鄰田飄散、指定實驗室分析的方法和範圍的要求，以促進對未推薦用於有機生產的物質的可靠檢測和量化、確保進行有機生產中農藥殘留檢測的實驗室是被指定的，並且確保將其指定傳達給國家參考實驗室（NRL），以促進其合作和知識共享、參考關於食品和飼料中農藥殘留分析的分析品質管制和方法確效程序的指引文件（SANTE / 11813/2017），以獲得一致的農藥殘留分析品質管制程序、對農藥殘留檢測結果的解釋和後續行動實施明確的指示，且其指示還應有助於確保預防措施的充分性。講者最後提到新版歐盟有機法規為歐洲理事會於 2018 年 5 月 22 日通過，並且即將在歐盟官方期刊上發表，此新版法規將於 2021 年 1 月 1 日起適用，重要之內容摘錄如下：有機經營者應保持適當的措施，以確保和避免有機生產污染的風險，並定期審查和調整措施。當主管機構或驗證機構等若在有機產品中檢測到不該存在的物質時：（a）應立即進行正式調查及（b）應暫時禁止將有關產品作為有機產品上市。歐盟委員會應按一致的規則採取行動。該機構並將「有機生產中農藥殘留控制」之調查結果集結成冊並發行 (如下圖)。



(圖片摘錄自講者提供投影片)

主題三：以芬普尼(Fipronil)案例討論監測策略的後續。由European Union Reference Laboratory for Pesticides in Food of Animal Origin and Commodities with High Fat Content (EURL-AO)-State Institute for Chemical and Veterinary Analysis (CVUA), Freiburg i. Br., Germany的Ralf Lippold發表演說。講者來自歐盟的參考實驗室(EURL-AO)，該實驗室主要針對動物源性及高脂肪含量之基質進行檢測。講者針對於2017年造成民眾恐慌之芬普尼雞蛋對歐盟農藥殘留監測計畫及後果進行討論。該事件源於2017年7月20日歐盟預警通報系統 (the Rapid Alert System for Food and Feed, RASFF)通報比利時檢驗出雞蛋中芬普尼殘留量高達0.72（後修正為1.2）mg/kg，肇因為濫用非法添加芬普尼的清潔劑Dega-16(不允許用於生產食品的動物上)。講者所在的實驗室(EURL-AO)在接收到來自德國主關當局相關的訊息後於8月2日在網頁上公佈分析方法。而比利時、德國及荷蘭這三個發現受汙染的雞蛋較多的國家紛紛封閉養雞場並進行檢驗。芬普尼的殘留定義為主成分(Fipronil)及其代謝物(Fipronil sulfone)之總和，以芬普尼表示之。歐盟與植物和動物源食品和飼料中的農藥容許量相關的法規(REGULATION (EC) NO 396/2005)在2017年1月1日起將鳥蛋、禽肉及禽脂中的芬普尼下修為0.005 mg/kg、0.005 mg/kg及0.006 mg/kg。事件爆發後，各實驗室便紛紛開始進行芬普尼檢測方法之開發，分別以液相層析串聯式質譜儀及液相層析串聯飛行式質譜儀或氣相層析串聯式質譜儀進行檢測，結果發現以液相層析串聯式質譜儀負電荷模式進行分析，可檢測到芬普尼主成分及其代謝物(Fipronil、Fipronil sulfon、Fipronil sulfide及、Fipronil desulfinyl)，其定量極限皆可達0.001 mg/kg。於2017年8月30日進行的SCoPaFF (Standing Committee on Plants, Animals, Food and Feed - Section Novel Food and Toxicological Safety of the Food Chain)討論，探討雞蛋樣品及其較為簡單之加工品(如蛋黃液及乾燥之蛋白粉或蛋黃粉

等)及稍為複雜之加工品(如義大利麵)之加工因子探討，由來自雞蛋樣品的檢驗結果指出，90-95%的芬普尼濃縮在蛋黃中，5-10%的濃縮在蛋白中。對於蛋黃中的計算，可假設為 100%，雞蛋樣品及其較為簡單之加工品之加工因子及建議簡述如下表：



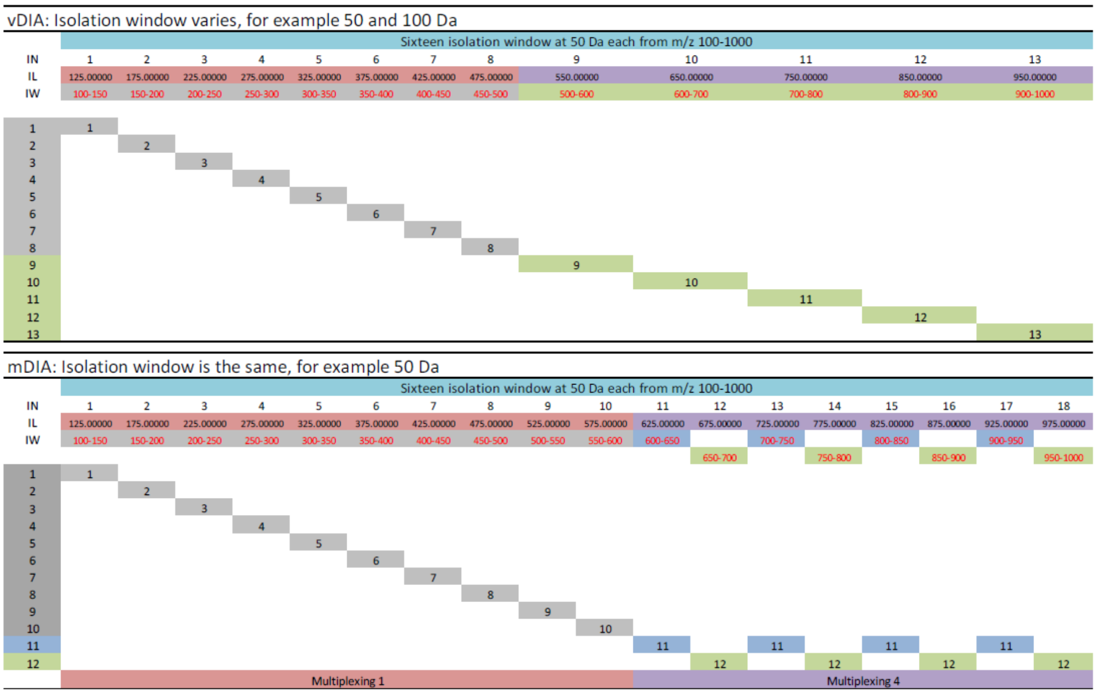
Product	Processing Factor	MRL applicable	Comments
Whole egg	1	0.005 mg/kg	MRL according Reg. 396/2005
Whole egg liquid	1	0.005 mg/kg	Equal to whole egg
Egg yolk liquid	3.125	0.016 mg/kg	32 % egg yolk in whole egg 100 % of Fipronil in egg yolk
Egg white liquid		< LOQ	68 % egg white in whole egg <10 % of Fipronil in egg white (< 0.00074 mg/kg in egg white)
Whole egg powder	4.28	0.021 mg/kg	Drying factor for whole egg liquid
Egg yolk powder	2.26 * 3.125	0.037 mg/kg	2,26 drying factor for egg yolk
Egg white powder	7,17	7.17 * LOQ	Liquid egg white was analysed 7.17 drying factor for egg white
		0.005 mg/kg	Level to be applied if no data for the liquid egg white available

(Ralf Lippold et al., 2018)

稍為複雜之加工品(如義大利麵)除考慮來自雞蛋中的芬普尼外亦需考慮來自麵粉(穀類)中的芬普尼。芬普尼為多用途物質 (同時可做為農藥、殺菌劑及動物用藥使用)，因本次事件委員會成立了特別監測計畫(Ad hoc Monitoring Programme)，針對類似芬普尼這種可能存在誤用疑慮之物質，提交了 12 種待監測品項(包含 Amitraz、Bifenthrin、Cypermethrin、Diazinon、Etoxazole、Fipronil、Flufenuxuron、Ivermectin、Pyridaben、Pyriproxyfen、Thiamethoxam 及 Triclorfon)，接著納入實驗室可用多重殘留方法進行分析之更多監測項目（計 56 種物質，包含殺蟎劑)。講者針對芬普尼事件提出之總結及建議如下：任何植物保護產品登記的同時必須有可用的分析用參考標準品(涉及殘留定義相關之所有標準品)、即使檢出值未超過 MRL，也要跟進任何不尋常的農藥殘留發現(特別是如果原產地在當地)、必須要擴大監測的範圍及品項，不僅僅是例行監測計畫的分析、同時需改善監管單位內、外溝通的方式及效率等，特別是當涉及主管當局內的不同部門時（例如涉及多用途 (同時可做為農藥、殺菌劑及動物用藥使用)物質之管制）。

主題四：基於化合物資料庫的軌道阱質譜(Q-Orbitrap)獨立資料獲取模式，用於篩選果蔬中 850 種農藥殘留。由 Canadian Food Inspection Agency, CFIA 的 Jian Wang 發表演說。該設計的目的在於基於精確質量測量，開發非目標資料獲得(Non-target data acquisition)的通用檢測方法，用於目標物分析。非目標資料獲得（即獨立資料獲取(data independent acquisition)），在超高液相層析儀串聯式軌道阱質譜(UHPLC/ESI Q-Orbitrap)中，超高液相層析儀可提供化合物分離之滯留時間(RT)，而軌道阱質譜可提供前驅物及其碎片的精確質量測量，該偵測系統提供了在較低μg/ kg 水準下的靈敏度。講者以 Full MS / dd-

MS^2(data dependent MS^2)模式用於鑑定及建立化合物資料庫和質譜資料庫；以 Full MS / vDIA（variable data independent acquisition）或 Full MS / mDIA（multiplexing data independent acquisition）用於目標篩選。vDIA 及 mDIA 模式主要差異在於質譜收取數據之質量選取範圍不同，vDIA 為非固定質量範圍選取(即變動質量範圍選取)收質譜圖；mDIA 則為固定質量範圍選取收質譜圖，兩者會造成化合物數據收取的點數及感度上有差異，示意圖如下：



The masses of 96% the pesticides in CDB (850) fall into the mass range from 100 – 500 m/z

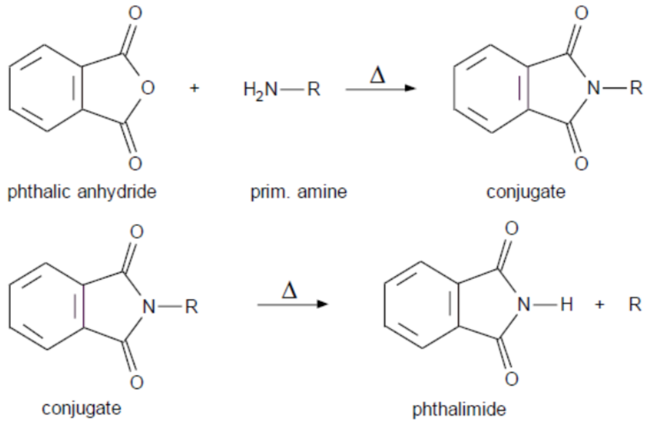
(Jian Wang et al., 2018)

講者在近兩年間選用上述不同的偵測模式於 10 種蔬果基質中，以兩種評定參數(暫定陽性篩選(tentative positive screening)及確定性陽性篩選(confirmatory positive screening))，及考量滯留時間、質量準確度及可接受的偽陰性率等三個參考標準下進行試驗，篩選約 850 項化合物。總結如下：超高液相層析儀串聯式軌道阱質譜(UHPLC/ESI Q-Orbitrap) Full MS / DIA 基於精確的質量測量，以非目標資料獲得(non-target data acquisition)的方式進行目標分析(target analysis)，也就是將樣品分析得到的數據與化合物資料庫(Compound Database, CDB)的數據依精確質量數等條件進行比對，以進行篩選，且超高液相層析儀串聯式軌道阱質譜(UHPLC/ESI Q-Orbitrap) Full MS/DIA 和化合物資料庫(CDB)具有很大的潛力，可用作篩選食品中大量農藥的檢測技術（基於風險的監測）和適用常規監測計畫中的高樣品通量（基於計畫的監測，應用較小型的 CDB(即 50 至 200 種農藥)）。

二.重要壁報展示內容

<u>與本組之重要業務相關壁報內容</u>

壁報一：Phthalimide – 福爾培(Folpet)的代謝物或不可避免的人工製品。由 Labor Friedle GmbH, Von-Heyden-Str. 11, 93105 Tegernheim (Regensburg), Germany 的 Nitsopoulos A.等人發表。該篇壁報同時也是分析方法之開發及應用領域之得獎壁報。根據 2016 年 1 月 18 日的歐盟 2016/156 號法規，對殺菌劑福爾培(Folpet)的殘留進行了新的定義，並於 2016 年 8 月 26 日生效：福爾培(Folpet)和 Phthalimide（簡稱 PI）的殘留量總和，表示為福爾培。福爾培屬於 phthalimide 類之殺菌劑，在較高溫度下迅速衰敗產生 PI，例如在氣相層析儀之注射器的高溫環境中。在植物中，PI 亦為福爾培之主要代謝產物。在乾燥產品中的常檢出高濃度的 PI，但卻沒有福爾培存在的任何跡象。PI 和 phthalic anhydride（簡稱 PSA）之間存在一個有趣的相關性，PSA 是一種普遍存在的環境化學物質，在特定條件下(特別是在高溫下)可以很容易地與初級氨基團反應(如氨基酸，胜肽等)形成 PI，如下圖所示。因此，很明顯的，用於測量福爾培和 PI 的常用分析技術-氣相層析質譜儀注射器之高溫進樣檢測模式，是產生偽陽性 PI 結果的潛在來源。



(Nitsopoulos A. et al., 2018)

檢測結果中的 PI 可能有四個來源：1.福爾培或益滅松(phosmet)的代謝產物、2.氣相層析儀在注射時福爾培的反應產物、3.由氣相層析儀注射器中的普遍存在的 PSA 與基質中的初級氨基團化合物的熱反應產生的人工製品或 4. 乾燥產品(如茶、乾燥香料等)製作過程中誘導產生的物質。作者發現可使用液相層析串聯式質譜儀技術和大氣壓化學電離（APCI）取代氣相層析串聯式質譜儀，在分析過程中可以排除 PI 的形成，但卻不可能將來自乾燥產品加工過程中衍生的 PI 與福爾培代謝物做區分。因此，福爾培的新殘留定義仍是一個問題，特別是在有機產品的農藥殘留檢測上可能造成誤判。

壁報二：應用於農藥標準品工作液混合劑之全自動稀釋工作站。由 Institut Kirchhoff Berlin GmbH, Oudenarder Straße 16, 13347 Berlin/D 及 Axel

Semrau GmbH & Co. KG, Stefansbecke 42, 45549 Sprockhövel 的 Rothmeier, S.等人發表，該篇壁報屬於其他領域，內容指出 Axel-Semrau®和 Institut Kirchhoff Berlin GmbH 兩家機構基於 CTC Analytics AG 的 CHRONECT Robotic 的 XYZ 機器人架構下，開發了一種全自動稀釋工作站，能夠在依據重量量測的控制下從標準品儲備液中配製出工作液混合劑。該程序符合 SANTE/11813/2017 的要求，所有配製相關資訊，如有效日期，批次，純度和最終分析物濃度均可輕鬆獲得。測試效能指出，具有 400 種分析物的標準品混合劑溶液可在 24 小時內自動混合(同樣的配製及文件製備的工作量若交由實驗室助理將需要 3-4 個工作天) ，其工作站之作業模式如下圖所示：

Dilution workstation

Fig.1: Overview about all stock and working standards from Database

Fig.2: Working standard mixture created by database, automatically prepared, gravimetrically corrected concentrations for each mixture in the database

Unique identification code for each standard controlled by barcode reader

Gravimetric control of solutions and pipetted volumes by 5 digit balance

Fig.3: PAL3 System

Peltier stack module: 12 racks with 54 positions: conditions between 4°C and 40°C

