

出國報告（出國類別：其他）

赴美國參加第 129 屆公定分析化學家協會 (AOAC)年會

服務機關：衛生福利部食品藥物管理署

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派赴國家：美國

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摘要

今年第 129 屆 AOAC 年會在美國加州洛杉磯舉行，會場位於洛杉磯商業中心內的 western Bonaventure 飯店之會議中心，場面盛大，全球約 1000 多名專家學者與會。藉由參加專題演講、壁報論文及分析儀器廠商展示，瞭解國際間檢驗技術之趨勢，並建立與此領域國際專家之交流管道，保持本署檢驗技術與國際接軌。本次年會專題演講的主題包括方法確效規範、動物用藥及化學殘留分析方法、微生物分析方法規範、重金屬、化粧品及色素添加物、統計分析方法、取樣方法探討、中藥(Asian Traditional Medicines, ATM)、膳食補充品(dietary supplements)之 GMP 規範挑戰、過敏原及病原性微生物等，演講內容豐富充實，學習到許多新知，也認識許多國際專家。方助理研究員受邀在會中以「New Blood 2015: Developing Methods for the Detection of Chemical analytes and Contaminants」議題進行口頭論文發表，題目為「Detection of diethyl yellow used illegally in processed soymilk curd by coupled LC-photodiode array detection and high resolution orbitrap MS」，會後反應熱烈，與國際專家有後續討論交流，藉此提高台灣能見度，另於大會安排之「Taiwan Section Business Meeting」發表專題演講，題目為「Hot food safety issues in Taiwan」，會後受到與會專家熱烈發問，並與相關領域國際專家留下聯絡資料。此外，本次會議本署共發表壁報論文 5 篇，為本署近年來在各領域之研究成果，主題分別為「Surveillance over 10 years for labeling legislation on genetically-modified food in Taiwan」、「Monitoring of hygiene quality in food produces in Taiwan in 2014」、「Detection of diethyl yellow used illegally in processed soymilk curd by coupled LC-photodiode array detection and high resolution orbitrap MS」、「Quantification of 143 pesticides in foods of animal origin using a modified QuEChERs method combined with LC-MS/MS and GC-MS/MS」及「Development of QuEChERs-based extraction and liquid chromatography-tandem mass spectrometry method for eugenol and tricaine methanesulfonate in fish muscle」，展示期間受到各國學者熱烈之詢問，也藉此機會展現台灣在檢驗分析領域之水準。

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目的

不法藥物及摻偽檢驗需借助儀器分析並與相關專家學者相互交流討論摻偽檢驗案例，參與研討會可了解近期國際不法藥物檢驗技術發展、參考他國分析方法及收集相關研究資訊，其成果可應用於本署研究檢驗業務，有助於未來研究計畫及相關檢驗業務之辦理。藥物及摻偽分析研究之創新日新月異，為能迅速掌握發展現況，參與研討會與國際先進國家之專家學者一同分享及討論最新發展，實為實際有效之方式。公定分析化學家協會(AOAC)在美國之年會是檢驗分析領域之年度盛事，AOAC 的重點研究領域與本署業務有高度相關性。有鑒於國際間食品及藥品安全事件層出不窮，分析技術日新月異，加上各類儀器設備不斷推陳出新，AOAC 年會成為極佳的交流舞台，各國專家與儀器公司專業人員齊聚，彼此切磋交流，為更理想的藥品及食品檢驗方法而努力。此行主要目的為汲取新知、拓展人脈，發表口頭論文 1 篇及壁報論文 5 篇，藉此增加台灣能見度並展現台灣實力。另於大會安排之「Taiwan Section Business Meeting」發表專題演講，並參加「Joint Asian Section Business Meeting」，與其他亞洲國家分會代表交流互動，建立溝通橋樑。

過程

與會同仁於 9 月 26 日自台北啟程，同日抵達美國洛杉磯，參加 9 月 27 日至 9 月 30 日的第 129 屆 AOAC 年會。今年共有約千名各國檢驗專家學者與會，包括許多先進國家政府單位實驗室代表，場面熱鬧。開幕式由現任 AOAC 理事長 Erick Konings 致詞，並表揚多位得獎人。今年的 keynote speech 是由任職於 Nestle (雀巢)的 NQAC Group Expert - Dr. Richard H. Stadler 帶來精采的演講，題目為「Analytical methods to verify food safety and integrity: needs and challenges」。主講者在演說中闡明食品衛生安全並不是只是設計給製造業者在製造時使用，整個從農場到筷子鏈中，都必須要注意，故需要快速的檢驗分析方法以應付這個目的。在化學殘留分析上，更需要導入目標物分析及非目標物分析以因應持續不斷的摻偽詐欺行為，整個演講內容摘要如下：1. 了解原料的價值跟經濟摻偽(economic adulteration)與產品安全危害的關係；2. 標準化(standardization)及協調化(harmonization)非標的物分析方法(untargeted method)用來偵測污染物及摻偽物質；3. 發展能符合國際規範的分析方法；4. 發展快速及經濟的分析方法；5. 發展國際平台藉以交流資訊。

在接連幾天的年會中，同仁在 Scientific Session 聆聽多場專題演講、瀏覽連續三天不同主題的壁報論文、參觀今年最新分析儀器設備、舉辦「Taiwan Section Business Meeting」與參加「Joint Asian Section Business Meeting」，行程忙碌但成果豐碩。茲將專題演講、壁報論文及台灣分會會議的重點分述於後。

一、專題演講：

今年 AOAC 專題演講之主題包括方法確效規範、動物用藥及化學殘留分析方法、微生物分析方法規範、重金屬、化粧品及色素添加物、統計分析方法、取樣方法探討、中藥(Asian Traditional Medicines, ATM)、膳食補充品(dietary supplements)之 GMP 規範挑戰、過敏原及病原性微生物等檢驗技術，共有 24 個 sessions，每一個 section 又各有 4-9 場演講，整體內容相當多元化，也均與本署檢驗業務息息相關。茲將各 session 主題分類彙整如下表，藉此有助瞭解現今檢驗安全分析領域較熱門的主題。

Analytical approaches to assess food authentically, or are you eating what you think you are?

Wiley award symposium: Innovative approaches to the analysis of veterinary drugs and chemical

contaminants in foods.

Norovirus detection in foods: Current status and roadmap to future validated methods.

Rapid methods for chemical contamination: Cell based assay, spectroscopy, portable devices and beyond.

Hot topics in cosmetics and color additives.

Regulatory microbiological criteria and rapid food micro methods: The European playground.

Analysis of metals and metals speciation in food.

The current impact of mycotoxins on food and dietary supplement safety.

Practical issues arising from statistical design and analysis of method validation studies.

New blood 2015: Developing methods for the detection of chemical analytes and contaminants.

Food allergens – Qua vadis?

Gluten measurement variation: Sampling, subsampling and analysis.

Genomics: Its HERE, now what do we do with it?

Asian traditional medicines (ATM)

LC-MS multi-class or multi-residue methods for analysis of veterinary drug in food.

PDE5 inhibitors in dietary supplements – the USP expert panel experience.

Analytical assessment of food sensory quality: bring two disciplines.

Analytical roundtable for regulators and the regulated: analytical laboratories and the dietary supplements cGMP challenge.

SPICES in the focus-Fraud and allergens. Why spices will remain a truly hot issue.

Analyses of carbohydrates and dietary fiber.

Ten years of the food emergency response network (FERN): integration of federal, state and local laboratories to improve the national food defense and food safety system.

Understanding cannabis and the challenges of cannabis testing laboratories.

Analytical challenges and reporting framework of results in perspective of sound method performance requirements.

Roundtable: progress and remaining challenges in the control of marine biotoxins.

本次年會專題演講主題與本署業務高度相關，主題繁多，於同一時段有三場演講同時進行，同仁僅能參加其中數場，茲將聽到的一些重點整理如下。

(一) 膳食補充品中 PDE-5 抑制物質的檢測(違法壯陽藥物篩檢)

美國 FDA Teresa Cain 談到使用 Ion trap data triggered scanning 及紫外光吸收光譜作為 PDE-5 的分析方法，可以快速篩檢檢體中含有 PDE-5 成分。另 John Edwards 則著重於研究核磁共振(NMR)光譜之應用於 PDE-5 的篩檢，透過 NMR 科技，樣品可以直接進樣分析，不須前處理，大大節省時間。Said Goueli 則是 Pomega 公司的代表，介紹了主要產品 Phosphodiesterase-5-inhibitor Assay 可以使用於非目標物(non-target)PDE-5 篩檢，該產品原理為使用酵素反應原理，針對所有具有 PDE-5 酵素抑制功能的物質做呈色反應，使檢體中具有 PDE-5 抑制功能的物質(壯陽類藥物)能被偵測到，對於非目標物，可再配合層析技術將其純化分離後定性。Anton Bzhelyansky 則描述 USP 對於膳食補充品的規範，上述 PDE-5 inhibitor 篩檢分析之發展，可供本署未來於類緣物研究方向參考。

(二) 化粧品及色素

美國 FDA 針對 14 種合法及不合法色素發展出定量方法，過去針對色素於規範上並沒有要求定量分析，由於目前在藥品及食品上色素使用越來越多，擔心有過量使用問題，因此 FDA 著手研發色素定量分析方法。該方法目前適用於飲料、明膠相關產品及乳製品等，方法定量極限為接近 1 ppm，值得本署參考。另有 2 位美國 FDA 學者討論到刺青顏料相關的檢驗分析，刺青是將刺青顏料注射到皮膚的表皮和真皮層中，刺青顏料必須不能溶解以避免擴散至其他地方，造成圖案模糊，因此刺青顏料是懸浮於溶劑中，通常是甘油、甲醇或是其他溶劑，刺青顏料必須為美國 FDA 公告可使用的合法色素(FD&C)。美國 FDA 認為刺青顏料應屬於化粧品，而顏料裡所含的色素應屬於著色劑添加物，但是並沒有任何一種色素被允許於注射用途而使用於化妝品類，市面上的刺青顏料製造商並沒有明確標示其內容物成分，因此有必要加以檢驗，X-ray diffraction 和 HPLC 等方法可以用來定義這些未知的刺青顏料色素，該方法調查了 30 個市售刺青顏料。此類問題亦值得本署留意。

另美國發生幾起因刺青而感染非結核性抗酸菌(nontuberculous mycobacteria)的病例，FDA 發展了一項 2 步驟的篩檢方法使用於快速偵測皮膚感染的原因。可疑的菌落從刺青顏料中分

離後，經過 2 種不同的 PCR 分析，再由 melting curve analysis。分離物鑑定則採用 2 種不同的 sequencing analysis，方法經過確效。使用選擇性培養基加上 2 步驟的初篩分析，再搭配後續的分類分析，該方法可以有效的鑑定出標的微生物及展現良好的回收率。

(三) 動物用藥及化學殘留分析

三段式四極桿質譜法是目前用來確認分析物的標準方法，該方法採用 1 個母離子及 2 個子離子來確認分析物。由於近十年來分析儀器不斷進步，而分析及確認方法也由以往的單一化合物進階至多重殘留分析，可一次分析數百個化合物。高解析度質譜近年發展快速，適合用來執行多重殘留分析，目前主流有飛行式質譜(TOF)、QTOF、軌道掃描式質譜(Orbitrap)、Q-orbitrap，這些高解析度質譜與傳統 QqQ 三段式四極桿質譜比較時，結論發現母離子的選擇影響分析方法選擇行甚鉅，高解析度質譜若取 1 個子離子時(<5ppm accuracy)其選擇性和傳統 QqQ 相等，似乎沒有改變傳統 QqQ 的必要。本署目前關於動物用藥及農藥殘留分析均使用三段式四極桿質譜法，符合國際潮流。

另外，藉由專題演講得知目前國際間關於動物用藥殘留檢驗之最新發展方向及重要的方法比對試驗。美國 Covance Laboratories Inc.的 Hui Zhao 提到，該實驗室正在開發 UHPLC-MS/MS 方法，可同步定量嬰兒奶粉中 150 種動物用藥，包括各類用藥如 amphenicols, anthelmintics, antinicrobiol growth promoters, antiprotozoals, beta-agonists, coccidiostats 及 antibiotics(包括 beta-lactams, macrolides, quinolones, sulfonamides, tetracyclines 等)。荷蘭食品安全局的 Bjorn Berendsen 提到，歐盟國家包括法國、瑞士及荷蘭等國正在執行一項方法比對試驗，比較不同類型質譜工具對於肌肉、牛乳、尿液及肝臟等基質中動物用藥殘留分析之結果。加拿大食品檢驗署(Canadian Food Inspection Agency)的資深科學家 Joe Boison，在演講中回顧近 30 年來動物用藥檢驗方法發展史，並提到現今檢驗趨勢朝向多重、快速、環保、高感度偵測器之發展，而該署今年正在研擬之檢驗方法是以 LC-QToF 質譜儀分析 17 種抗球蟲藥(anticoccidial drugs)以及其他 129 種動物用藥。

(四) 摻偽分析

由於酒類的高經濟價值，常常發生以經濟利益為目的的偽酒、仿冒酒及摻偽酒，以美國肯德基州為例，2010 年威士忌的產值高達 26 億美元，一些特別的酒，例如：限量酒、陳年酒更是特別容易被仿冒。氣相層析儀搭配火焰離子化偵測器或質譜儀常被使用來分析威士忌及酒中的揮發性化合物，若威士忌中摻有其他來源的酒精則可以透過和真正的威士忌比較其揮發性化合物組成來判斷。這項技術也可應用於製造廠的品質管理上，用來判斷目前的加工方法是否有別或改變產品揮發性成分。該報告使用超高效能液相層析搭配高解析度飛行式質譜

儀，搭配逆相層析管柱用來分析酒中的非揮發性成分，這些成分可以成功地被管柱分開，經過高解析度質譜分析後，可以得到精確分子量，這項技術用來鑑定產品的真偽，可以立即分辨出低價劣品的酒摻雜入高價高品質的酒中。

美國第一件有紀錄的果汁摻假是 80 年代使用高效液相層析(HPLC)來偵測的，但是自從那時起，一些專業的摻假廠商，就懂得使用調配的方式來達到掩蔽摻假的手段，於是分析果汁中氫和碳原子的同位素方法被發展出來鑑定真偽，植物依其行光合作用的方式可以分成兩種類，即 C3 植物和 C4 植物，而 C3 植物和 C4 植物累積的碳同位素不同，因此可以用來判斷果汁中摻雜其他來源的糖或是酸。另一種方式是 90 年代發展出利用多醣(oligosaccharide)的組成分布來判斷，可以用來鑑別果汁中加入糖漿。在歐洲，DNA 鑑定方法已被使用於鑑定柳橙汁摻橘子汁，全美估計約有 10%的橘子汁被加入柳橙汁中而沒有任何標示。最新的鑑別方法可以是使用核磁共振(NMR)來偵測氫元子的訊號，經過 15 分鐘的信號擷取，再由電腦軟體配合統計資訊，直接判斷真偽，並將可能摻假之果汁進一步由其它儀器確認。