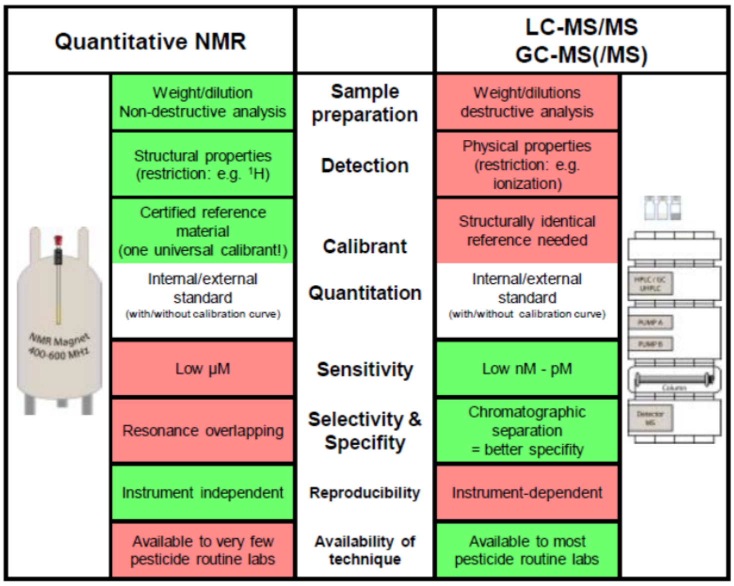
Vortex Mixer Module tool → remixing

Capping and decapping tool → no replacement of septum after piercing necessary

Pipetting tool for using disposable pipette tips → no risk of carryover

(Rothmeier S. et al., 2018)

壁報三：定量核磁共振(qNMR)對農藥標準品儲備液的長期穩定性監測結果。由 Chemischen und Veterinäruntersuchungsämter (CVUA) Stuttgart 的 H. Zipper 等人發表。CVUA 為位於德國南部的巴登-符騰堡州的四個官方食品控制和動物健康相關的實驗室之一。該壁報亦屬於其他領域，農藥殘留分析時的一個重要錯誤來源是分析所使用之標準品的降解。目前，液相層析串聯式質譜儀和氣相層析串聯式質譜儀是用於測試農藥標準品穩定性的最廣泛使用的技術。這些技術對混合物的測試具有敏感性和專一性，但若要符合量測不確定性要求，則需要多次進樣（通常至少 5 次）才能達到符合規定所需的準確度。與質譜儀相比，qNMR 的測量靈敏度相對低，但主要優點是不需要是相同的化合物做為參考標準，而只需要一個與目標分析物無關的通用標準。該技術為非破壞性偵測，使得樣品可以在幾年的時間內保持用於測量。qNMR 與質譜儀之比較如下：



Quantitative NMR		LC-MS/MS GC-MS(/MS)
Weight/dilution Non-destructive analysis	Sample preparation	Weight/dilutions destructive analysis
Structural properties (restriction: e.g. ^{1}H)	Detection	Physical properties (restriction: e.g. ionization)
Certified reference material (one universal calibrant!)	Calibrant	Structurally identical reference needed
Internal/external standard (with/without calibration curve)	Quantitation	Internal/external standard (with/without calibration curve)
Low µM	Sensitivity	Low nM - pM
Resonance overlapping	Selectivity & Specifity	Chromatographic separation = better specifity
Instrument independent	Reproducibility	Instrument-dependent
Available to very few pesticide routine labs	Availability of technique	Available to most pesticide routine labs

(H. Zipper et al., 2018)

選取數支農藥標準品儲備液(濃度為 1 mg/mL)進行分析後，結果顯示：雖然必須考慮一些缺點（例如共振重疊，技術僅適用於極少數農藥檢測之常規實驗室），但結果仍表明 qNMR 是評估純標準品純度和農藥標準品儲備液穩定性的可靠技術。另外該實驗室在特定儲存條件下的儲備液之研究結果將被導入 EURL Data Pool 網站的化合物穩定性資料庫。

叁、心得

本次研討會因經費核定因素，僅能一人出席會議，若要兩人以上出席就必須自行補貼，因研討會內容與本所各重要業務皆甚為相關，若有同伴一起蒐集資訊相信會更為完整，因此稍感可惜。慕尼黑為位於德國南部的古老城市，發展較早，因此街上有古老的建築(如教堂等)及現代化建築並立，形成特別的景緻，人們感覺生活悠閒、步調緩慢，氣候舒適且有便捷的大眾交通系統，在緊湊的研討會行程

結束後，可把握短暫的時間體驗當地生活。由於慕尼黑當地之物價高於台灣，在食等基本生活上的開銷較大。因台灣時間比德國快 6 個小時，常常當地時間凌晨 4-5 點就會醒來，下午 5-6 點時就感覺精神不濟，但在研討會期間仍希望能盡量打起精神吸收資訊，把業務相關發展帶回所內供同仁參考。然而，由於大會演講及壁報涵蓋議題廣泛，在有限的時間內謹能就各重點議題節錄相關資訊。除研討會之主題演講與壁報展示外，大會也安排了一些贊助廠商展示最新的研發成果及儀器設備等。在休息時間及餐敘期間不乏看見與會的各國代表進行溝通與討論，值得注意的是在研討會中較少看到來自亞洲的與會者，多數來自歐洲各國及美加等地。慕尼黑當地的商店(除了餐廳之外)營業時間多只到晚間 6-7 點，因此利用研討會結束後的時間至當地的瑪莉恩廣場等地探訪，體驗當地風情。

本次研討會演講及壁報展示內容與國內食品安全、農藥殘留檢驗等重要議題及與本所之重要業務如風險評估、農藥登記審查及檢測技術開發等皆甚為相關，且非常充實精要，期能將此次研討會所帶回之資訊應用及精進於業務上，達成與國際接軌、與世界並進之目標。

慕尼黑當地街景-1

慕尼黑當地街景-2

研討會會場

研討會入口

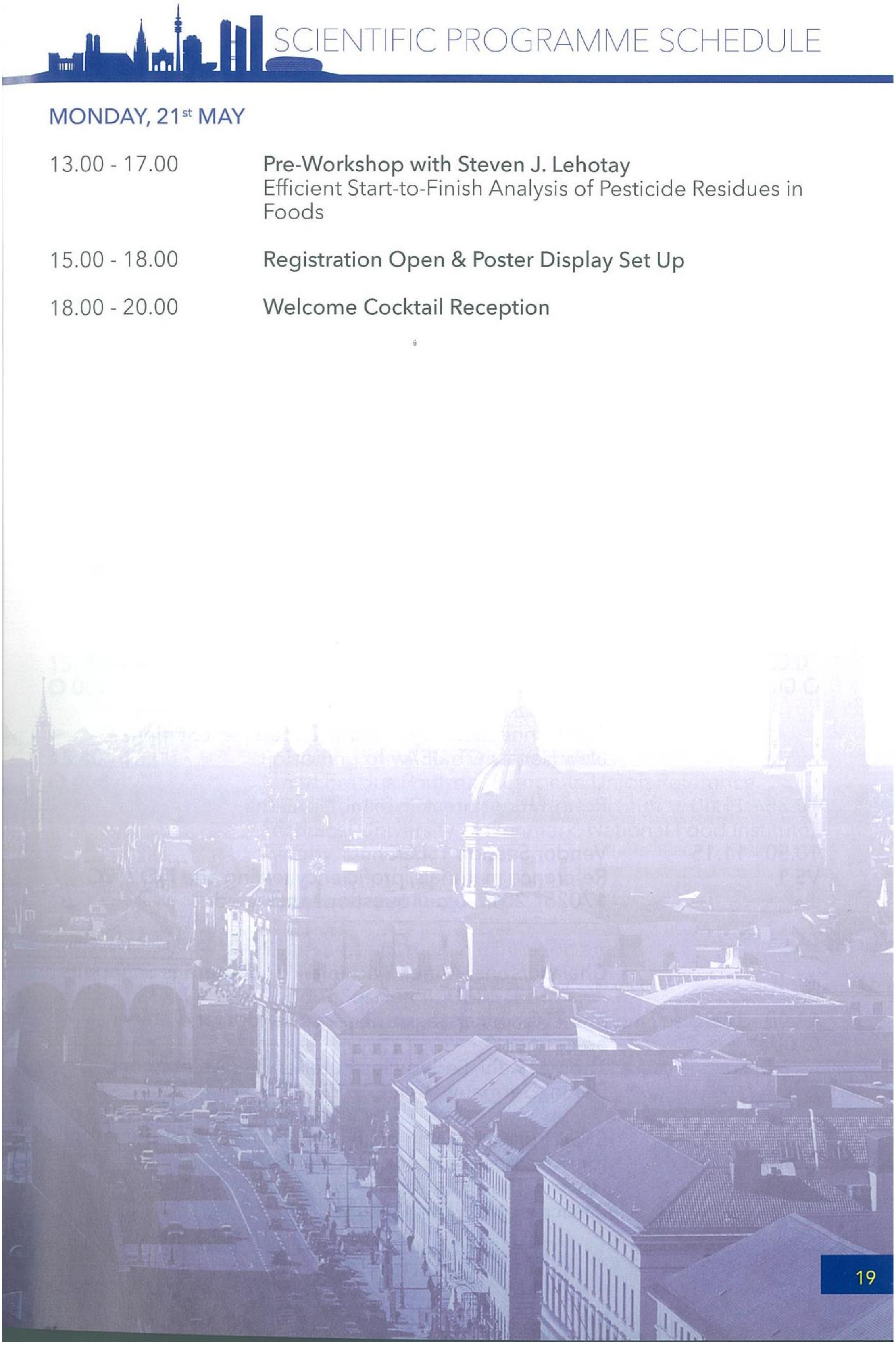
肆、建議

一、 建立自動化農藥殘留檢驗技術：在農藥標準品工作液配製部分，已有廠商開發標準品工作液混合劑之全自動配製工作站(詳壁報分享二) ，在檢驗方法部分，目前廣泛使用之樣品前處理方法為 QuEChERS，於會場中亦看到廠商開發以 QuEChERS 為基礎之萃取及純化管柱搭配自動化工作站，銜接氣相層析串聯式質譜儀及液相層析串聯式質譜儀進行分析，力求將農藥殘留檢測的過程一步步朝向自動化發展。隨著智慧工業的進步與機器人及人工智能的發展，若國內能對相關技術投注更多的心力及成本，並時刻關注國際發展，相信未來農藥殘留檢驗工作能以自動化/半自動化之方式進行，強化檢驗之效率及量能。

二、 建立高通量之目標物篩選分析技術，現行質譜檢驗技術之發展已從氣相層析串聯式質譜儀及液相層析串聯式質譜儀之檢測技術朝向高解析式質譜儀(如飛行式質譜及軌道阱質譜等)，因後者具有較高的解析度，能測得待測物之精準質量，進而與內建之化合物資料庫進行比對，在樣品中未知物的定性分析上具有高精準度及更高通量的特性，不僅僅是針對已知目標物的分析(如現行公告方法之表列藥劑清單)，更能對食品及環境中之潛在汙染物質進行鑑別，為國人的健康安全做更嚴謹的把關。

三、 鼓勵所內同仁多參與歐洲農藥殘留研討會(EPRW)：本次大會討論主題如有機農產品中的農藥殘留檢測控制、風險評估及溝通、芬普尼雞蛋事件等都與國內食品安全議題有高度相關性，雖然地區及國情不同，但於政策面或執行面上所面臨到問題與瓶頸卻是相似的，同仁參與此種大型研討會，除了可接觸與檢驗方法相關的新知外，也能即時掌握國際重點食安議題及相應對策。研討會最後一天大會預告 2020 年的第 13 屆歐洲農藥殘留研討會(EPRW)將於西班牙舉行，希望能多鼓勵由不同領域的同仁與會，以互相討論，一起蒐集更全面之資訊。

附錄一：大會之議程表(摘錄自大會手冊)



SCIENTIFIC PROGRAMME SCHEDULE

MONDAY, 21st MAY

13.00 - 17.00	Pre-Workshop with Steven J. Lehotay Efficient Start-to-Finish Analysis of Pesticide Residues in Foods
15.00 - 18.00	Registration Open & Poster Display Set Up
18.00 - 20.00	Welcome Cocktail Reception

SCIENTIFIC PROGRAMME SCHEDULE

TUESDAY, 22nd MAY

8.30	Registration Open
	Chairpersons: Lutz Alder and Magnus Jezussek
9.00 - 9.10	**Introduction and Welcome** Magnus Jezussek, Bavarian Health and Food Safety Authority, Erlangen, Germany
9.10 - 9.25	**Opening Speech** Magnus Jezussek, Bavarian Health and Food Safety Authority, Erlangen, Germany
9.25 - 9.35	**Greetings and Opening** Andreas Zapf, President of Bavarian Health and Food Safety Authority, Erlangen, Germany
9.35 - 10.05 O 001	**Risk communication with a focus on pesticide residues** Roland Solecki, Federal Institute for Risk Assessment, Berlin, Germany
10.05 - 10.35 O 002	**Bees and Pesticides: Challenges in Measurement and Toxicology** Brian Eitzer, Department of Analytical Chemistry, The Connecticut Agricultural Experiment Station, New Haven, CT, USA
10.35 - 11.40	Refreshment break in exhibition area
10.50 - 11.15 VS 1	**Vendor Session 1: LGC** **Reference materials, proficiency testing and ISO / IEC 17025 : 2017 - your questions answered.**
	Chairpersons: Anneli Widenfalk and Marloes Schepens
11.40 - 12.00 O 003	**The TTC concept as an all purpose tool for dietary risk assessment?** Thomas Kuhl, Federal Institute for Risk Assessment, Berlin, Germany
12.05 - 12.25 O 004	**EFSA PRIMo revision 3: an updated risk assessment tool for risk assessment of pesticide residues** Hermine Reich, European Food Safety Authority - Pesticides Unit, Parma, Italy

12.30 - 12.50 O 005	**Cumulative exposure and risk** Polly Boon, National Institute for Public Health and the Environment (RIVM), Bilthoven, Netherlands
12.50 - 13.05	**Questions and Discussion**
13.05 - 14.50	Lunch break in exhibition area
13.20 - 13.55 VS 2	**Vendor Session 2: Bruker Daltonics** **Minimising false positives in pesticide analysis:** **The power of high resolution mass spectrometry**
14.10 - 14.45 VS 3	**Vendor Session 3: Shimadzu Europa GmbH** **In food we trust – the full solution in pesticide analysis**

Chairpersons: Despo Christodoulou and Antonio Valverde

14.50 - 15.10 O 006	**Analytical strategies in pesticide exposure assessment through human biomonitoring** Hans Mol, RIKILT - Wageningen University & Research, Wageningen, Netherlands
15.15 - 15.35 O 007	**Formulations of plant protection products – formulation techniques and its influence on residue behavior** Christian Sowa, BASF SE, Limburgerhof, Germany
15.40 - 16.00 O 008	**Poisoning of wildlife with pesticides** Mette Erecius Poulsen, European Union Reference Laboratory for Cereals and Feeding Stuff, Technical University of Denmark, National Food Institute, Lyngby, Denmark
16.00 - 16.15	**Questions and Discussion**
16.15 - 17.10	Refreshment break in exhibition area
16.35 - 17.00 VS 4	**Vendor Session 4: GERSTEL** **Automated Sample Handling for efficient Pesticide analysis**