茶葉及香料植物在近 20 年來需求量大增，這些作物強調天然、高品質及無汙染，而這些宣稱常常和其產地連結在一起，例如茶葉的產地就含其品質緊緊相連，消費者相信某地方產的茶葉品質特別好，因此，茶葉及香料植物常常有假冒產地的情形發生。感應耦合電漿光譜儀(ICP-OES)可以偵測元素組成(矽、鈉、鎂、鐵、鉀)而找出可能的摻假，當香料植物中含有高量的矽及鈉時，常常發現其摻有低價的香料植物及其他植物。ICP-MS 則可以用來偵測微量重金屬，一些例子中可以發現許多含有高量重金屬例如鉛，常常是摻有鉻化鉛或氧化鉛的摻假香料。

(五) 中藥(Asian Traditional Medicines, ATM)

槲蕨植物的乾草或是萃取物在中藥裡稱為骨碎補原產於中國南部。植物化學家分析骨碎補中的化學成分，找出其主要成分為類黃酮類(flavonoids)、phenylpropanoids 以及 triterpenes 作為強身健骨的藥方，在中醫中主要用於治療骨質疾病，像是骨質疏鬆、骨折等。現代藥學研究中也指出骨碎補萃取物具有刺激骨細胞增生的活性。此研究廣泛的收集市面上的骨碎補萃取物產品進行分析，研究結果指出經過與真實骨碎補萃取物比較，發現市售產品部分含有違法添加物，因此進而開發逆相液相層析搭配光二極體偵測器方法用來偵測實骨碎補萃取物中的二個主要化合物 neoeriocitrin 和 naringin 及進行指紋圖譜分析，此研究結果可以用來確保市售產品的品質，或追蹤不法廠商，促進無摻假產品的品質。

另一位學者則說明使用 HPTLC 用於鑑定草藥的真偽及正確品種，草藥在經過乾燥加工後，其外觀可能會產生變化，若是不小心或是刻意混入其他藥草中，其除了影響藥效之外，

有些植物甚至具有毒性，因此，如何鑑別草藥的真偽是相當重要的。該學者說明利用高效薄層析系統進行草藥品種及摻假鑑別，並展現快速及有效的分析方式。

(六) 口頭發表

方助理研究員受邀在會中以「New Blood 2015: Developing Methods for the Detection of Chemical analytes and Contaminants」議題進行口頭論文發表，題目為「Detection of diethyl yellow used illegally in processed soymilk curd by coupled LC-photodiode array detection and high resolution orbitrap MS」。簡報內容如下：

AOAC Annual meeting & Exposition
May 31-06, Los Angeles CA 2015

FDA

AOAC

Detection of Diethyl Yellow Dye Used Illegally in Processed Soymilk Curd by Coupled LC-Photodiode Array Detection and High Resolution Orbitrap MS

Ming-Chih Fang, Ph.D.
Researcher, Division of Research and Analysis
Taiwan Food and Drug Administration

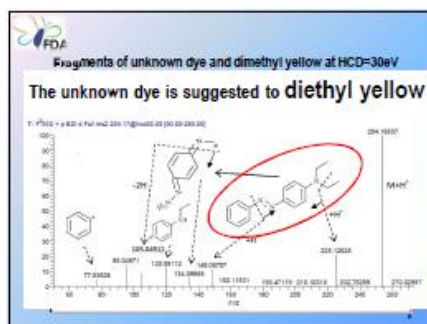
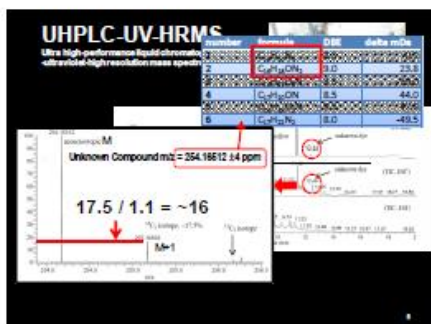
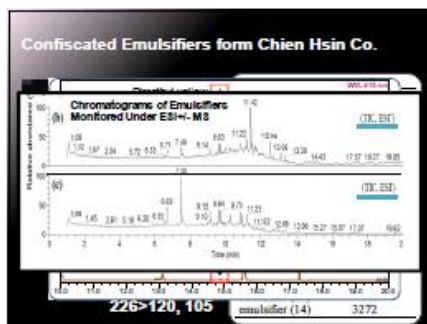
Dimethyl Yellow adulterated in dried bean curd uncovered by Hong Kong authorities

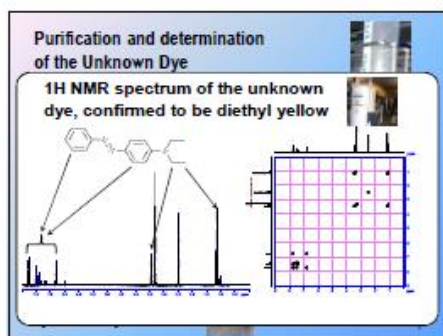
- Formula: C₁₄H₁₅N₃
- Butter yellow
- Liver tumor, carcinogen

CN(C)C1=CC=C(C=C1)/N=C2C=CC(=C2)N

Where was the Dye Come From?

product / additive	dimethyl yellow (mg/kg)
Soy sauce	ND
Seasoning powder	ND
Caramel color	ND
Liquid flavor	ND
square tofu skin	3.8
rectangle deep fried tofu skin	5.0
fried oil	9.2
rectangle deep fried tofu skin emulsifier	1792





二、壁報論文：

今年年會共有 280 篇來自世界各地的壁報論文展示，主題涵蓋藥品及食品安全分析之各領域，應用化學、微生物或分子生物技術檢驗。本署今年發表 5 篇壁報論文，為近年來在各領域之研究成果，主題分別為「Surveillance over 10 years for labeling legislation on genetically-modified food in Taiwan」、「Monitoring of hygiene quality in food produces in Taiwan in 2014」、「Detection of diethyl yellow used illegally in processed soymilk curd by coupled LC-photodiode array detection and high resolution orbitrap MS」、「Quantification of 143 pesticides in foods of animal origin using a modified QuEChERS method combined with LC-MS/MS and GC-MS/MS」及「Development of QuEChERS-based extraction and liquid chromatography-tandem mass spectrometry method for eugenol and tricaine methanesulfonate in fish muscle」，展示期間受到各國學者熱烈之詢問，也藉此機會展現台灣在食品分析領域之水準。

茲將各壁報論文主題分類彙整如下表，有助瞭解現今食品安全分析領域較熱門的主題。

1. Detection and measurement of natural toxins
2. Food nutrition and food allergen
3. General methods, quality assurance and accreditation
4. Authenticity
5. Emerging issues in food safety and security
6. Microbiological methods
7. Analysis of non-foodborne contaminants and residues
8. Botanicals and dietary supplements
9. Performance tested methods

10. Water and wastewater analysis

本次年會壁報主題繁多，茲將一些重點整理如下。

(一)黴菌毒素分析

An improved QuEChERS method for LC-MS stermination of multiresidue mycotoxins in grains

「LC-MS/MS 之 QuEChERS 方法檢驗穀物中多重殘留的黴菌毒素」

該研究以 QuEChERS 方法用於 LC-MS/MS 針對 14 種黴菌毒素，用在稻米、全穀之麵粉、玉米粉及米粉的黴菌毒素分析之進行評估。在這四種物質中，大多數的毒素，包括黃麴毒素 (Aflatoxin)、伏馬鐮孢毒素 (Fumonisin)、赭麴毒素 (Ochratoxin)、T-2 毒素及 HT-2 毒素皆有好的回收率。然而，建議的基質分散固相萃取 (d-SPE) 之淨化方法，只適用於使用高感度的儀器。該研究探討修飾或替代的萃取和淨化條件，並應用於分析穀物樣品中的黴菌毒素。目標為改善回收率及淨化效果，以提供更多的儀器更適合的方法。

(二)過敏原分析

LC-MS/MS detection of peanut and almond allergens in spices. 「利用液向層析串連二級質譜 (LC-MS/MS) 分析香料中花生及杏仁過敏原」

在北美及歐洲因最近研究發現香料中過敏原的存在，因此回收了許多食品，美國 FDA 建議對花生過敏的民眾應避免含有研磨小茴香或小茴香粉末的產品，因部分產品中驗出未標示之花生蛋白，食品標準局(FSA)更發布紅椒之過敏警示，因於 3 項紅椒產品中驗出杏仁蛋白並要求回收，歐洲 RASFF(Rapid Alert System for Food and Feed)入口指出在含有紅椒粉及 Pilli-Pilli powder 的產品中發現含有未標示之花生殘留，民眾知道食品的安全及真實是很重要的，必須發現食品供應鏈中潛在的缺失並採取必要的因應措施以保護消費者，需要正確及可靠的分析方法來監測食品供應鏈及修正錯誤標示，此次研究提供香料中花生及杏仁的檢測方法，將樣品萃取蛋白質後將其還原、烷基化並以胰蛋白酶水解後以逆向液向層析串連二級電噴灑質譜分析，利用 SCIEX QTRAP 4500 MRM 分析以提高偵測之選擇性，每個過敏原至少監測 12 個離子片段 (transitions, 3 transitions for 4 peptides) 以減少基質干擾造成之偽陽性。

Going against the grain-using targeted proteomics for gluten quantification and wheat detection. 「利用目標蛋白質體學(Targeted Proteomics)進行麩質(gluten)定量及小麥檢測」

麩質為小麥、裸麥、大麥及燕麥中一群蛋白質的總稱，乳糜瀉(coeliac disease)為一具基因感受性人中在攝入麩質後引起之小腸免疫疾病，目前針對乳糜瀉或麩質耐受性不良(約 7 千萬)的病人唯一治療方法僅有終生避免攝取含麩質之食物，因此無麩質食品非常常見，但現今方法因

使用非特異性抗體偵測而會產生交叉反應，故很難正確偵測無麩質食品中是否真不含麩質，加工處理食品經蛋白質修飾及水解使偵測更為困難，針對 16 種重要麥片利用 SDS-PAGE、西方墨點法及 LC-MS/MS 分析全蛋白質體，以建立麩質體(gluteome)並選擇麩質和小麥之特異性肽標籤以進行質譜定量分析，小麥特異性肽標籤可於 14 種小麥中測出並共佔了小麥基因變異性的 80%，可以幫助麵粉中小麥污染的檢測，在大麥啤酒中發現高量的麩質水解，此結果與 ELISA 分析呈現低麩質之結果一致，大麥啤酒中的水解殘餘片段產生 ELISA 麩質分析中劑量性抑制，因此以質譜方式建立麩質及其水解物精確定量分析方法是必須的。

(三)植物成分分析

Analysis of distribution of phytochemicals in biological samples by using MALDI imaging mass spectrometry 「利用基質輔助雷射脫附游離影像質譜儀 (MALDI Imaging Mass Spectrometry)分析生物樣品中植物化學成分分布」

具生物活性的化學物質之空間分佈在闡述生物或藥理作用機制上是不可缺少的，像是生物利用率和生物轉化。該研究開發了一種原位無標記成像技術，應用於多酚類的生物轉化之可視化。方法則建立了基質輔助雷射脫附游離質譜影像技術 (MALDI-mass spectrometry imaging technique)，可於哺乳動物組織中直接觀察沒食子兒茶素-3-沒食子酸酯 (epigallocatechin-3-O-gallate, EGCG)。離子化用於 MALDI-MS 之分析物，需要最佳的基質。該研究為木麻黃素 (strictinin)及槲皮素 (quercetin)進行了 40 個潛在的基質篩選，以基質輔助雷射脫附游離飛行質譜儀 (MALDI-TOF-MS)在正電及負電模式下進行分析。並以餵食木麻黃素 (strictinin)或槲皮素 (quercetin)之小鼠的腎臟的冷凍切片，來進行植化素的檢測。植化素並非以傳統的 MALDI-TOF-MS 來檢測，而改以 MALDI-QIT-TOF-MS 進行。相同的切片在相同的基質下進行 MALDI 分析。從有給藥的腎臟切片中得到 m/z 633 或 m/z 301 之離子訊息。基質塗層是利用一種新的昇華方法 iMLayer 進行。這讓槲皮素 (quercetin)的第 2 階段代謝物可視化。利用這種影像技術，發現木麻黃素 (strictinin)及槲皮素 (quercetin)的第 2 階段代謝物在腎臟腔室中 (腎盂、腎髓質及腎皮質)的分佈位置模式不同，特別是在腎盂中的含量最高。該結果意味著，在經口攝取之後，被吸收的植化素或許很快地被排出體外。此研究呈現了高感度的 MALDI-MSI 技術，用於哺乳動物組織中植化素之可視化。

(四)色素分析

Simple quality control qualification of FD&C colors from sport drinks and fruit juice beverages using automated solid phase extraction and a portable spectrometer. 「使用自動固相萃取以及攜帶式光譜儀對運動飲料以及果汁飲料當中的色素做簡易的品質控管」

美國 FDA 調整了使用在食品、化粧品、藥品以及醫療器械當中的顏色添加劑的規範。在聯邦食品、藥品和化粧品法案當中任何顏色添加劑都需要是合法的。這些條款由 FDA 所監督並且通過美國聯邦法規，FDA 也釋出新的通過認證之顏色添加劑以及其使用用途的訊息。美國聯邦法規 21 章第 74 條中有九種合法色素在美國是可以被添加在食物當中的。每個可以添加在食物、藥物以及化粧品(FD&C)的色素在美國需要通過一連串全面性的安全測試才可以被使用。色素在運動飲料或是果汁飲料中可以創造出視覺上效果使得顏色符合其口味。許多運動飲料以及果汁使用不同濃度的藍色一號和黃色五號來調出適合萊姆、西瓜或是一些熱帶口味的顏色。該研究展示了如何利用 SmartPrep Extractor 的自動化固相萃取來有效分離和純化運動飲料和果汁當中的藍色一號以及黃色五號色素，以及使用攜帶式的光譜儀的定性分析來確定色素是否存在。

(五)成分分析

Characterization of a new total nutrient standard reference material: protein drink mix. 「營養素標準參考物質:蛋白質混合飲料」

運動營養是一個 240 億美元的產業，而且補充蛋白質的方式越來越常見甚至超過了健身。販賣蛋白粉在 2015 年預計可以到達 45 億，運動員的目標是透過增加蛋白質的攝取來提高其表現，而非運動員的目的則是提高其整體健康。根據蛋白粉產品上的標示，不管是作為食品或是膳食補充品的含量都是不固定的，且消費者認為其產品的營養含量是正確的，而那些已知或未知的成分通常都被隱蔽起來。為了加強蛋白粉以及其混合飲料之監管和實驗室品質保證，美國國家標準與技術局(NIST)發展了蛋白質混合飲料的認證參考物質(SRM)。這標準品含有營養元素、維他命、膽固醇、胺基酸以及脂肪酸。除了提供蛋白質補充品的製造商以及實驗室的檢測外，SRM3252 對於食品行業也是一個適合而且經過認證的認證參考物質。

三、參加台灣分會會議及亞洲聯合分會會議：

AOAC 台灣分會(Taiwan Section)成立於 2002 年，當時由藥檢局廖俊亨局長、孫慈悌副局長及美國 FDA 的周家璜博士等人積極促成，是台灣在此領域國際活動上之重要成果。目前 AOAC Sections Worldwide 包括 Europe Section、India Section、Japan Section、China Section、Latin American-Caribbean Section、Lowlands Section (Belgium, Luxembourg and The Netherlands)、Taiwan Section 及 Thailand Section 等 8 個分會，每年 AOAC 年會皆有專屬時段及會議室供 AOAC 台灣分會舉辦「Taiwan Section Business Meeting」，此為台灣戮力多年經營之成果。本年由台灣分會何國榮理事長及同仁舉辦台灣分會會議，本次共有約 30 人參加，多