17.10 - 17.55	**POSTER SESSION I**

WEDNESDAY, 23rd MAY

8.30	Registration Open
9.00 - 9.10	Announcements

* * *

	THEMED DAY: "RESIDUES IN ORGANIC PRODUCTS" **Chairpersons: Sonja Masselter and André de Kok**
9.10 - 9.30 O 009	**Dealing with pesticide residues in organic as a process based quality and sustainability scheme** Jan Plagge, IFOAM EU Group / Bioland - Verband für organisch-biologischen Landbau e.V., Mainz, Germany
9.35 - 9.55 O 010	**EU audits on pesticide residue controls in organic production** Jan von Kietzell, Food and Health Audits and Analysis, European Commission, Grange, Dunsany, County Meath, Ireland
10.00 - 10.20 O 011	**Analytical challenges for the evaluation of pesticide residues in organic crops** Amadeo Fernandez-Alba, European Union Reference Laboratory for Pesticide Residues in Fruit and Vegetables, Universidad de Almería-Edificio de Química, Almeria, Spain
10.20 - 10.35	**Questions and Discussion**
10.35 - 11.40	Refreshment break in exhibition area
10.50 - 11.15 VS 5	**Vendor Session 5: AGILENT** **New Tools for Pesticide and Environmental Pollutant Analysis by GC-Triple Quad and GC/Q-TOF Mass Spectrometry**

* * *

	Chairpersons: Sonja Masselter and André de Kok
11.40 - 12.00 O 012	**The cultivation of organic salads: market opportunities and growing difficulties** Giovanni Roncareggi, La Linea Verde Società Agricola SpA, Direzione Qualità, Manerbio, Italy
12.05 - 12.25 O 013	**Challenges in production of organic baby food** Norbert Fuchsbauer, HiPP-Werk Georg Hipp OHG, Pfaffenhofen, Germany

12.30 - 12.50 O 014	**Endogenous formation of fosetyl in wine: conditions of vinification, refinement and role of yeast** Loris Tonidandel, Edmund Mach foundation, San Michele all'Adige, Italy
12.50 - 13.05	**Questions and Discussion**
13.05 - 14.50	Lunch break in exhibition area
13.20 - 13.55 VS 6	Vendor Session 6: Waters S.A.S. **Determination of pesticide residues in fruit and vegetable commodities by GC-MS/MS**
14.10 - 14.45 VS 7	Vendor Session 7: THERMO FISHER SCIENTIFIC **New Innovative Triple Quadrupole MS Technologies for Unstoppable Performance and Confident Quantitation of Pesticide Residues in Foods**

	Chairpersons: Sonja Masselter and André de Kok
14.50 - 15.10 O 015	**Official Control of organic products in the Netherlands - Roles and results** Henk A. van der Schee, Netherlands Food and Consumer Product Safety Authority (NVWA), Utrecht, Netherlands
15.15 - 15.35 O 016	**Illegal practices in organic farming: can occurrence of pesticide metabolites detected in crops provide the evidence?** Jana Hajslova, University of Chemistry and Technology, Prague, Czech Republic
15.40 - 16.00 O 017	**Control of Organic Food in Switzerland** Andreas Schürmann, Kantonales Labor Zurich, Zurich, Switzerland
16.00 - 16.15	**Questions and Discussion**
16.15 - 17.10	Refreshment break in exhibition area
16.35 - 17.00 VS 8	Vendor Session 8: Axel Semrau GmbH & Co. KG **New automated methods for sample preparation and detection of pesticides in food**

17.10 - 17.55	**POSTER SESSION II**

20.00	**GALA DINNER** Ticket required

THURSDAY, 24th MAY

8.30	Registration Open
9.00 - 9.10	Announcements

	Chairpersons: Lutz Alder and Magnus Jezussek
9.10 - 9.30 O 018	**Overview of pesticide-relevant compounds originating from sources other than pesticide use** Michelangelo Anastassiades, European Union Reference Laboratory for Single Residue Methods, CVUA Stuttgart, Fellbach, Germany
9.35 - 9.45 O 019	**Selective analysis of glyphosate and other polar organophosporous compounds in foods of plant origin using on-line ligand-exchange SPE-HPLC-MS/MS** Eric Eichhorn, CVUA Stuttgart, Fellbach, Germany
9.45 - 9.55 O 020	**Evaluation of supercritical fluid chromatography coupled to tandem mass spectrometry for pesticide residues in food** Maria Murcia Morales, Universidad de Almería, Almería, Spain
10.00 - 10.20 O 021	**Pesticide residue from grape to wine: monitoring during winemaking by liquid chromatography-tandem mass spectrometry** Céline Franc, Univ. Bordeaux, ISVV, Villenave d'Ornon Cedex, France
10.20 - 10.35	Questions and Discussion
10.35 - 11.40	Refreshment break in exhibition area
10.50 - 11.15 VS 9	Vendor Session 9: THERMO FISHER SCIENTIFIC Analysis of Polar Ionic Pesticides using High Performance Ion Chromatography coupled with High Resolution Accurate Mass Spectrometry

	Chairpersons: Finbarr O'Regan and Ionara Pizzutti
11.40 - 12.00 O 022	**Regulations for MRL and risk on "Other Foods"** Carmen Tiu, Dow AgroSciences LLC, Indianapolis, USA

12.05 - 12.25 O 023	**The Fipronil case - consequences for monitoring strategies** Ralf Lippold, European Union Reference Laboratory for Pesticides in Food of Animal Origin, CVUA Freiburg, Freiburg, Germany
12.30 - 12.50 O 024	**Phtalimide. A metabolite of Folpet or an artefact produced in the GC from other sources?** Andreas Hentschel, Institut Kirchhoff Berlin GmbH, Berlin, Germany
12.50 - 13.05	**Questions and Discussion**
13.05 - 14.50	Lunch break in exhibition area
13.20 - 13.55 VS 10	**Vendor Session 10: SCIEX** **The use of a Q-TOF in a contract laboratory for routine Pesticide Analysis in food and feed**
14.10 - 14.45	**Vendor Session 11: AGILENT** **Further improvements in pesticide residue analysis in food by applying GC-Triple Quadrupole MS/MS technologies**

Chairpersons: Patrizia Pelosi and Sherry Garris

14.50 - 15.10 O 025	**Resolved: Sample processing should be assessed during method validation and routine quality control** Steven J. Lehotay, USDA Agricultural Research Service, Eastern Regional Research Center, Wyndmoor, United States
15.15 - 15.35 O 026	**Assessment of the effectiveness and benefits of different calibration techniques for quantifying pesticide residues** Sadat Nawaz, Fera Science Limited, York, United Kingdom
15.40 - 15.50 O 027	**Comparison of different cleanup procedures and method validation for pesticides in food of animal origin using GC-MS/MS** Silja Laufer, CVUA Freiburg, Freiburg, Germany
15.50 - 16.00 O 028	**Studies on the pesticide residues levels in soybean sprouts: method development and pesticides dynamics** Florencia Jesús, Universidad de la República, Paysandú, Uruguay
16.00 - 16.15	**Questions and Discussion**

16.15 - 17.10	Refreshment break in exhibition area
16.35 - 17.00 VS 12	**Vendor Session 12: Merck** Sample Preparation for Fatty & Complex Food Matrices - New tools for SPE & QuEChERS
17.10 - 17.55	POSTER SESSION III

FRIDAY, 25th MAY

8.30	Registration Open
9.00 - 9.10	Announcements
	Chairpersons: Susanne Ekroth and Steve Lehotay
9.10 - 9.30 O 029	**Use of LC and GC-Orbitrap for the quantitation of pesticide residues in fruit and vegetables** Jim Garvey, The Department of Agriculture, Food and the Marine, Celbridge, Ireland
9.35 - 9.55 O 030	**The design of Q-Orbitrap data independent acquisition experiments for target screening ~850 pesticide residues in fruits and vegetables based on a compound database** Jian Wang, Canadian Food Inspection Agency, Calgary, Canada
10.00 - 10.20 O 031	**Can LC-HRMS (Q-TOF) replace LC-MS Triple quad mass spectrometers?** André de Kok, NVWA – Netherlands Food and Consumer Product Safety Authority, Wageningen, Netherlands
10.20 - 10.35	Questions and Discussion
10.35 - 11.40	Refreshment break in exhibition area
11.40 - 13.00	Poster awards & closing remarks
13.00 - 14.00	Lunch break in exhibition area
14.00 - 16.00	Poster demounting

附錄二：心得分享簡報內容

參加第12屆歐洲農藥殘留研討會報告

服務機關：行政院農業委員會農業藥物毒物試驗所
出國人員：王熙宇 技佐
派赴國家：德國(慕尼黑)
出國日期：107年5月19日至5月29日

目的:

歐洲農藥殘留研討會（EPRW）每兩年由一個不同的歐洲成員國舉辦，介紹和討論食品和飲料中農藥殘留領域的最新概念和發展。第12屆研討會於德國慕尼黑舉行，其係由巴伐利亞健康和食品安全管理局（Bavarian Health and Food Safety Authority）主辦，與會人數計超過500人。主要討論之四大議題如下：

（一）風險評估及溝通
（二）有機產品中的農藥殘留
（三）農藥殘留之監控
（四）農藥殘留之分析方法

目的:

本次研討會涵蓋近期關注之議題，並邀請歐洲及美加地區之風險評估及農藥殘留相關領域專家蒞臨演講，提供與會世界各地之政府單位、商業實驗室、監管機構、食品製造商及農藥製造商等單位代表交流研討之平台，並將演講及壁報投稿摘要集結成冊，提供與會人員參考。

總計約有160篇之壁報發表，內容分為以下四個領域：

（一）分析方法之開發及應用

（二）監管議題和監控

（三）毒理學及攝食量評估

（四）其他主題等

另有耗材或儀器供應商等舉辦新型儀器及分析技術之展示會，亦有研發技術相關之壁報論文發表計約40篇。

本所參與發表:

會場設有壁報區，提供各國與會代表發表研究成果，本次參與研討會除瞭解歐洲地區近期於食品安全及農藥殘留領域關注之議題及相關分析技術之發展外，本所亦參與發表: 承接之衛福部委辦計畫成果 -「開發利用氣相層析串聯質譜儀及液相層析串聯質譜儀於動物產品中分析多重農藥殘留方法」。

2/27/2018 12th European Pesticide Residue Workshop - Abstract Submission System

Abstract Preview - Step 3/4

- print version -

Topic: PD Development and Application of Analytical Methods

Title: Development of a method for analysis of the multi-pesticide residues in animal products using LC/MS/MS and GC/MS/MS.

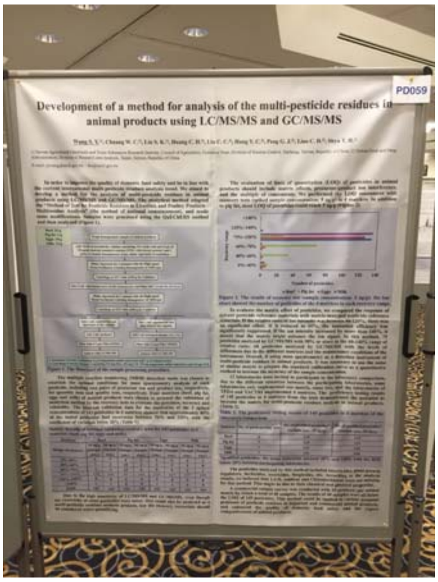
Author(s): Wang S.Y.[1], Chuang W.C.[1], Lin S.K.[1], Huang C.H.[1], Liu C.C.[2], Hung Y.C.[2], Peng G.J.[2], Liao C.D.[2], Shyu T.H.[1]

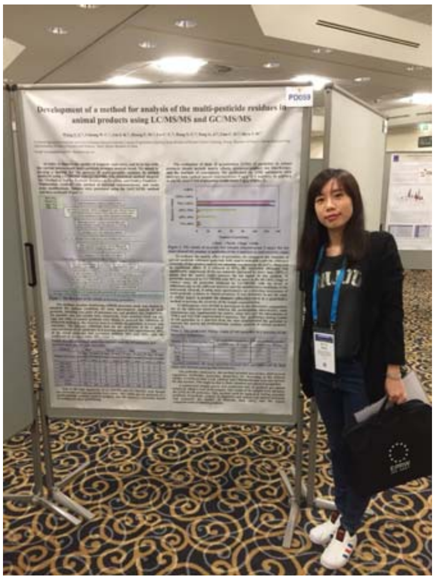
Institute(s): *[1]Taiwan Agricultural Chemicals and Toxic Substances Research Institute, Council of Agriculture, Executive Yuan, Division of Residue Control, Taichung, Taiwan, Republic of China, [2]Taiwan Food and Drug Administration, Division of Research and Analysis, Taipei, Taiwan, Republic of China*

Text: In order to improve the quality of domestic food safety and be in line with the current international multi-pesticide residues analysis trend. We aimed to develop a method for the analysis of multi-pesticide residues in animal products using LC/MS/MS and GC/MS/MS. The validation of analytical method included the optimal conditions for the instruments, sample recovery, data reproducibility, reliability and accuracy. The analytical method adopted the "Method of Test for Pesticide Residues in Livestock and Poultry Products - Multiresidue Analysis" (the method of national announcement), and made some modifications. Samples were processed using the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) method and then analyzed. The multiple reaction monitoring (MRM) detection mode was chosen to establish the optimal conditions for mass spectrometry analysis of each pesticide, including two pairs of precursor ion and product ion, respectively, for quantity ions and quality ions, respectively. For the internal validation, we analyzed the recoveries of two concentrations of 143 pesticides in 4 matrices including beef, milk, eggs and pig fat. In both concentrations of recovery experiments, the recoveries of Chinomethionat, 2,4-D and Amitraz in animal products were not between 70% and 120%. This might be due to their chemical and physical properties. Approximately 80% of the tested pesticides resulted in recoveries between 70% and 120% with the coefficient of variation below 20%. Due to the high sensitivity of LC/MS/MS and GC/MS/MS, even though the recoveries of some pesticides were lower, they could also be analyzed as a multi-pesticide residues analysis projects, but the recovery correction should be considered when quantifying. The evaluation of limit of quantitation (LOQ) of pesticides in animal products should include matrix effects, precursor/product ion interference, and the multiple of concentrate. In addition to pig fat, most LOQ of pesticides could reach 0.005 ppm. 12 laboratories were invited to participate in the laboratory comparison, and the proficiency testing result of 145 pesticides in 4 matrices from the tests demonstrated the potential to increase the matrix for multi-pesticide residues analysis in animal products. A commercial sample survey was conducted with 10 products per animal matrix by which a total of 40 samples. The results of 40 samples were all below the LOQ of 145 pesticides. This method could be applied to various potential problems of pesticide residues in imported and commercial animal products, and enhanced the quality of domestic food safety and the export competitiveness of animal products.