為任職於美國官方及民間機構的台灣人。在一個小時的時間內皆以英語進行，理事長先介紹台灣分會今年舉辦的活動及成果，後由方助理研究員進行專題演講，分享台灣近年發生的食安事件及本署研發之分析檢驗方法，接著大家就檢驗技術及熱門檢驗話題進行熱烈討論，就各自專業領域交流，場面熱鬧，與會專家皆肯定台灣在近年食安事件發生時能夠及時研擬與國際接軌之檢驗方法。現場並備有台灣茶、月餅及鳳梨酥，充滿濃濃的台灣味，與會者皆表示明年還要來參加。除了台灣分會會議圓滿成功之外，同仁也參加「**Joint Asian Section Business Meeting**」，與包括日本、中國、印度及泰國等分會之理事長及會員交流互動，討論熱門檢驗技術議題，建立聯絡管道。

專題演講之內容以台灣在民國 100 年發生的順丁烯二酸酐化製澱粉事件開場，不肖業者以只允許工業使用之順丁烯二酸酐化製澱粉違法製造粉圓等加工食品販售，事件之經過包括如何研發檢驗方法及市售產品稽查等。接下來以 102 年發生的大統長基公司違法添加銅葉綠素於食用油中混充橄欖油為例子，本署積極開發檢驗方法，使用 HPLC-UV 及 HPLC-MS/MS 方法配合固相萃取匣可以有效分析橄欖油中銅葉綠素殘留。關於非標的物檢驗方面則以塑化劑和豆乾中發現二乙基黃為例，我國出口的豆干在香港被檢驗出含有違法色素二甲基黃，經過本署積極調查，發現其來源為乳化劑，並從其中另發現另一違法未知色素，經過同仁不斷調查分析，進一步從檢體中純化出此未知色素，後續由高解析度質譜及核磁共振光譜確認此未知色素為二乙基黃，口頭發表之簡報如下：

AOAC Annual Meeting & Exposition
Sep 27-30, Los Angeles CA 2013

Taiwan Section Business Meeting
Hot Food Safety Issues In Taiwan

Ming-Chih Fang, Ph.D.
Researcher, Division of Department of Research and Analysis
Taiwan Food and Drug Administration

中華民國食品藥物管理署
Taiwan Food and Drug Administration

Over 200 diseases are caused by unsafe food containing harmful bacteria, parasites, viruses, **chemical** substances.

2 million It is estimated that two million **deaths** occur every year from contaminated food or drinking water.

Are you expecting me?

World Health Organization

Hot Food Safety Issues in Taiwan
Target Analysis

2011 Phthalate Plasticizer in drinks, jam, jelly, capsule food

2012 ND or ND

2013 Metals, Antipyrine, Methyl Starch, Quabampyril in China Oil

2014 Dyes in Tofu Products & Oil Adulteration

2015 MgCO₃ Recycled Vinegar

Non-target Analysis

Bubble tea, Pearl tea

chemical modified starch

- chewy
- firm texture
- anti-shear
- anti-freezing
- stable
- anti-retrogradation

Examples of Modified Starches

Starch acetate

Acetic anhydride

Starch acetate

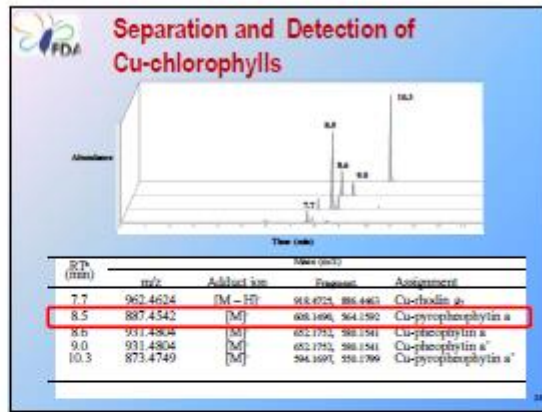
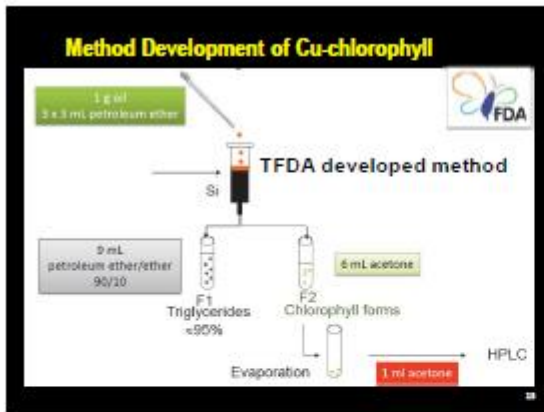
Starch acetate

Maleic Anhydride Modified Starch

- Low gelatinization temp.
- Stable
- High viscosity
- Improve texture quality

Pathway of the esterification and hydrolysis of starch maleate

(Tse et al., JFDA 2014)



食品安全 責任安心

Jan. 27, 2014. European chemist expert delegation TFDA Laboratory Visit and Oil Event Discussion Meeting

March 11, 2004. Meeting of Chemists on Method of Analysis for Olive Oils and Olive Pomace Oils.

Agreement:
The IOC chemistry experts will set up a ring-test to the method developed by the Taiwan experts on several pomace oils.

衛生福利部
食品藥物管理署 歡迎至本署網站查詢更多資訊 <http://www.fda.gov.tw/>

Hot Food Safety Issues in Taiwan

Practical Application on Nontarget Analysis

2011

Phthalate Plasticizer in drinks, jam, jelly, capsule food

Dyes in Yofu Products

Where's Waldo / Target ?

Characteristic Boy

Characteristic

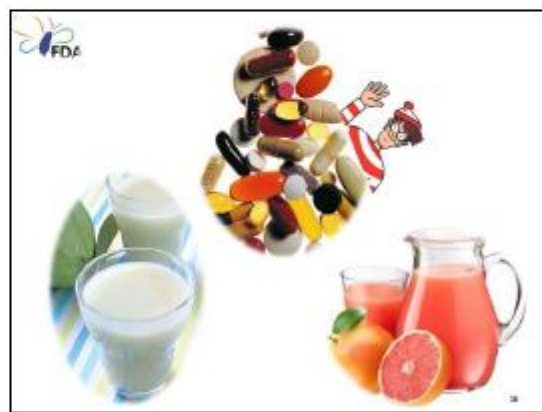
Hat ? ? ?

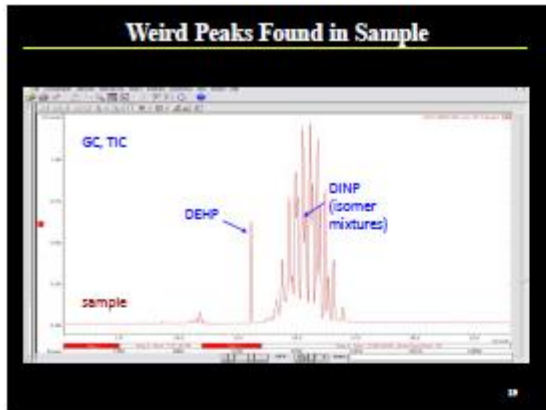
Glasses ? ? ?

Red-white stripes

Brown hair

Non-target Analysis





Why Phthalates Present in Food?

Plasticizer: Bis(2-ethylhexyl) phthalate (DEHP)

Probiotic supplement

600 ppm ? unreasonable

Chemical structure of Bis(2-ethylhexyl) phthalate (DEHP) is shown. A probiotic supplement is also depicted. The text indicates that 600 ppm of DEHP is unreasonable.