Preferred Presentation Type: Poster Presentation

Conference: 12th European Pesticide Residue Workshop · Abstract: A-952-0002-00063 · **Status: Submitted**



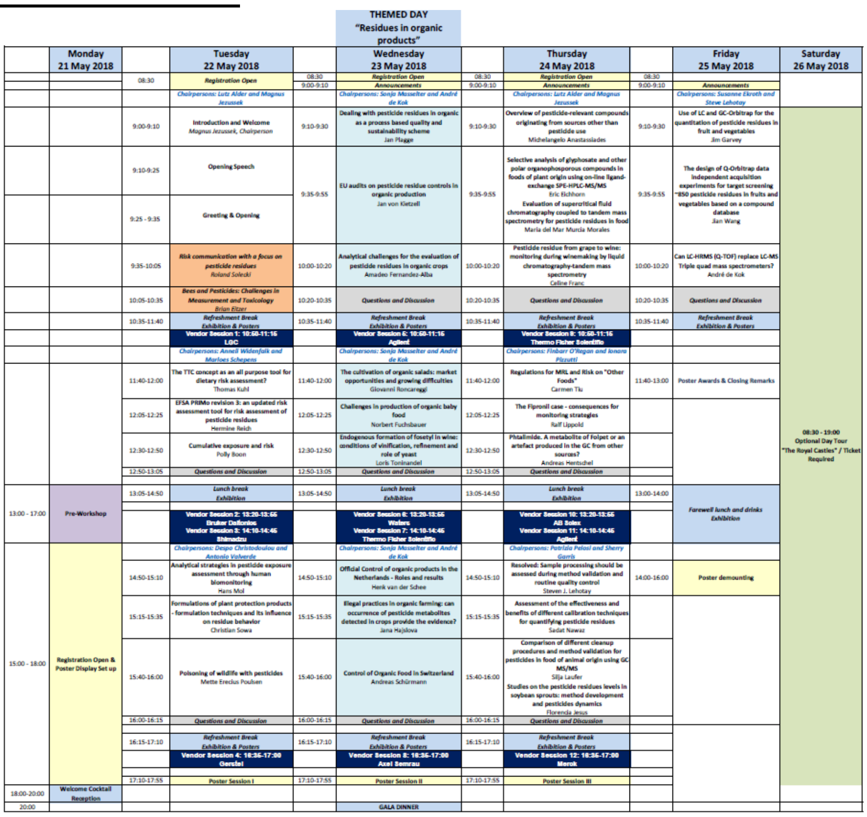


過程-研討會舉辦地點及提供資料:

地點:Holiday Inn Munich City Centre。

(Picture taken from Holiday Inn Homepage)

過程-大會提供之簡要行程表:



					THEMED DAY "Residues in organic products"					
	Monday 21 May 2018		Tuesday 22 May 2018		Wednesday 23 May 2018		Thursday 24 May 2018		Friday 25 May 2018	Saturday 26 May 2018
		08:30	*Registration Open*	08:30	*Registration Open*	08:30	*Registration Open*	08:30		
				9:00-9:10	*Announcements*	9:00-9:10	*Announcements*	9:00-9:10	*Announcements*	
			Chairpersons: Lutz Alder and Magnus Jezussek		*Chairpersons: Sonja Masselter and André de Kok*		*Chairpersons: Lutz Alder and Magnus Jezussek*		*Chairpersons: Susanne Ekroth and Steve Lehotay*	
		9:00-9:10	Introduction and Welcome *Magnus Jezussek, Chairperson*	9:10-9:30	Dealing with pesticide residues in organic as a process based quality and sustainability scheme Jan Plagge	9:10-9:30	Overview of pesticide-relevant compounds originating from sources other than pesticide use Michelangelo Anastassiades	9:10-9:30	Use of LC and GC-Orbitrap for the quantitation of pesticide residues in fruit and vegetables Jim Garvey	08:30 - 19:00 Optional Day Tour "The Royal Castles" / Ticket Required
		9:10-9:25	Opening Speech	9:35-9:55	EU audits on pesticide residue controls in organic production Jan von Kietzell	9:35-9:55	Selective analysis of glyphosate and other polar organophosporous compounds in foods of plant origin using on-line ligand-exchange SPE-HPLC-MS/MS Eric Eichhorn Evaluation of supercritical fluid chromatography coupled to tandem mass spectrometry for pesticide residues in food Maria del Mar Murcia Morales	9:35-9:55	The design of Q-Orbitrap data independent acquisition experiments for target screening ~850 pesticide residues in fruits and vegetables based on a compound database Jian Wang	
		9:25 - 9:35	Greeting & Opening							
		9:35-10:05	*Risk communication with a focus on pesticide residues* *Roland Solecki*	10:00-10:20	Analytical challenges for the evaluation of pesticide residues in organic crops Amadeo Fernandez-Alba	10:00-10:20	Pesticide residue from grape to wine: monitoring during winemaking by liquid chromatography-tandem mass spectrometry Celine Franc	10:00-10:20	Can LC-HRMS (Q-TOF) replace LC-MS Triple quad mass spectrometers? André de Kok	
		10:05-10:35	*Bees and Pesticides: Challenges in Measurement and Toxicology* *Brian Eitzer*	10:20-10:35	*Questions and Discussion*	10:20-10:35	*Questions and Discussion*	10:20-10:35	*Questions and Discussion*	
		10:35-11:40	*Refreshment Break* *Exhibition & Posters*	10:35-11:40	*Refreshment Break* *Exhibition & Posters*	10:35-11:40	*Refreshment Break* *Exhibition & Posters*	10:35-11:40	*Refreshment Break* *Exhibition & Posters*	
			Vendor Session 1: 10:50-11:15 **LGC**		**Vendor Session 5: 10:50-11:15** **Agilent**		**Vendor Session 9: 10:50-11:15** **Thermo Fisher Scientific**			
			Chairpersons: Anneli Widenfalk and Marloes Schepens		*Chairpersons: Sonja Masselter and André de Kok*		*Chairpersons: Finbarr O'Regan and Ionara Pizzutti*			
		11:40-12:00	The TTC concept as an all purpose tool for dietary risk assessment? Thomas Kuhl	11:40-12:00	The cultivation of organic salads: market opportunities and growing difficulties Giovanni Roncareggi	11:40-12:00	Regulations for MRL and Risk on "Other Foods" Carmen Tiu	11:40-13:00	Poster Awards & Closing Remarks	
		12:05-12:25	EFSA PRIMo revision 3: an updated risk assessment tool for risk assessment of pesticide residues Hermine Reich	12:05-12:25	Challenges in production of organic baby food Norbert Fuchsbauer	12:05-12:25	The Fipronil case - consequences for monitoring strategies Ralf Lippold			
		12:30-12:50	Cumulative exposure and risk Polly Boon	12:30-12:50	Endogenous formation of fosetyl in wine: conditions of vinification, refinement and role of yeast Loris Toninandel	12:30-12:50	Phtalimide. A metabolite of Folpet or an artefact produced in the GC from other sources? Andreas Hentschel			
		12:50-13:05	*Questions and Discussion*	12:50-13:05	*Questions and Discussion*	12:50-13:05	*Questions and Discussion*			
13:00 - 17:00	Pre-Workshop	13:05-14:50	*Lunch break* *Exhibition*	13:05-14:50	*Lunch break* *Exhibition*	13:05-14:50	*Lunch break* *Exhibition*	13:00-14:00	*Farewell lunch and drinks* *Exhibition*	
			Vendor Session 2: 13:20-13:55 **Bruker Daltonics** **Vendor Session 3: 14:10-14:45** **Shimadzu**		**Vendor Session 6: 13:20-13:55** **Waters** **Vendor Session 7: 14:10-14:45** **Thermo Fisher Scientific**		**Vendor Session 10: 13:20-13:55** **AB Sciex** **Vendor Session 11: 14:10-14:45** **Agilent**			
15:00 - 18:00	Registration Open & Poster Display Set up		*Chairpersons: Despo Christodoulou and Antonio Valverde*		*Chairpersons: Sonja Masselter and André de Kok*		*Chairpersons: Patrizia Pelosi and Sherry Garris*			
		14:50-15:10	Analytical strategies in pesticide exposure assessment through human biomonitoring Hans Mol	14:50-15:10	Official Control of organic products in the Netherlands - Roles and results Henk van der Schee	14:50-15:10	Resolved: Sample processing should be assessed during method validation and routine quality control Steven J. Lehotay	14:00-16:00	Poster demounting	
		15:15-15:35	Formulations of plant protection products - formulation techniques and its influence on residue behavior Christian Sowa	15:15-15:35	Illegal practices in organic farming: can occurrence of pesticide metabolites detected in crops provide the evidence? Jana Hajslova	15:15-15:35	Assessment of the effectiveness and benefits of different calibration techniques for quantifying pesticide residues Sadat Nawaz			
		15:40-16:00	Poisoning of wildlife with pesticides Mette Erecius Poulsen	15:40-16:00	Control of Organic Food in Switzerland Andreas Schürmann	15:40-16:00	Comparison of different cleanup procedures and method validation for pesticides in food of animal origin using GC MS/MS Silja Laufer Studies on the pesticide residues levels in soybean sprouts: method development and pesticides dynamics Florencia Jesus			
		16:00-16:15	*Questions and Discussion*	16:00-16:15	*Questions and Discussion*	16:00-16:15	*Questions and Discussion*			
		16:15-17:10	*Refreshment Break* *Exhibition & Posters*	16:15-17:10	*Refreshment Break* *Exhibition & Posters*	16:15-17:10	*Refreshment Break* *Exhibition & Posters*			
			Vendor Session 4: 16:35-17:00 **Gerstel**		**Vendor Session 8: 16:35-17:00** **Axel Semrau**		**Vendor Session 12: 16:35-17:00** **Merck**			
		17:10-17:55	Poster Session I	17:10-17:55	Poster Session II	17:10-17:55	Poster Session III			
18:00-20:00	Welcome Cocktail Reception									
20:00					GALA DINNER					

臺灣與德國時差約6小時

過程-大會提供摺頁:

由於大會演講及壁報涵蓋風險評估、農藥殘留監控、有機農產品農藥殘留檢驗及農藥殘留分析方法開發等，討論議題眾多， 謹就各重點議題節錄與本組業務較為相關之重要內容及國際發展趨勢進行分享。

EPRW
2018 · MUNICH

12th EUROPEAN PESTICIDE RESIDUE WORKSHOP
Pesticides in Food and Drink
22nd – 25th May 2018 | Munich, Germany

POCKET PROGRAMME

MONDAY, 21st MAY

13.00 - 17.00	Pre-Workshop with Steven J. Lehotay Efficient Start-to-Finish Analysis of Pesticide Residues in Foods
15.00 - 18.00	Registration Open & Poster Display Set Up
18.00 - 20.00	Welcome Cocktail Reception

TUESDAY, 22nd MAY

8.30	Registration Open
	Chairpersons: Lutz Alder and Magnus Jezussek
9.00 - 9.10	Introduction and Welcome Magnus Jezussek
9.10 - 9.25	Opening Speech Magnus Jezussek
9.25 - 9.35	Greetings and Opening Andreas Zapf
9.35 - 10.05 O 001	Risk communication with a focus on pesticide residues Roland Solecki
10.05 - 10.35 O 002	Bees and Pesticides: Challenges in Measurement and Toxicology Brian Eitzer
10.35 - 11.40	Refreshment break in exhibition area
10.50 - 11.15 VS 1	Vendor Session 1: LGC Reference materials, proficiency testing and ISO / IEC 17025 : 2017 - your questions answered.
	Chairpersons: Anneli Widenfalk and Marloes Schepens
11.40 - 12.00 O 003	The TTC concept as an all purpose tool for dietary risk assessment? Thomas Kuhl
12.05 - 12.25 O 004	EFSA PRIMo revision 3: an updated risk assessment tool for risk assessment of pesticide residues Hermine Reich
12.30 - 12.50 O 005	Cumulative exposure and risk Polly Boon
12.50 - 13.05	Questions and Discussion
13.05 - 14.50	Lunch break in exhibition area
13.20 - 13.55 VS 2	Vendor Session 2: Bruker Daltonics Minimising false positives in pesticide analysis: The power of high resolution mass spectrometry
14.10 - 14.45 VS 3	Vendor Session 3: Shimadzu Europa GmbH In food we trust - the full solution in pesticide analysis
	Chairpersons: Despo Christodoulou and Antonio Valverde
14.50 - 15.10 O 006	Analytical strategies in pesticide exposure assessment through human biomonitoring Hans Mol
15.15 - 15.35 O 007	Formulations of plant protection products - formulation techniques and its influence on residue behavior Christian Sowa
15.40 - 16.00 O 008	Poisoning of wildlife with pesticides Mette Erecius Poulsen
16.00 - 16.15	Questions and Discussion
16.15 - 17.10	Refreshment break in exhibition area
16.35 - 17.00 VS 4	Vendor Session 4: GERSTEL Automated Sample Handling for efficient Pesticide analysis
17.10 - 17.55	POSTER SESSION I

WEDNESDAY, 23rd MAY

8.30	Registration Open
9.00 - 9.10	Announcements
	THEMED DAY: "RESIDUES IN ORGANIC PRODUCTS" Chairpersons: Sonja Masselter and André de Kok
9.10 - 9.30 O 009	Dealing with pesticide residues in organic as a process based quality and sustainability scheme Jan Plagge
9.35 - 9.55 O 010	EU audits on pesticide residue controls in organic production Jan von Kietzell
10.00 - 10.20 O 011	Analytical challenges for the evaluation of pesticide residues in organic crops Amadeo Fernandez-Alba

1.

10.20 - 10.35	Questions and Discussion
10.35 - 11.40	Refreshment break in exhibition area
10.50 - 11.15 VS 5	Vendor Session 5: AGILENT New Tools for Pesticide and Environmental Pollutant Analysis by GC-Triple Quad and GC/Q-TOF Mass Spectrometry
	Chairpersons: Sonja Masselter and André de Kok
11.40 - 12.00 O 012	The cultivation of organic salads: market opportunities and growing difficulties Giovanni Roncareggi
12.05 - 12.25 O 013	Challenges in production of organic baby food Norbert Fuchsbauer
12.30 - 12.50 O 014	Endogenous formation of fosetyl in wine: conditions of vinification, refinement and role of yeast Loris Tonidandel
12.50 - 13.05	Questions and Discussion
13.05 - 14.50	Lunch break in exhibition area
13.20 - 13.55 VS 6	Vendor Session 6: Waters S.A.S. Determination of pesticide residues in fruit and vegetable commodities by GC-MS/MS
14.10 - 14.45 VS 7	Vendor Session 7: THERMO FISHER SCIENTIFIC New Innovative Triple Quadrupole MS Technologies for Unstoppable Performance and Confident Quantitation of Pesticide Residues in Foods
	Chairpersons: Sonja Masselter and André de Kok
14.50 - 15.10 O 015	Official Control of organic products in the Netherlands - Roles and results Henk A. van der Schee
15.15 - 15.35 O 016	Illegal practices in organic farming: can occurrence of pesticide metabolites detected in crops provide the evidence? Jana Hajslova
15.40 - 16.00 O 017	Control of Organic Food in Switzerland Andreas Schürmann
16.00 - 16.15	Questions and Discussion
16.15 - 17.10	Refreshment break in exhibition area
16.35 - 17.00 VS 8	Vendor Session 8: Axel Semrau GmbH & Co. KG New automated methods for sample preparation and detection of pesticides in food
17.10 - 17.55	POSTER SESSION II
20.00	GALA DINNER (Ticket required)

THURSDAY, 24th MAY

8.30	Registration Open
9.00 - 9.10	Announcements
	Chairpersons: Lutz Alder and Magnus Jezussek
9.10 - 9.30 O 018	Overview of pesticide-relevant compounds originating from sources other than pesticide use Michelangelo Anastassiades
9.35 - 9.45 O 019	Selective analysis of glyphosate and other polar organophosporous compounds in foods of plant origin using on-line ligand-exchange SPE-HPLC-MS/MS Eric Eichhorn
9.45 - 9.55 O 020	Evaluation of supercritical fluid chromatography coupled to tandem mass spectrometry for pesticide residues in food Maria Murcia Morales
10.00 - 10.20 O 021	Pesticide residue from grape to wine: monitoring during winemaking by liquid chromatography-tandem mass spectrometry Céline Franc
10.20 - 10.35	Questions and Discussion
10.35 - 11.40	Refreshment break in exhibition area
10.50 - 11.15 VS 9	Vendor Session 9: THERMO FISHER SCIENTIFIC Analysis of Polar Ionic Pesticides using High Performance Ion Chromatography coupled with High Resolution Accurate Mass Spectrometry
	Chairpersons: Finbarr O'Regan and Ionara Pizzutti
11.40 - 12.00 O 022	Regulations for MRL and risk on "Other Foods" Carmen Ti
12.05 - 12.25 O 023	The Fipronil case - consequences for monitoring strategies Ralf Lippold

2.