Emulsifier, Clouding Agent

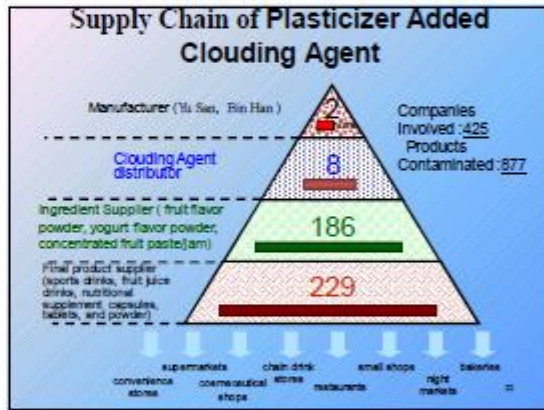
Diglyceride

DINP, DEHP

Glycerol, relatively unstable

phthalate, very stable

Chemical structures of Diglyceride, DINP, and DEHP are shown. Diglyceride is labeled as 'Glycerol, relatively unstable' and phthalate is labeled as 'phthalate, very stable'.



Dimethyl Yellow adulterated in dried bean curd uncovered by Hong Kong authorities

- Formula: C₁₄H₁₅N₃
- Butter yellow
- Liver tumor, carcinogen

Chemical structure of Dimethyl Yellow is shown. Images of dried bean curd products are also included.

Dimethyl Yellow in the Ingredients of a Tofu Product



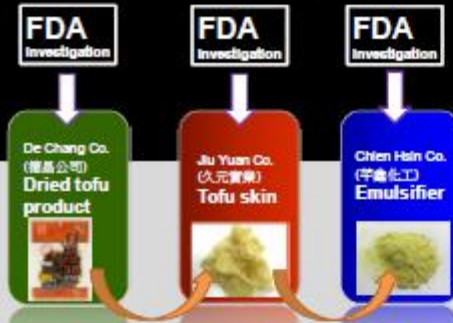
ingredient	dimethyl yellow (mg/kg)
soy sauce	ND*
seasoning powder	ND
caramel color	ND
liquid flavor	ND
deep fried tofu skin	8.8
sugar	ND
black pepper	ND

Where was the Dye Come From?



product / additive	dimethyl yellow (mg/kg)
square tofu skin	3.8
rectangular deep fried tofu skin	5.0
fried oil	9.2
striped deep fried tofu skin	520
emulsifier	1792

FDA Traced Banned Dye Back to Firms



Confiscated Emulsifiers from Chien Hsin Co. (千鑫化工)

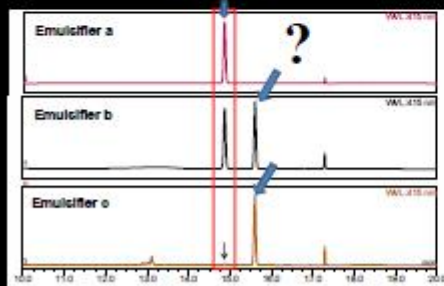


	dimethyl yellow (mg/kg)
emulsifier (1)	1368
emulsifier (2)	112800
emulsifier (3)	ND
emulsifier (4)	13316
emulsifier (5)	40
emulsifier (6)	95604
emulsifier (7)	928
emulsifier (8)	ND
emulsifier (9)	43040
emulsifier (10)	ND
emulsifier (11)	ND
emulsifier (12)	3680
emulsifier (13)	47760
emulsifier (14)	3272

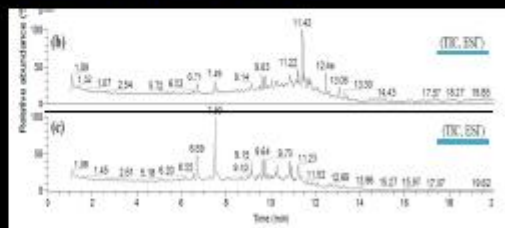
By LC/MS/MS
226>120, 105

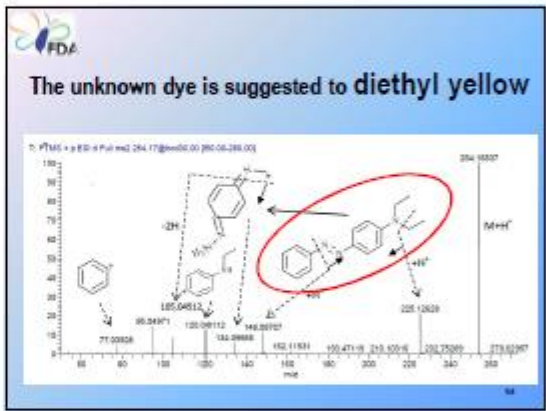
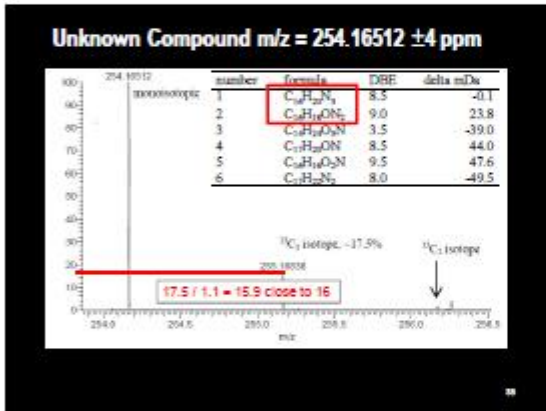
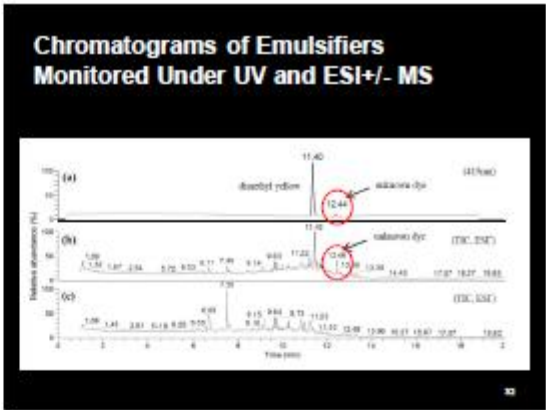
Chromatograms of Emulsifiers

Dimethyl yellow



Chromatograms of Emulsifiers Monitored Under ESI+/- MS





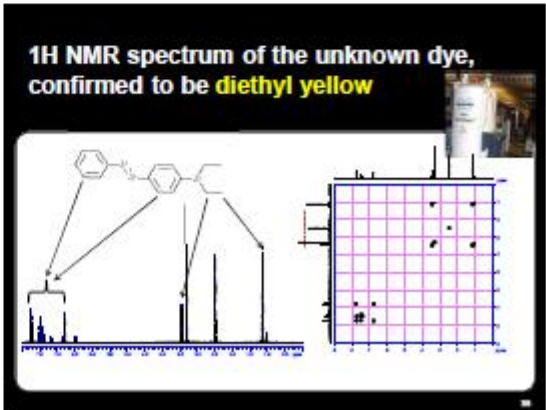
Purification of the Unknown Dye

GPC
gel permeation chromatography

silica gel chromatography

recrystallization

1.9 x 30 cm, 5mL/min
Cyclohexane/ethyl acetate





Emulsifiers

Emulsifier No.	Approval status (No./Yes)	Approval status (No./Yes)
Emulsifier 1	2466	87161
Emulsifier 2	112608	142
Emulsifier 3	907	387168
Emulsifier 4	123254	82322
Emulsifier 5	40	83428
Emulsifier 6	95304	142
Emulsifier 7	828	88812
Emulsifier 8	907	182796
Emulsifier 9	68260	25486
Emulsifier 10	907	28412
Emulsifier 11	907	142
Emulsifier 12	9080	48428
Emulsifier 13	87792	24958
Emulsifier 14	8272	142