12.30 - 12.50 O 024	Phtalimide. A metabolite of Folpet or an artefact produced in the GC from other sources? Andreas Hentschel
12.50 - 13.05	Questions and Discussion
13.05 - 14.50	Lunch break in exhibition area
13.20 - 13.55 VS 10	Vendor Session 10: SCIEX The use of a Q-TOF in a contract laboratory for routine Pesticide Analysis in food and feed
14.10 - 14.45	Vendor Session 11: AGILENT Further improvements in pesticide residue analysis in food by applying GC-Triple Quadrupole MS/MS technologies
	Chairpersons: Patrizia Pelosi and Sherry Garris
14.50 - 15.10 O 025	Resolved: Sample processing should be assessed during method validation and routine quality control Steven J. Lehotay
15.15 - 15.35 O 026	Assessment of the effectiveness and benefits of different calibration techniques for quantifying pesticide residues Sadat Nawaz
15.40 - 15.50 O 027	Comparison of different cleanup procedures and method validation for pesticides in food of animal origin using GC-MS/MS Silja Laufer
15.50 - 16.00 O 028	Studies on the pesticide residues levels in soybean sprouts: method development and pesticides dynamics Florencia Jesús
16.00 - 16.15	Questions and Discussion
16.15 - 17.10	Refreshment break in exhibition area
16.35 - 17.00 VS 12	Vendor Session 12: Merck Sample Preparation for Fatty & Complex Food Matrices - New tools for SPE & QuEChERS
17.10 - 17.55	POSTER SESSION III

FRIDAY, 25th MAY

8.30	Registration Open
9.00 - 9.10	Announcements
	Chairpersons: Susanne Ekroth and Steve Lehotay
9.10 - 9.30 O 029	Use of LC and GC-Orbitrap for the quantitation of pesticide residues in fruit and vegetables Jim Garvey
9.35 - 9.55 O 030	The design of Q-Orbitrap data independent acquisition experiments for target screening ~850 pesticide residues in fruits and vegetables based on a compound database Jian Wang
10.00 - 10.20 O 031	Can LC-HRMS (Q-TOF) replace LC-MS Triple quad mass spectrometers? André de Kok
10.20 - 10.35	Questions and Discussion
10.35 - 11.40	Refreshment break in exhibition area
11.40 - 13.00	Poster awards & closing remarks
13.00 - 14.00	Lunch break in exhibition area
14.00 - 16.00	Poster demounting

SATURDAY, 26th MAY

8.30 - 19.00	Optional Day Tour "The Royal Castles" Departing Holiday Inn Hotel at 8:30 Ticket required

3.

EPRW
2018 · MUNICH

12th EUROPEAN PESTICIDE RESIDUE WORKSHOP
22nd – 25th May 2018 · MUNICH · GERMANY

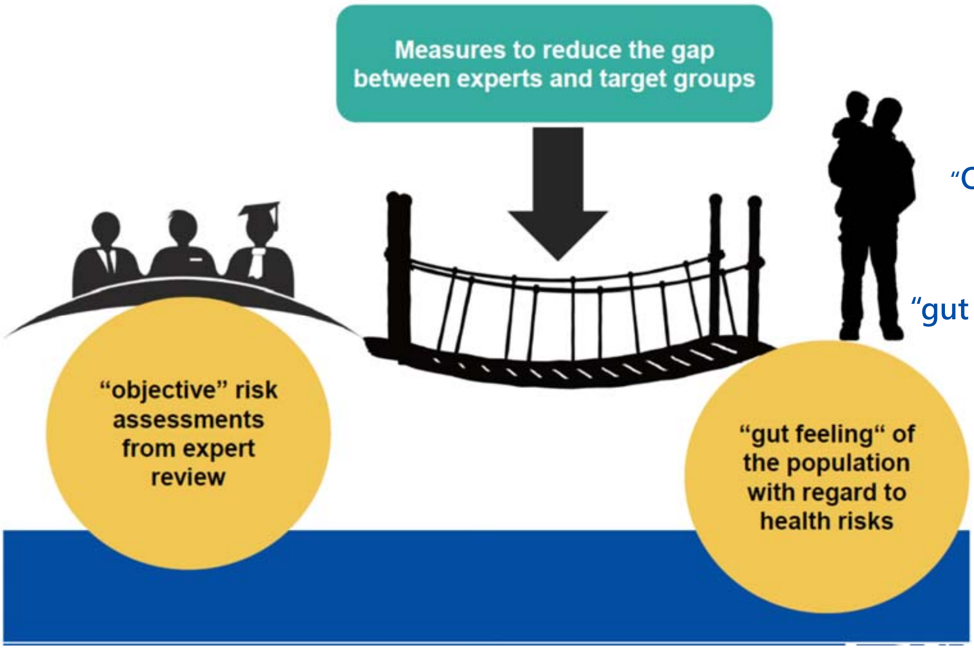
Oral Presentation
-風險評估及溝通
-有機農產品中的農藥殘留

O01- Risk communication with a focus on pesticide residues
O10- EU audits on pesticide residue controls in organic production

O01- Risk communication with a focus on pesticide residues

Speaker: Roland Solecki (Department Pesticide Safety German Federal Institute for Risk Assessment)

風險溝通的總體目標



Measures to reduce the gap between experts and target groups

“objective” risk assessments from expert review

“gut feeling“ of the population with regard to health risks

“Objective risk” = hazard × exposure

The objective risk is based on criteria of risks measurable by natural sciences.

“gut feeling” = Subjective Risk Perception

Sociocultural factors

Effective risk communication requires knowledge and understanding of the perception of the target group.

低估 vs 高估風險 (人們通常傾向低估自然產生的風險，高估人為來源的風險)

Eurobarometer 2010 – risks associated with human nutrition

Pesticide residues in food (19%)

Food pathogens (12%)

Gene technology (8%)

New technologies (1%)

‘Intuitive Toxicology‘

Underestimation of natural risks like mildew toxins

Mildews produce aflatoxins, which cause liver cancer

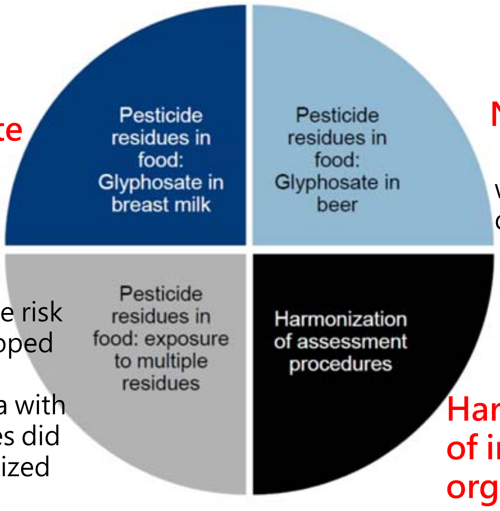
Legend of the gracious mother nature

- **可用於評估主觀風險認知的方法:** Delphi study、consumer conference 、population survey、focus group 、**media analysis and social media analysis**.
- 最近在BfR關於農藥殘留的媒體分析顯示，大多數關於農藥殘留的文章都提到了健康風險。僅在少數關於農藥殘留的文章中提到了效益，而絕大多數的文章沒有提到任何效益。
- 一方面，大眾對食品中的農藥殘留有高度的認知。 但另一方面，對與農藥殘留相關的食品消費行為影響卻很小。

2016年於德國有關植物保護產品的代表性群體調查顯示

- 在過去的兩年裡，有七成的消費者在媒體上接收到有關農藥殘留的報導
- 三分之二的人們認為食品中的農藥殘留普遍受到禁止(即食品中不允許有農藥殘留)
- 十分之三的人們關注有關嘉磷塞(Glyphosate)的報導

農藥殘留領域的溝通挑戰:



No residues of glyphosate detectable in breast milk

No health risk from glyphosate in beer

"In order to ingest quantities of glyphosate that would pose a health risk, an adult would have to drink roughly 1000 liters of beer in one day."

- Methodologies for cumulative risk assessment have been developed and are already in use
- Evaluation of monitoring data with respect to cumulative residues did not reveal formerly unrecognized health risks.

Harmonized and transparent procedures of international authorities and organization's necessary

總結:

近期風險溝通的挑戰:

- 妥善處理影響風險認知的因素
- 改進評估風險認知的方法
- 納入風險認知研究，為目標群體提供資訊(為不同的目標群體選擇溝通工具)
- 與公眾展開更有效的風險溝通

人類健康風險評估的創新挑戰:

- 納入國際間研究的結果
- 改進國際間公認的指導和指引
- 整合協調累積風險評估的方法
- 考慮設定容許量(MRL)的適當混合效應
- 加強科學合作和能力養成
- 根據匯入資料建立最新數據庫
- 評估程序更加透明和一致性
- 保持並改進高水準的科學專業知識
- 防止人類的健康受到農藥有害的影響
- 實現消費者的選擇自由

15 YEARS Science in the Service of Humanity

BfR Bundesinstitut für Risikobewertung

O10- EU audits on pesticide residue controls in organic production

Speaker: JAN VON KIETZELL (European Commission DG Health and Food Safety)

- 歐洲委員會衛生和食品安全總司(European Commission’s Directorate-General for Health and Food Safety)主管範圍包含食品、動物健康、動物福祉、**有機生產**、**農藥殘留**，污染物等。
- 該機構針對**有機生產中的農藥殘留檢測**執行一項計畫，該計畫之執行背景為:
  1.農藥殘留檢測為有機生產中的一個控制方式
  2.自2014年起，法規要求需查驗5%的有機操作者
  3.幫助歐盟會員國實施有機生產中農藥殘留檢測的有效控制
- 於2014年12月向所有會員國發送問卷，調查有機生產中的農藥殘留檢測情況，隨後在2015年和2016年間針對5個會員國(英國、波蘭、德國、西班牙及芬蘭)進行了一系列的審視。

調查結果顯示:

- 農藥殘留檢驗的取樣對象包括: 食品、飼料、葉子 、土壤及水; 樣品取樣之階段包括: 生產、加工、零售及進口
- 雖然有關於採樣程序的官方指導文件，但在生產階段的採樣通常沒有明確的程序（例如樹葉、土壤和水），且官方採樣程序**不適用於識別**鄰田農藥飄散

- 主管當局估計，含有農藥殘留的樣品中有三分之一與飄散有關，其可能來自採樣人員實施錯誤的採樣程序，導致檢驗結果的解釋可能會受到不適合其目的的採樣程序影響
- 在參與檢驗的實驗室及分析方法部分，**缺乏分析方法(如分析的品項範圍及其定量極限等)的官方標準**會對控制系統產生負面影響

調查門檻 - 行動值(action level)的設定:

- 某些驗證機構在決定是否啟動調查(行動值)之前會納入加工因子作為考量（例如香料的加工因子最高可到10)
- 將量測不確定度與定量極限聯繫起來在技術上是不正確的，任何等於或高於定量極限的結果都可以量化。

調查的程序:

- 正式的程序: 在調查過程中，有機農產品會被封鎖且認定為未經認證（低農藥殘留的情況例外）
- 各個驗證機構調查的程度和性質各不相同
- 某些驗證機構在檢出低農藥殘留的情況下（例如0.01-0.02 mg / kg）會向有機生產者發出信函，通知他們結果，並要求解釋
- 在葉子上經常檢測到農藥殘留，一些驗證機構會應用數學模型來確定農藥殘留是否來自使用未推薦農藥而沒有至現場調查

- 如果有機生產者已採取足夠的預防措施，則認為**鄰田飄散**和其他污染原因是可以接受的
- **並沒有官方標準**來決定預防措施的充分性，採用逐案判斷，不適用一致的規則
- 在某些會員國會進行系統性的現場調查，逐案跟進、並訪問鄰近的慣行農場，取得樣本、檢查這些鄰近慣行農場的用藥記錄等

執法和結果回報

- 在5個會員國中的2個國家，所有檢測到定量極限以上的農藥殘留都導致了執法行動和裁罰
- 5個會員國中沒有一個具有固定的行動值，超過該行動值將採取執法行動
- 都有定期通知主管當局的程序

關於執法的結論

- 有機生產中的農藥殘留檢測是確定與農藥殘留有關的問題的合適工具
- 歐盟之指引提供了充分的資訊，可用以逐案調查農藥殘留檢測
- 農藥殘留檢測的結果解釋和後續行動的**官方標準差異**阻礙了對於合乎規定的處理的**一致性**，特別是在低濃度的農藥殘留檢測結果下尤其明顯

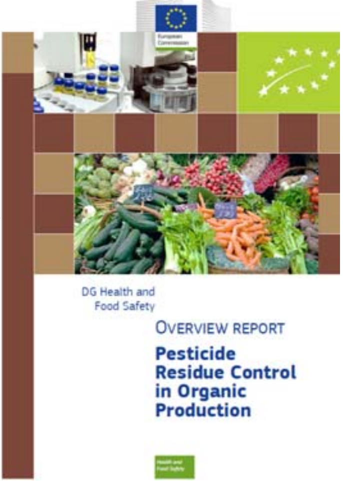
會員國的主管機構應考慮:

- 在生產過程中對農藥殘留分析的採樣程序實施明確的指示

- 在適當的情況下，**採樣程序**應適用於識別鄰田飄散
- 指定實驗室分析的**方法和範圍的要求**，以促進對未推薦用於有機生產的物質的可靠檢測和量化
- 確保進行有機生產中農藥殘留檢測的實驗室是被**指定的**
- 確保將其指定傳達給國家參考實驗室（NRL），以促進其合作和知識共享
- 參考關於食品和飼料中農藥殘留分析的**分析品質管制和方法確效程序的指引文件**（**SANTE / 11813/2017**），以獲得一致的農藥殘留分析品質管制程序
- 對農藥殘留檢測**結果的解釋和後續行動實施明確的指示**
- 其指示還應有助於確保**預防措施的充分性**

新版歐盟有機法規

- 歐洲理事會於2018年5月22日通過，即將在歐盟官方期刊上發表
- 將於**2021年1月1日**起適用
- 有機經營者應保持適當的措施，以確保和避免有機生產污染的風險並定期審查和調整措施
- 主管機構或驗證機構等若在有機產品中檢測到不該存在的物質時：（a）應**立即進行正式調查**及（b）應**暫時禁止**將有關產品作為有機產品上市
- 歐盟委員會應**按一致的規則**採取行動



DG Health and Food Safety

OVERVIEW REPORT

Pesticide Residue Control in Organic Production

12th EUROPEAN PESTICIDE RESIDUE WORKSHOP
22nd – 25th May 2018 · MUNICH · GERMANY

Oral Presentation
-農藥殘留之監控
-農藥殘留之分析方法

O23- The Fipronil Case - Consequences for Monitoring Strategies
O30- The design of Q-Orbitrap data independent acquisition experiments for target screening ~850 pesticide residues in fruits and vegetables based on a compound database

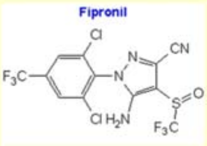
---

O23- The Fipronil Case - Consequences for Monitoring Strategies

Speaker: Ralf Lippold (European Union Reference Laboratory for Pesticides in Food of Animal Origin and Commodities with High Fat Content (EURL-AO)-State Institute for Chemical and Veterinary Analysis (CVUA), Freiburg i. Br., Germany)

- 源起: 2017年7月20日歐盟預警通報系統 (the Rapid Alert System for Food and Feed, RASFF)通報比利時檢驗出雞蛋中芬普尼(Fipronil)殘留量高達0.72（後為1.2）mg / kg
- 濫用非法添加芬普尼的清潔劑Dega-16(不允許用於生產食品的動物上)
- EURL AO於8月2日在網頁上公佈分析方法
- 比利時、德國及荷蘭這三個發現受汙染的雞蛋較多的國家紛紛封閉養雞場並進行檢驗

- REGULATION (EC) NO 396/2005:
  - Residue definition: fipronil (sum fipronil + sulfone metabolite (MB46136) expressed as fipronil) (F)


Fipronil


Fipronil-Sulfone

  - Other metabolites are fipronil-sulfide and fipronil-desulfinyl

Most relevant analyte in egg: Fipronil-sulfon

- REGULATION (EC) NO 396/2005:
(MRL of pesticides in or on food and feed of plant and animal origin)
  - 0.015 mg/kg for bird´s eggs until 31.12.2016
  - **0.005* mg/kg for bird´s eggs from 01.01.2017**
  - 0.015 mg/kg for poultry muscle until 31.12.2016
  - **0.005* mg/kg for poultry muscle from 01.01.2017**
  - 0.020 mg/kg for poultry fat until 31.12.2016
  - **0.006 mg/kg for poultry fat from 01.01.2017**

建立分析動物源食品的方法

	QuEChERS-AO	SweEt	EN 1528 (DFG S 19)
Sample weight	5 g	5 g	5 g
Extraction	10 mL acetonitrile Citrate buffer NaCl $MgSO_4$	10 mL ethyl acetate Na_2SO_4 PSA C_{18}	Mixing with 50 g Na_2SO_4 Extraction with petroleum ether Filtration and removal of solvent Determination of fat content
	Shake (10 min) centrifuge (5 min at 2000 g)	Shake (30 min) centrifuge (6 min at 2000 g)	Redissolve fat for GPC in ethyl acetate/cyclo hexane
clean-up	6 mL supernatant: $MgSO_4$ PSA	Filtrate GPC	1. GPC -> Solvent exchange 2. Silica gel columns
	Shake (10 min) centrifuge (5 min at 2000 g)		Sampling of fractions Removal of solvent 0,5 mL final volume
Detection system (typical)	LC-MS/MS or LC-Q-ToF	LC-MS/MS (or GC-MS/MS with further clean up)	GC-MS/MS

Results for
- Fipronil
- Fipronil-sulfon
- Fipronil-sulfide
- Fipronil-desulfinyl

ESI+: No signals (tested up to 0.040 mg/kg)

ESI-: LOQ of 0.001 mg/kg for all analytes

加工因子探討

- Processing factors were discussed at the SCoPaFF (30.08.2017):

(Standing Committee on Plants, Animals, Food and Feed - Section Novel Food and Toxicological Safety of the Food Chain)

- average fat content egg: 10 %
- average fat content egg yolk: 32.6 %
- proportion egg yolk in whole egg: 32 %
- proportion egg white in whole egg: 68 %

Data indicate that 90-95 % of fipronil is concentrated in egg yolk and 5-10 % in egg white.

For calculation on egg yolk, 100 % is assumed

Product	Processing Factor	MRL applicable	Comments
Whole egg	1	0.005 mg/kg	MRL according Reg. 396/2005
Whole egg liquid	1	0.005 mg/kg	Equal to whole egg
Egg yolk liquid	3.125	0.016 mg/kg	32 % egg yolk in whole egg 100 % of Fipronil in egg yolk
Egg white liquid		< LOQ	68 % egg white in whole egg <10 % of Fipronil in egg white (< 0.00074 mg/kg in egg white)
Whole egg powder	4.28	0.021 mg/kg	Drying factor for whole egg liquid
Egg yolk powder	2.26 * 3.125	0.037 mg/kg	2,26 drying factor for egg yolk
Egg white powder	7,17	7.17 * LOQ	Liquid egg white was analysed 7.17 drying factor for egg white
		0.005 mg/kg	Level to be applied if no data for the liquid egg white available

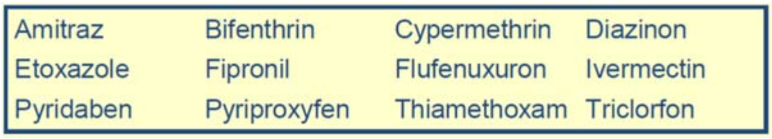
較“複雜”的蛋製品

E.g. pasta: sources for Fipronil are eggs and cereals

- **Regarding The Fipronil Case:**
  As Fipronil was not detected in cereals for several years the rule was to set Fipronil from cereals to zero (not to the LOQ of the laboratory).

特別監測計畫(Ad hoc Monitoring Programme):

- 因為可能存在誤用之疑慮，委員會提交了12種待監測品項:



Amitraz	Bifenthrin	Cypermethrin	Diazinon
Etoxazole	Fipronil	Flufenuxuron	Ivermectin
Pyridaben	Pyriproxyfen	Thiamethoxam	Triclorfon

- 接著納入實驗室可用多重殘留方法進行分析之更多監測項目（56種物質，包含殺蟎劑)

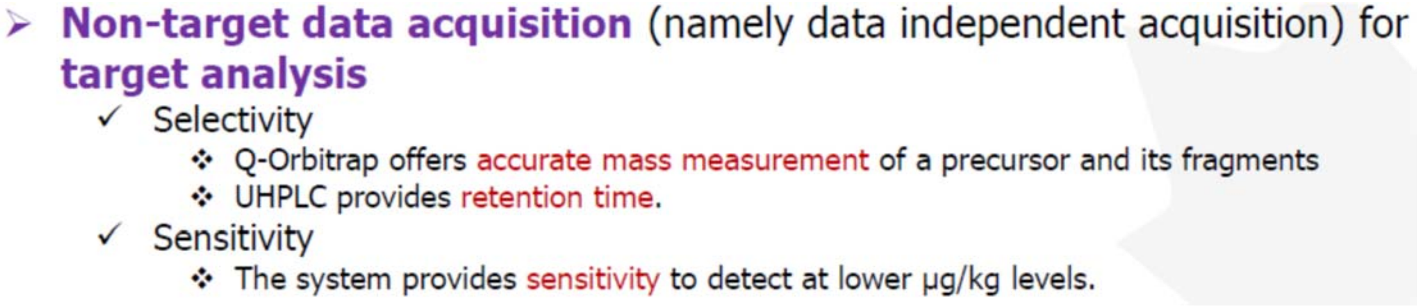
總結及建議:

- **任何植物保護產品登記的同時必須有可用的分析用參考標準品(涉及殘留定義相關之所有標準品)**
- **即使檢出值未超過MRL，也要跟進任何不尋常的農藥殘留發現(特別是如果原產地在當地)**
- **必須要擴大監測的範圍及品項 - 不僅僅是例行監測計畫的分析**
- **改善監管單位內、外溝通的方式及效率等，特別是當涉及主管當局內的不同部門時（例如涉及多用途 (同時可做為農藥、殺菌劑及動物用藥使用)物質之管制）**

O30- The design of Q-Orbitrap data independent acquisition experiments for target screening ~850 pesticide residues in fruits and vegetables based on a compound database

Speaker: Jian Wang (Canadian Food Inspection Agency, CFIA)

- Develop a generic detection approach of non target data acquisition for target analysis based on accurate mass measurement.
- **UHPLC/ESI Q-Orbitrap** application for target screening using Full MS/vDIA (variable data independent acquisition) or Full MS/mDIA (multiplexing data independent acquisition).



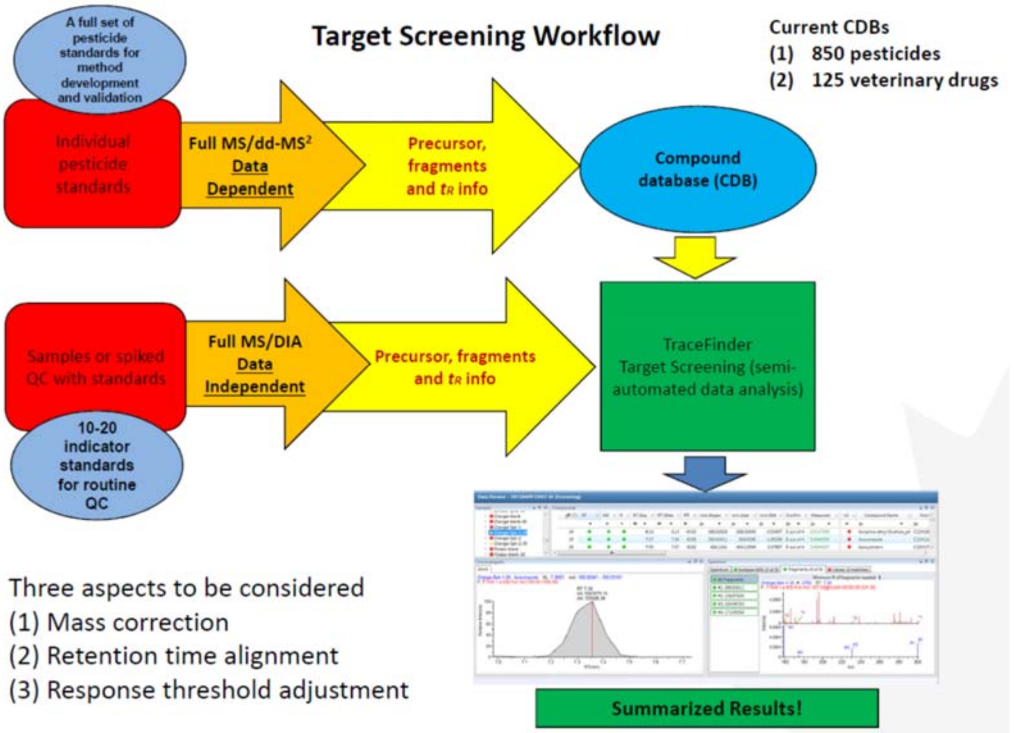
➢ **Non-target data acquisition** (namely data independent acquisition) for **target analysis**
  - ✓ Selectivity
    - ❖ Q-Orbitrap offers accurate mass measurement of a precursor and its fragments
    - ❖ UHPLC provides retention time.
  - ✓ Sensitivity
    - ❖ The system provides sensitivity to detect at lower µg/kg levels.

Instrumentation

UHPLC/ESI Q-Orbitrap system consisted of a Q Exactive mass spectrometer (ThermoFisher Scientific, Germany) and an Accela 1250 LC pump and an Accela open autosampler

Q-Orbitrap

- Full MS/dd-MS^2: Full MS at 70,000 FWHM and dd-MS^2 (data dependent MS^2) at 35,000 FWHM
  - ✓ Product ion spectrum for identification, compound database and mass spectral library
- Full MS/vDIA (variable data independent acquisition) or Full MS/mDIA (multiplexing data independent acquisition) at 35,000 FWHM. Full MS at 70,000 FWHM
  - ✓ Target screening



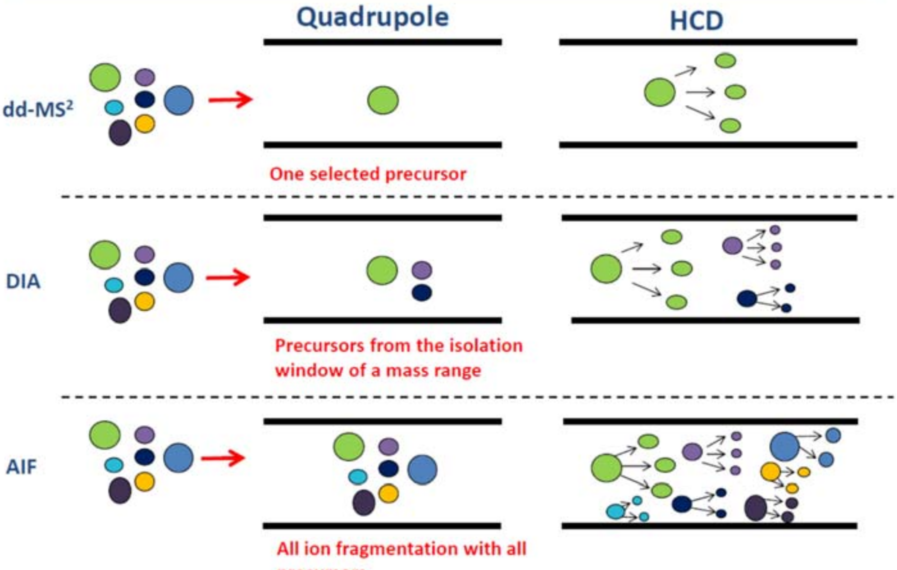
Target Screening Workflow

Current CDBs
(1) 850 pesticides
(2) 125 veterinary drugs

Three aspects to be considered
(1) Mass correction
(2) Retention time alignment
(3) Response threshold adjustment

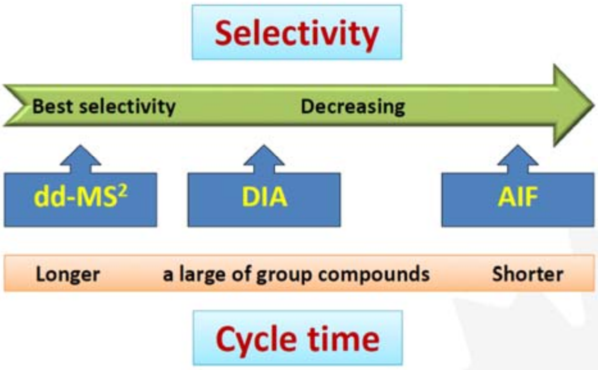
---

dd-MS^2, DIA, and AIF: to acquire product ions or fragments for identification or target screening

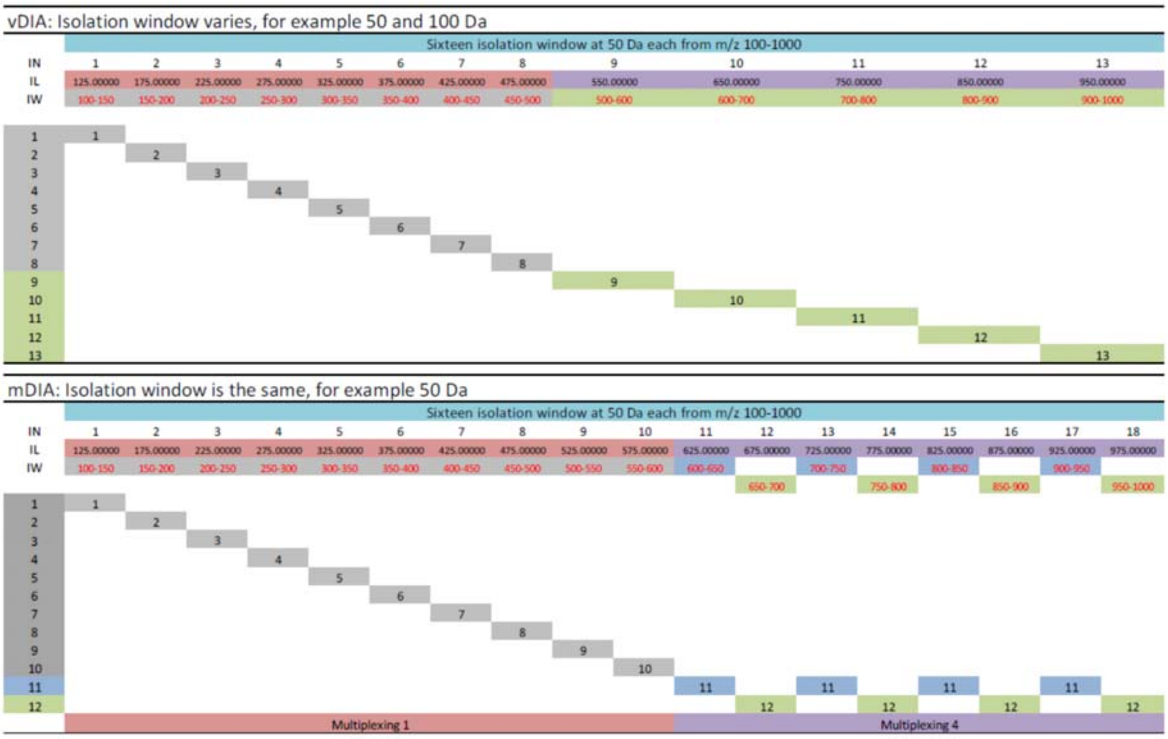


Reference: Zhu et al. Anal. Chem. 2014, 86, 1202–1209

不同的前驅物篩選模式及其專一性與cycle time之比較



Full MS/vDIA or Full MS/mDIA



vDIA: Isolation window varies, for example 50 and 100 Da

	Sixteen isolation window at 50 Da each from m/z 100-1000												
IN	1	2	3	4	5	6	7	8	9	10	11	12	13
IL	125.00000	175.00000	225.00000	275.00000	325.00000	375.00000	425.00000	475.00000	550.00000	650.00000	750.00000	850.00000	950.00000
IW	100-150	150-200	200-250	250-300	300-350	350-400	400-450	450-500	500-600	600-700	700-800	800-900	900-1000

mDIA: Isolation window is the same, for example 50 Da

	Sixteen isolation window at 50 Da each from m/z 100-1000																	
IN	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IL	125.00000	175.00000	225.00000	275.00000	325.00000	375.00000	425.00000	475.00000	525.00000	575.00000	625.00000	675.00000	725.00000	775.00000	825.00000	875.00000	925.00000	975.00000
IW	100-150	150-200	200-250	250-300	300-350	350-400	400-450	450-500	500-550	550-600	600-650		700-750		800-850		900-950	
												650-700		750-800		850-900		950-1000