Tofu products

Code	Product	Approval status (No./Yes)	Approval status (No./Yes)
10001	Soft Tofu (silken)	11	28.4
10002	Soft Tofu (silken)	60	142
10003	Soft Tofu (silken)	11.3	142
10004	Soft Tofu (silken)	11.4	142
10005	Soft Tofu (silken)	3	38.2
10006	Soft Tofu (silken)	60	142
10007	Soft Tofu (silken)	118	142
10008	Soft Tofu (silken)	218	142
10009	Soft Tofu (silken)	264	142
10010	Soft Tofu (silken)	176	11.4
10011	Soft Tofu (silken)	248	142
10012	Soft Tofu (silken)	268	142
10013	Soft Tofu (silken)	288	142
10014	Soft Tofu (silken)	3	21.4
10015	Soft Tofu (silken)	180	142
10016	Soft Tofu (silken)	140	142
10017	Soft Tofu (silken)	148	142





Thank you for your attention

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心得及建議

心得

此次口頭論文發表有不錯的效果，美國食品藥物管理局 Deborah Nebenzahl 從事食品中著色劑檢驗研究，對於同仁發表的主題非常有興趣，除了熱烈討論外，也留下聯絡方式，日後有檢驗資訊互通合作的機會。而 Texas State Chemist 的 Susie Y. Dai 博士則推薦同仁投稿於他們的期刊(Journal of Regulatory Science)中。建議往後同仁參加研討會時也能爭取發表口頭論文的機會，能見度及參與感會比張貼壁報論文高很多。於台灣分會會議時，由於有專題演講，使得參與台灣分會之旅外台灣人能就相關議題討論，會議進行非常熱絡，透過提問與回答，加上互相討論，即使會議結束後許多與會人士仍沒離開，繼續交換名片及討論相關議題，提供了一個非常棒的擴展人際交流場合。研討會中收集了最新國際檢驗資訊及最新國際關切事務，能了解國外目前在關心什麼，例如合法著色劑的定量分析(過去只有定性，並無規定使用量)。另外，在儀器方面，雖然有報告指出二級低解析度質譜仍舊為目前研究使用之儀器主流，但高解析度質譜已漸漸普及，未來確認分析物的標準也許會改變得更嚴謹。

建議

- (一) AOAC 年會主題與本署業務高度相關，且著重在方法開發、確效評估等，學習成果可立即應用在本署檢驗工作上，值得持續派員參加此會議。
- (二) 分析檢驗之趨勢，已全面進展到質譜分析，高解析度質譜儀(high resolution mass)也應用於藥品及食品檢驗，非標的物分析技術(non-target)日受重視，值得本署參考增加非標的物檢驗分析之研究。
- (三) 建議往後同仁參加研討會時也能爭取發表口頭論文的機會，能見度及參與感會比張貼壁報論文高很多。
- (四) 此行與各領域國際級專家建立友好關係，除了見到最近一年曾邀請來台演講的美國藥典(USP)專家 Dr. Anton Bzhelyansky 及 Jeffrey Moore、歐洲 Eurofins 檢驗專家 David Hammond、瑞士食品控制局專家 Anton Kaufmann 之外，也結識食品風味專家 Dr. Roger J. Bleiler 及 Dr. Ian Ronningen、美國農業部食品安全專家 Oliver Ou、質譜專家 Bjorn Berendsen 及 Gareth Cleland、化學物質鑑定專家 Marianita Perez-Gonzalez 等人，都是各領域頂尖專家。日後可邀請來台演講，分享最新研究成果。

照片



會場入口



儀器商展示區



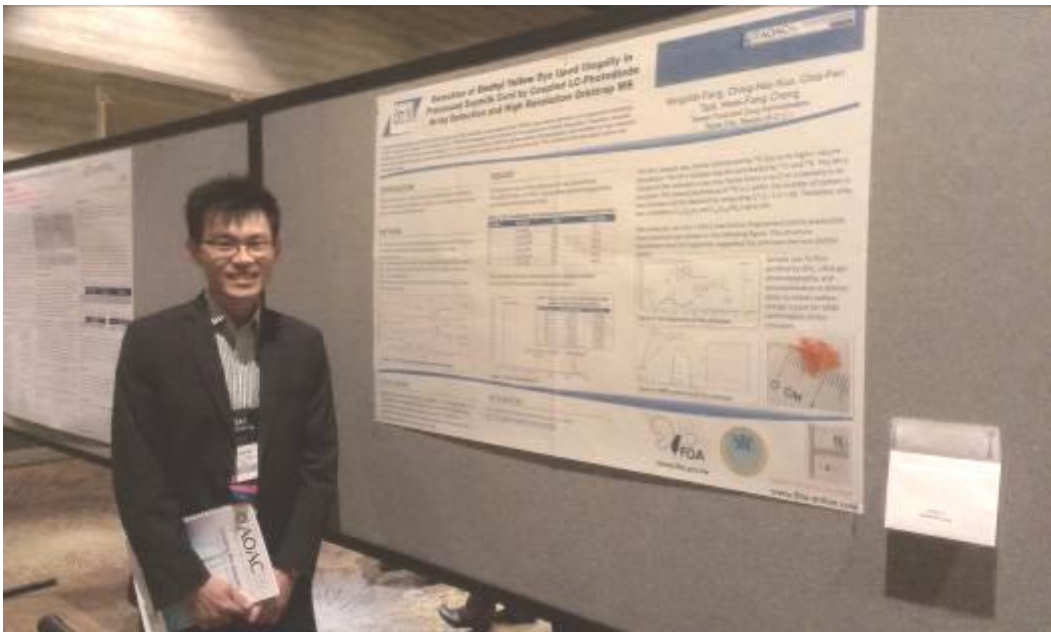
壁報論文展示區



同仁發表口頭論文



壁報論文發表



壁報論文發表



Taiwan Section Business Meeting



(AOAC 亞洲分會聯合會議)

SCHEDULE AT A GLANCE

SATURDAY, SEPTEMBER 26, 2015

9:00am – 5:00pm	Level 2 Reg Area	Registration Open
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SUNDAY, SEPTEMBER 27, 2015

7:30 am – 7:30pm	Level 2 Reg Area	Registration Open
1:00pm – 4:30pm	Palos Verdes	TOLM Training Session: Method Development Done Right so Method Validation is Light
1:00pm – 4:30pm	San Gabriel	Symposium: Analytical Approaches to Assess Food Authenticity, or Are You Eating What You Think You Are?
1:00pm – 6:00pm	San Pedro	Expert Review Panel – Microbiology Methods
6:30pm – 9:30pm	CA Ballroom	Exhibit Hall Grand Opening & President's Welcome Reception