The masses of 96% the pesticides in CDB (850) fall into the mass range from 100 – 500 m/z

---

近期選用三種不同分析方法進行測試

Method 1
Full MS/mDIA: Loop count 12; Isolation window 52 Da; MSX 4

Method 2
Full MS/vDIA: Loop count 8; Isolation window 52 Da, and Loop count 5; Isolation window 104 Da; MSX 1

Method 3
Full MS/mDIA: Loop count 20; Isolation window 26 Da; MSX 5

儀器設定之參數

Parameters

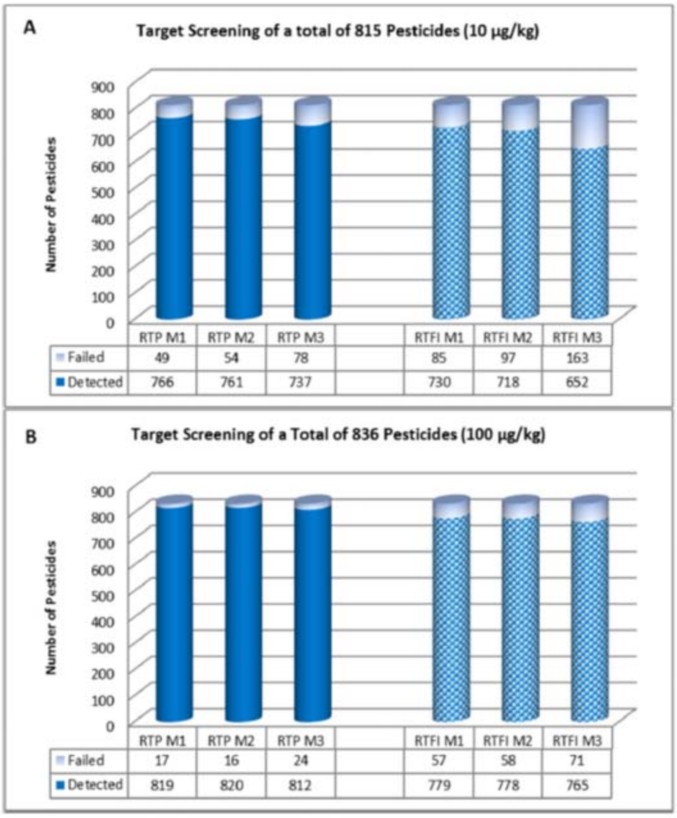
1.Loop count (cycle time)
2.MSX count (selectivity and sensitivity, split on injection time)
3.Isolation window (cycle time and selectivity)
4.NCE Steps (sensitivity, split on Injection Time)

分析方法效能評定之參數及標準

- Parameters
  - **RTP** (tentative positive screening): **R**etention **T**ime and accurate mass of **P**recursor by Full MS
  - **RTFI** (confirmatory positive screening): **R**etention **T**ime and accurate masses of a precursor and its **F**ragment **I**on by Full MS/DIA

- Criteria
  - Retention time: ±0.5 min (reference to CDB)
  - Mass accuracy: ≤5 ppm
  - An acceptable false-negative rate of ≤5%

Results of 2-Year Work



Target Screening of a total of 815 Pesticides (10 µg/kg)

	RTP M1	RTP M2	RTP M3	RTFI M1	RTFI M2	RTFI M3
Failed	49	54	78	85	97	163
Detected	766	761	737	730	718	652

Target Screening of a Total of 836 Pesticides (100 µg/kg)

	RTP M1	RTP M2	RTP M3	RTFI M1	RTFI M2	RTFI M3
Failed	17	16	24	57	58	71
Detected	819	820	812	779	778	765

CDB: 850 pesticides

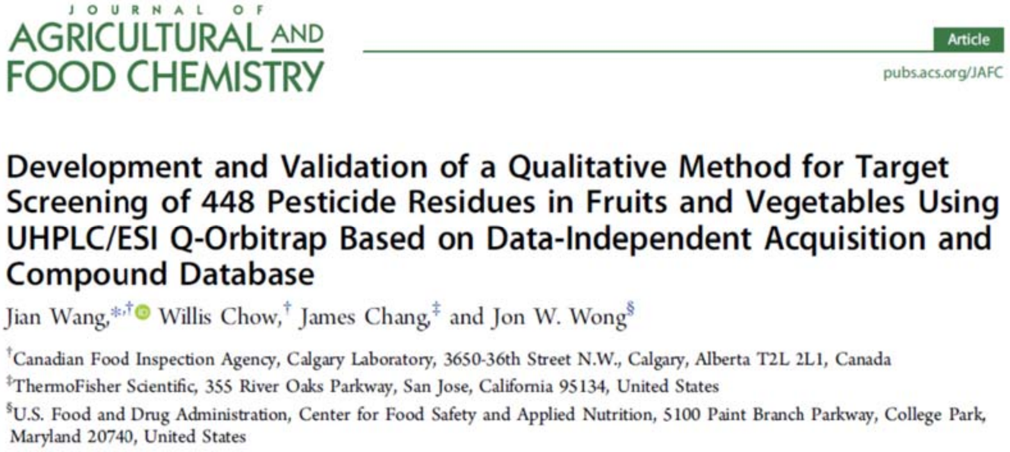
M1: mDIA (IW: 50 Da)
M2: vDIA (IW: 50 and 100 Da)
M3: mDIA (IW: 25 Da)

RTP: precursor + RT
RTFI: precursor + fragment + RT

- By RTP, the validated methods (Method 1 and 2) are capable of screening about 760 and 820 pesticides at 10 and 100 µg/kg, respectively, in fruits and vegetables.
- By RTFI, the methods screen about 720 and 780 pesticides at 10 and 100 µg/kg, respectively.

總結:

- UHPLC / ESI Q-Orbitrap Full MS / DIA基於精確的質量測量，以非目標數據獲得(non-target data acquisition)的方式進行目標分析(target analysis) ，也就是將樣品分析得到的數據與化合物資料庫(Compound Database, CDB)的數據依精確質量數等條件進行比對，以進行篩選。
- UHPLC/ESI Q-Orbitrap Full MS/DIA 及化合物資料庫(CDB)具有很大的潛力，可用作篩選食品中大量農藥的檢測技術（基於風險的監測）和適用常規監測計畫中的高樣品通量（基於計畫的監測， 應用較小型的CDB(即50至200種農藥)）。



JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Development and Validation of a Qualitative Method for Target Screening of 448 Pesticide Residues in Fruits and Vegetables Using UHPLC/ESI Q-Orbitrap Based on Data-Independent Acquisition and Compound Database

Jian Wang,*,† Willis Chow,† James Chang,‡ and Jon W. Wong§

†Canadian Food Inspection Agency, Calgary Laboratory, 3650-36th Street N.W., Calgary, Alberta T2L 2L1, Canada
‡ThermoFisher Scientific, 355 River Oaks Parkway, San Jose, California 95134, United States
§U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, 5100 Paint Branch Parkway, College Park, Maryland 20740, United States

12th EUROPEAN PESTICIDE RESIDUE WORKSHOP
22nd – 25th May 2018 · MUNICH · GERMANY

Poster
-分析方法之開發及應用
-其他主題

PD048- Phthalimide – Metabolite of Folpet or unavoidable artefact
PO023- Fully automated dilution workstation for pesticides working standard mixtures
PO026- Long Term Stability Monitoring of Pesticide Stock Solutions by Quantitative NMR – Results

---

PD048

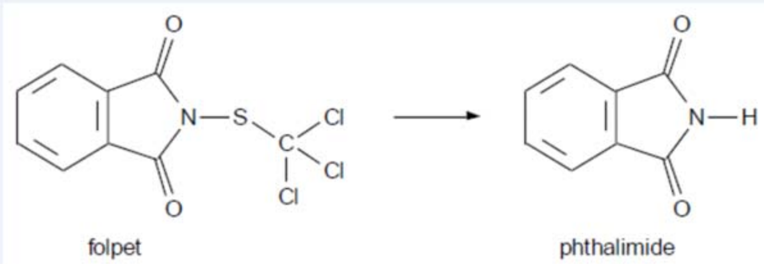
LABOR FRIEDLE GMBH

Phthalimide – Metabolite of Folpet or unavoidable artefact

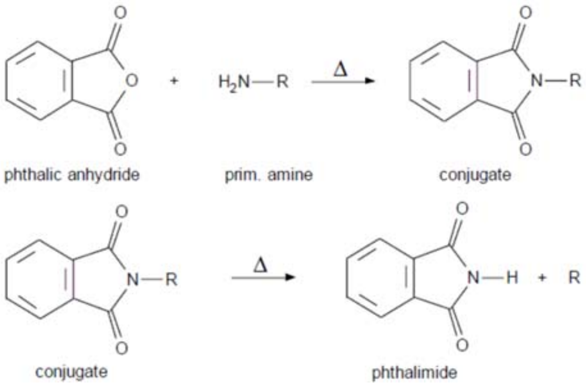
Nitsopoulos A., Wollein G., Friedle A.
Labor Friedle GmbH, Von-Heyden-Str. 11, 93105 Tegernheim (Regensburg), Germany

- Based on Regulation (EU) 2016/156 dated 18 January 2016 a new definition of residue concerning the fungicide folpet was given, entered into force 26 August 2016: “Sum of folpet and phthalimide, expressed as folpet.”
- Folpet belongs to the group of phthalimide fungicides, which quickly decay at higher temperatures, e.g. in a gaschromatographic injector. The bond breaking takes place on the nitrogen (N), so that the final product is phthalimide.
- In plants folpet is also metabolized to phthalimide as the **major metabolite**.

POSTER WINNER!



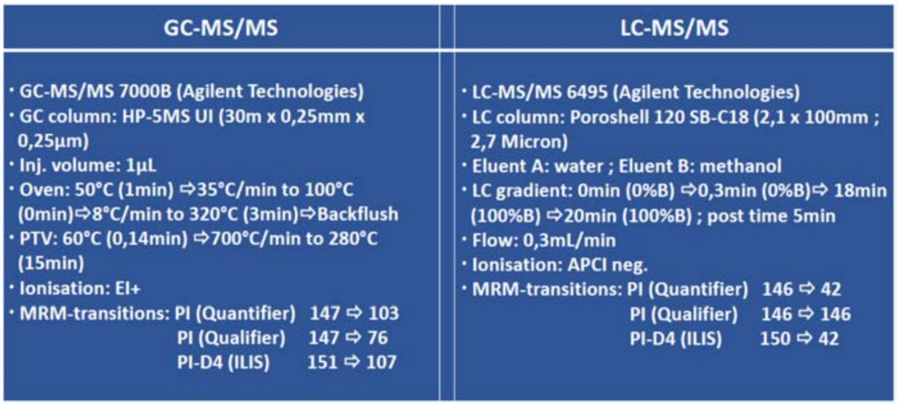
- Partially high concentrations in **dried products** - without the slightest indication of folpet.
- An interesting correlation between the presence of **phthalimide (PI) and phthalic anhydride (PSA)**, an ubiquitous environmental chemical, which can easily react under specific conditions (esp. higher temperatures) with primary amino groups (like present in amino acids, peptides, etc.) to form phthalimide.
- As a consequence, it is obvious that the common analytical technique for measuring folpet and PI - **the hot injection GC-detection - is a potential source** for the generation of false positive levels of PI.



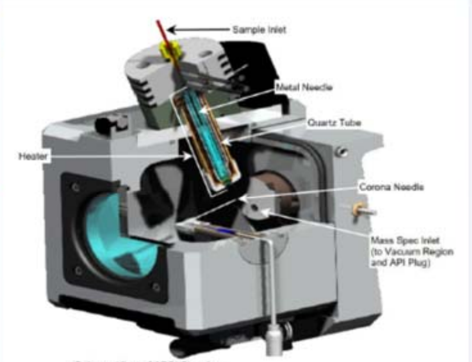
- Phthalimide can be:

(I) a **metabolite** of folpet or phosmet, (II) **reaction product** of folpet during GC injection, (III) an **artefact** resulting from thermic reaction of the ubiquitously occurring phthalic anhydride with primary amino compounds of the matrix either in GC-injector or (IV) of **process-induced origin** especially in dried products .

- We showed that it is possible to exclude formation of phthalimide during analysis, using **LC-MS/MS**-technique with atmospheric pressure chemical ionisation (**APCI**) instead of GC-MS/MS, but there is no chance to differ phthalimide as folpet metabolite from process-induced origin

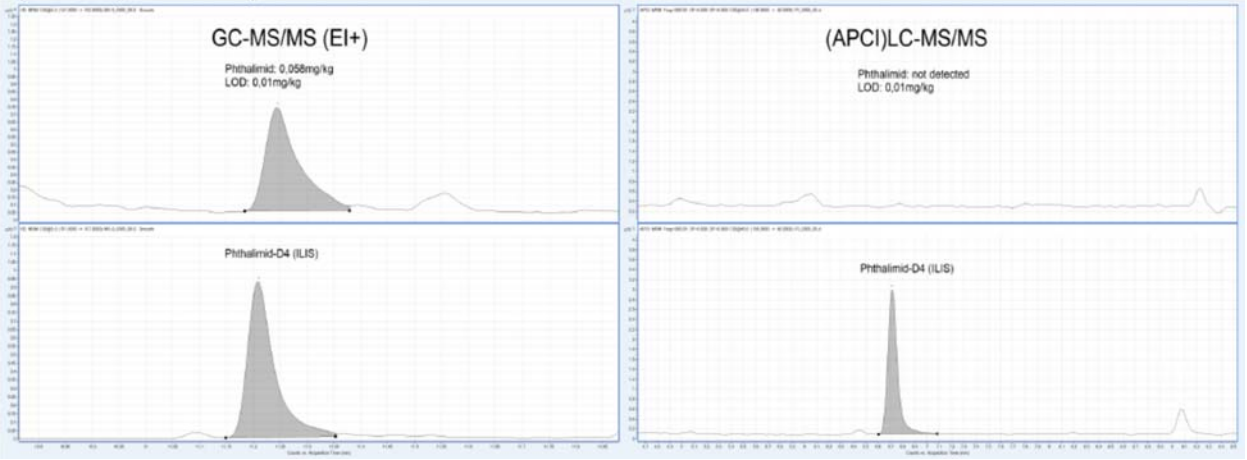


GC-MS/MS	LC-MS/MS
• GC-MS/MS 7000B (Agilent Technologies) • GC column: HP-5MS UI (30m x 0,25mm x 0,25µm) • Inj. volume: 1µL • Oven: 50°C (1min) ⇨35°C/min to 100°C (0min)⇨8°C/min to 320°C (3min)⇨Backflush • PTV: 60°C (0,14min) ⇨700°C/min to 280°C (15min) • Ionisation: EI+ • MRM-transitions: PI (Quantifier) 147 ⇨ 103 PI (Qualifier) 147 ⇨ 76 PI-D4 (ILIS) 151 ⇨ 107	• LC-MS/MS 6495 (Agilent Technologies) • LC column: Poroshell 120 SB-C18 (2,1 x 100mm ; 2,7 Micron) • Eluent A: water ; Eluent B: methanol • LC gradient: 0min (0%B) ⇨0,3min (0%B)⇨ 18min (100%B) ⇨20min (100%B) ; post time 5min • Flow: 0,3mL/min • Ionisation: APCI neg. • MRM-transitions: PI (Quantifier) 146 ⇨ 42 PI (Qualifier) 146 ⇨ 146 PI-D4 (ILIS) 150 ⇨ 42



Cutaway View of APCI Chamber

- Samples of dried parsley were **spiked with 1ppm PSA** and measured both with the **GC-MS/MS and the (APCI)LC-MS/MS** system after **QuEChERS extraction** and clean-up.
- The following chromatograms show that there is a strong and precise signal of PI in case of GC-MS/MS arising from previous artefact formation. In case of the **(APCI)LC-MS/MS** there is **no detection of PI**.



It is not possible to differ phthalimide as folpet metabolite from process-induced origin - folpet's new residue definition is a problem especially for organic products

---

PO023

Fully automated dilution workstation for pesticides working standard mixtures

Rothmeier, S.[1], Nestola, M.[2], Hentschel, A.[1], Fischer, F.[1], Becker, E.[1] Kirchhoff, E.[1]
[1]Institut Kirchhoff Berlin GmbH, Oudenarder Straße 16, 13347 Berlin/D
[2]Axel Semrau GmbH & Co. KG, Stefansbecke 42, 45549 Sprockhövel

- Axel-Semrau® and Institut Kirchhoff Berlin GmbH developed based on the CHRONECT Robotic XYZ robots from CTC Analytics AG a **fully automated dilution workstation** which is able to produce **working standard mixtures** from stock solutions under gravimetric control.
- This procedure complies with the requirements of **SANTE**, all relevant information like date of expiry, batch, purity and final analyte concentration (gravimetrically controlled) are easily accessible for each stock standard solution and working standard solution mixtures.
- A standard mixture solution with 400 analytes could be mixed automated within 24 hours. A laboratory assistant would spend 3-4 working days (including documentation).

Dilution workstation

Fig.1: Overview about all stock and working standards from Database

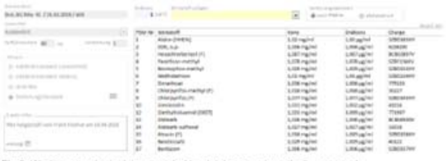


Fig.2: Working standard mixture created by database, automatically prepared, gravimetrically corrected concentrations for each mixture in the database

Unique identification code for each standard controlled by barcode reader

Gravimetric control of solutions and pipetted volumes by 5 digit balance

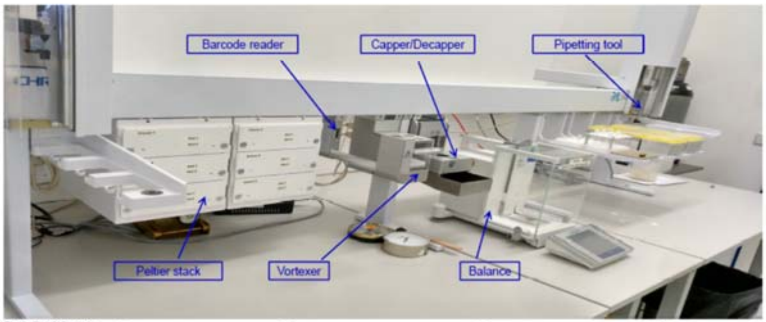


Fig.3: PAL3 System

Peltier stack module: 12 racks with 54 positions: conditions between 4°C and 40°C

Vortex Mixer Module tool → remixing

Capping and decapping tool → no replacement of septum after piercing necessary

Pipetting tool for using disposable pipette tips → no risk of carryover

---

PO026

Long Term Stability Monitoring of Pesticide Stock Solutions by Quantitative NMR – Results

H. Zipper, S. Ackermann, E. Scherbaum, M. Anastassiades
E-Mail: Hubert.Zipper@cvuas.bwl.de

cvua STUTTGART
Chemisches und
Veterinäruntersuchungsamt
Stuttgart

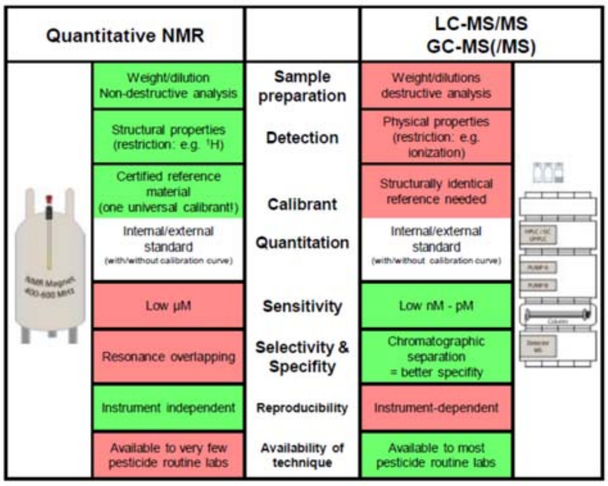
one of the 4 official food control and animal health laboratories of Baden-Wuerttemberg

- A significant source of **error** in pesticide residue analysis is the degradation of neat standards, standards in stock solutions, working solutions and sample extracts.
- Currently **LC-MS/MS and GC-MS(/MS)** are the most widely employed techniques for testing the stability of pesticides.
- These techniques are sensitive and selective enough for testing of mixtures, but **measurement uncertainty requires multiple injections (typically ≥5)** to achieve the accuracy required for reliable conclusions about compliance with the stipulated thresholds.

Quantitative NMR - an Alternative! ?

- Compared with mass spectrometry, qNMR yields relatively low-sensitivity measurements, but a major advantage is that **the reference standard does not need to be the identical material, but only one universal standard unrelated to the target analyte**.
- The **non-destructive nature** of this technique makes it possible for samples to be kept for measurements over the course of several years, e.g. in flame-sealed NRM tubes.

A comparison of the main characteristics of qNMR and chromatographic techniques is shown here:



Quantitative NMR		LC-MS/MS GC-MS(/MS)
🟩 Weight/dilution Non-destructive analysis	**Sample preparation**	🟥 Weight/dilutions destructive analysis
🟩 Structural properties (restriction: e.g. ^1H)	**Detection**	🟥 Physical properties (restriction: e.g. ionization)
🟩 Certified reference material (one universal calibrant!)	**Calibrant**	🟥 Structurally identical reference needed
Internal/external standard (with/without calibration curve)	**Quantitation**	Internal/external standard (with/without calibration curve)
🟥 Low µM	**Sensitivity**	🟩 Low nM - pM
🟥 Resonance overlapping	**Selectivity & Specifity**	🟩 Chromatographic separation = better specifity
🟩 Instrument independent	**Reproducibility**	🟥 Instrument-dependent
🟥 Available to very few pesticide routine labs	**Availability of technique**	🟩 Available to most pesticide routine labs

Experiments

- Pesticide stock solutions were prepared at 1 mg/mL in acetonitrile, in formic acid-acidified (0.4 Vol.%) acetonitrile (started in 05/2015) and/or deuterated acetonitrile (started in 07/2017), filled in NMR-tubes, flame-sealed and stored at 4°C. 1H-NMR spectra were recorded at 400 MHz (Bruker Avance 400).
- The certified reference standards **3,5-dinitrobenzoic acid** or **prochloraz** were used as universal calibration standards.

Results

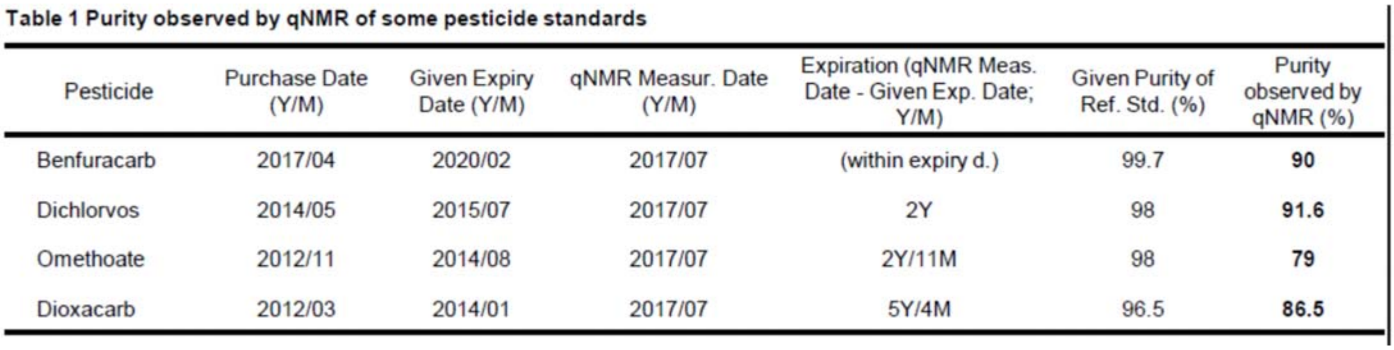
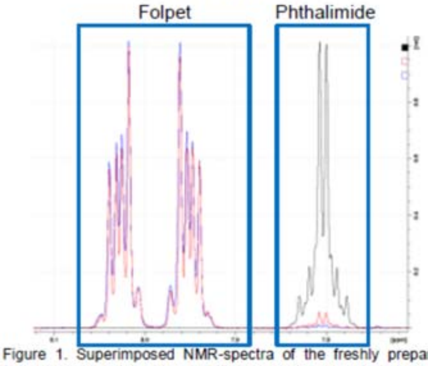


Table 1 Purity observed by qNMR of some pesticide standards

Pesticide	Purchase Date (Y/M)	Given Expiry Date (Y/M)	qNMR Measur. Date (Y/M)	Expiration (qNMR Meas. Date - Given Exp. Date; Y/M)	Given Purity of Ref. Std. (%)	Purity observed by qNMR (%)
Benfuracarb	2017/04	2020/02	2017/07	(within expiry d.)	99.7	**90**
Dichlorvos	2014/05	2015/07	2017/07	2Y	98	**91.6**
Omethoate	2012/11	2014/08	2017/07	2Y/11M	98	**79**
Dioxacarb	2012/03	2014/01	2017/07	5Y/4M	96.5	**86.5**


Stability Monitoring of Folpet Stock Solution

NMR-signals of

Figure 1. Superimposed NMR-spectra of the freshly prepared folpet stock solution using acidified acetonitrile as solvent (blue), of the same solution after 2 years of storage (red) and of a phthalimide-stock solution (black). Phthalimide was identified in the 2-year-old folpet stock solution (red NMR-signals at 7.8 ppm).

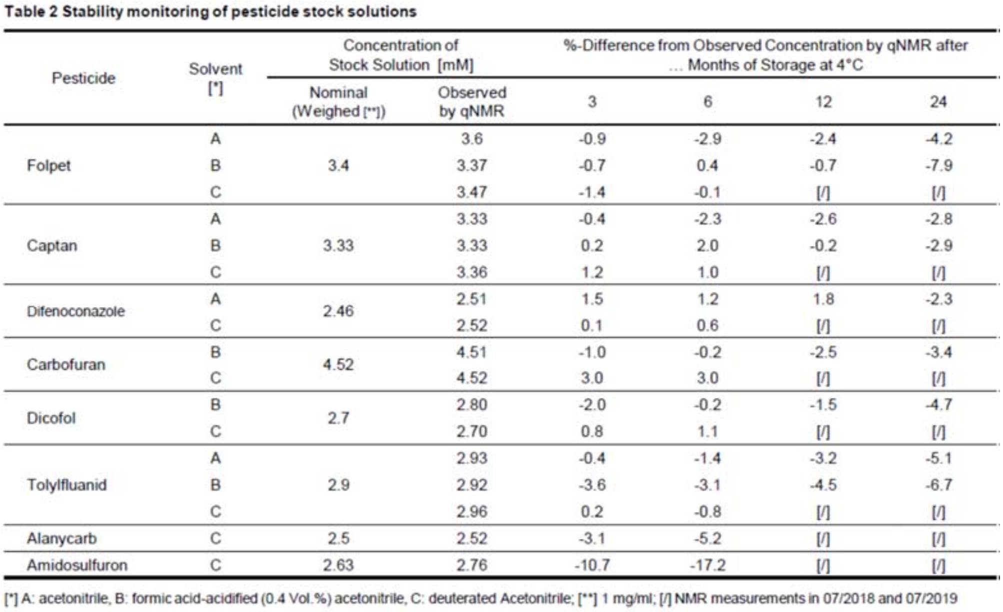


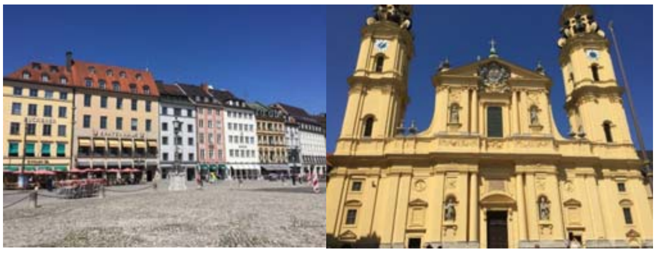
Table 2 Stability monitoring of pesticide stock solutions

Pesticide	Solvent [*]	Concentration of Stock Solution [mM] Nominal (Weighed [**])	Concentration of Stock Solution [mM] Observed by qNMR	%-Difference from Observed Concentration by qNMR after … Months of Storage at 4°C: 3	6	12	24
Folpet	A	3.4	3.6	-0.9	-2.9	-2.4	-4.2
	B		3.37	-0.7	0.4	-0.7	-7.9
	C		3.47	-1.4	-0.1	[/]	[/]
Captan	A	3.33	3.33	-0.4	-2.3	-2.6	-2.8
	B		3.33	0.2	2.0	-0.2	-2.9
	C		3.36	1.2	1.0	[/]	[/]
Difenoconazole	A	2.46	2.51	1.5	1.2	1.8	-2.3
	C		2.52	0.1	0.6	[/]	[/]
Carbofuran	B	4.52	4.51	-1.0	-0.2	-2.5	-3.4
	C		4.52	3.0	3.0	[/]	[/]
Dicofol	B	2.7	2.80	-2.0	-0.2	-1.5	-4.7
	C		2.70	0.8	1.1	[/]	[/]
Tolylfluanid	A	2.9	2.93	-0.4	-1.4	-3.2	-5.1
	B		2.92	-3.6	-3.1	-4.5	-6.7
	C		2.96	0.2	-0.8	[/]	[/]
Alanycarb	C	2.5	2.52	-3.1	-5.2	[/]	[/]
Amidosulfuron	C	2.63	2.76	-10.7	-17.2	[/]	[/]

[*] A: acetonitrile, B: formic acid-acidified (0.4 Vol.%) acetonitrile, C: deuterated Acetonitrile; [**] 1 mg/ml; [/] NMR measurements in 07/2018 and 07/2019

Summary: Although some drawbacks have to be considered (e.g. resonance overlapping, technique is available only to very few pesticide routine labs) the outcome of this study indicates that **qNMR is a reliable technique to assess the purity of neat standards and the intrinsic stability of pesticide stock solutions at specified storage conditions**. The results of this study will be imported into the compound stability database of the EURL DataPool-website.

心得概要



- 本次研討會因經費核定因素，僅能一人出席會議，因研討會內容與本所各重要業務皆甚為相關，若有同伴一起蒐集資訊相信會更為完整。
- 由於慕尼黑當地之物價高於台灣，在食等基本生活上的開銷較大。因台灣時間比德國快6個小時，於研討會期間有時差問題，但仍希望能盡量吸收資訊，把業務相關發展帶回所內供同仁參考。
- 由於大會演講及壁報涵蓋議題廣泛，在有限的時間內謹能就各重點議題節錄相關資訊。除研討會之主題演講與壁報展示外，大會也安排了一些贊助廠商展示最新的研發成果及儀器設備等。
- 在休息時間及餐敘期間不乏看見與會的各國代表進行溝通與討論，值得注意的是在研討會中較少看到來自亞洲的與會者，多數來自歐洲各國及美加等地。
- 本次研討會演講及壁報展示內容與國內食品安全、農藥殘留檢驗等重要議題及與本所之重要業務如風險評估、農藥登記審查及檢測技術開發等皆甚為相關，且非常充實精要，期能將此次研討會所帶回之資訊應用及精進於業務上，達成與國際接軌、與世界並進之目標。

建議


13th European Pesticide Residue Workshop

EPRW 2020 - SPAIN

- 建立自動化農藥殘留檢驗技術
- 建立高通量之目標物篩選分析技術
- 鼓勵所內同仁多參與歐洲農藥殘留研討會(EPRW)

感謝聆聽，敬請指正