MONDAY, SEPTEMBER 28, 2015

7:00am – 8:00am	Santa Monica A	TDRM Executive Committee Meeting
7:30am – 5:00pm	Level 2 Reg Area	Registration Open
8:00am – 8:30am	San Bernardino	Exhibitor/Partner Presentation: SCIEX
8:15am – 10:15am	San Pedro	AOAC INTERNATIONAL Board of Directors Meeting
9:00am – 9:30am	San Bernardino	Exhibitor Presentation: ANKOM Technology
9:15am – 10:15am	Beaudry B	Latin America Section Business Meeting
10:00am – 10:30am	San Bernardino	Exhibitor/Partner Presentation: Pickering Laboratories
10:00am – 10:30am	Catalina Foyer	Continental Breakfast <i>L3</i>
10:30am – 12:00pm	Catalina	Keynote Address and Awards Ceremony <i>L3</i>
12:00pm – 1:00pm	CA Ballroom	Poster Author Presentations
12:00pm – 5:00pm	CA Ballroom	Exhibit Hall Open
12:00pm – 5:00pm	CA Ballroom	Poster Presentations: Detection and Measurement of Natural Toxins, Food Nutrition and Food Allergens, and General Methods, Quality Assurance and Accreditation
12:15pm – 12:45pm	San Bernardino	Exhibitor Presentation: Phenomenex
1:00pm – 1:30pm	Santa Anita	H.W. Wiley Award Address
1:30pm – 3:00pm	Santa Anita	Wiley Award Symposium: Innovative Approaches to the Analysis of Veterinary Drugs and Chemical Contaminants in Foods
1:30pm – 3:00pm	Santa Barbara	Symposium: Norovirus Detection in Foods: Current Status and Roadmap to Future Validated Methods <i>lobby</i>
1:30pm – 3:00pm	San Gabriel	Symposium: Rapid Methods for Chemical Contamination – Cell Based Assay, Spectroscopy, Portable Devices and Beyond
1:30pm – 7:30pm	San Pedro	Expert Review Panel – Fertilizer Methods
3:00pm – 3:30pm	CA Ballroom	Refreshment Break
3:00pm – 3:30pm	San Bernardino	Exhibitor Presentation: Thomson Instrument Company
3:30pm – 5:00pm	Santa Anita	Symposium: Hot Topics in Cosmetics and Color Additives <i>lobby</i>

3:30pm – 5:00pm	Santa Barbara	Symposium: Regulatory Microbiological Criteria and Rapid Food Micro Methods – The European Playground
3:30pm – 5:00pm	San Gabriel	Symposium: Analysis of Metals and Metals Speciation in Food
5:00pm – 5:30pm	San Bernardino	Exhibitor Presentation: Food Safety Solutions, Inc./Food Microbiological Laboratories, Inc.
5:00pm – 6:30pm	Plaza Pool Deck	New Member Welcoming Reception
5:00pm – 6:30pm	Santa Monica C	ALACC Meeting
5:00pm – 7:00pm	Hollywood Ballroom	Chemical Contaminants and Residues in Food Community Meeting
5:00pm – 7:00pm	Palos Verdes	Cosmetic and Color Additives Meeting
5:00pm – 7:30pm	Santa Monica A	Marine and Freshwater Toxins Community Meeting
6:00pm – 7:00pm	San Fernando	Taiwan Section Business Meeting
6:00pm – 7:00pm	Santa Monica B	Japan Section Business Meeting
6:30pm – 7:30pm	Beaudry B	Reception for TOLM Members, co-sponsored by Microbiologics
6:30pm – 7:30pm	Santa Monica D	Central Section Business Meeting
7:00pm – 8:00pm	Santa Monica B	Joint Asian Sections Business Meeting

TUESDAY, SEPTEMBER 29, 2015

7:15am – 8:15am	Catalina	Exhibitor/Partner Presentation: Waters Corporation
7:30am – 5:00pm	Level 2 Reg Area	Registration Open
7:45am – 8:15am	Lower Level Foyer	Refreshment Break
8:15am – 9:45am	Santa Anita	Symposium: Oral Posters from Dietary Supplements and Botanicals
8:15am – 9:45am	San Gabriel	Symposium: The Current Impact of Mycotoxins on Food and Dietary Supplement Safety
8:15am – 9:45am	Santa Barbara	Symposium: Practical Issues Arising from Statistical Design and Analysis of Method Validation Studies
8:30am – 5:00pm	San Fernando	SPIFAM Expert Review Panel
9:00am – 11:00am	Beaudry B	Water/Wastewater Community Meeting
9:45am – 10:15am	San Bernardino	Partner Presentation: Covance Laboratories, Inc.
10:00am – 10:30am	CA Ballroom	Refreshment Break
10:00am – 12:00pm	Beaudry A	Committee on Statistics Meeting
10:00am – 5:00pm	CA Ballroom	Poster Presentations: Analysis of Foodborne Contaminants and Residues, Authenticity, Cosmetics and Color Additives, Emerging Issues in Food Safety and Security, and Microbiological Methods
10:00am – 5:00pm	CA Ballroom	Exhibit Hall Open
10:15am – 11:45am	Santa Anita	TDRM Symposium: Use of CRMs and/or RMs in Method Validation and Maintaining Accreditation According to ISO/IEC 17025
10:15am – 11:45am	San Gabriel	Symposium: New Blood 2015 – Developing Methods for the Detection of Chemical Analytes and Contaminants
10:15am – 11:45am	Santa Barbara	Symposium: Food Allergens – Qua Vadis?
11:45am – 1:15pm	Santa Monica B	Contaminants Subgroup Meeting-Veterinary Drugs

SCHEDULE AT A GLANCE

12:00pm – 1:00pm	CA Ballroom	Poster Author Presentations
12:00pm – 1:00pm	Catalina	Exhibitor/Partner Presentation: Agilent Technologies
12:30pm – 2:30pm	San Pedro	Committee on Sections Meeting
1:00pm – 1:30pm	San Bernardino	Exhibitor/Partner Presentation: RIKILT – Institute of Food Safety; Sponsored by Thermo Scientific
1:00pm – 2:30pm	Los Feliz	Agricultural Materials Community Meeting
1:00pm – 4:00pm	Palos Verdes	AOAC Research Institute Advisory Council Meeting
1:30pm – 2:30pm	Santa Monica A	TDLM Executive Committee Meeting
1:30pm – 3:00pm	Santa Monica B	Contaminants Subgroup Meeting–Metals
2:00pm – 2:30pm	CA Ballroom	Refreshment Break
2:00pm – 2:30pm	San Bernardino	Exhibitor/Partner Presentation: Shimadzu Scientific Instruments
3:00pm – 4:30pm	Santa Barbara	Symposium: Gluten Measurement Variation – Sampling, Subsampling and Analysis
3:00pm – 4:30pm	San Gabriel	Symposium: Genomics – It's HERE, Now What Do We Do with It?
3:00pm – 4:30pm	Santa Anita	TDRM Workshop: How Do I Set Up a Proper Inter Laboratory Comparison with Testing Materials that I Have Prepared Myself?
4:30pm – 5:00pm	San Bernardino	Exhibitor Presentation: Horizon Technology Inc.
4:30pm – 6:00pm	Wilshire G	Membership Committee Meeting
4:30pm – 6:00pm	Santa Monica B	Contaminants Subgroup Meeting–Environmental and Emerging Contaminants
4:30pm – 7:30pm	San Pedro	Mycotoxin Community Meeting
4:30pm – 7:30pm	Los Feliz	Editorial Board Meeting
4:45pm – 6:45pm	Catalina	Food Allergens Community Meeting
5:00pm – 6:00pm	Beaudry B	TDRM Members Meeting
5:00pm – 6:30pm	Santa Monica C	Europe Section Executive Committee Meeting
5:30pm – 6:00pm	San Bernardino	Exhibitor Presentation: Bruker Optics, Inc.
6:00pm – 7:00pm	Palos Verdes	TDRM Members Reception, co-sponsored by Silliker, Cerilliant, and Synutra Pure
6:15pm – 7:45pm	Santa Monica B	Contaminants Subgroup Meeting–Pesticides
6:30pm – 7:30pm	Beaudry A	China Section Business Meeting

WEDNESDAY, SEPTEMBER 30, 2015

7:30am – 8:00am	San Bernardino	Exhibitor Presentation: U.S. Pharmacopelal Convention (USP)
7:45am – 8:15am	Lower Level Foyer	Refreshment Break
8:00am – 10:00am	Beaudry B	Expert Review Panel for Proprietary Food Allergens – Gluten
8:00am – 12:00pm	Level 2 Reg Area	Registration Open
8:15am – 9:45am	Santa Anita	Symposium: Asian Traditional Medicines (ATM)
8:15am – 9:45am	San Gabriel	Symposium: LC-MS Multi-Class or Multi-Residue Methods for Analysis of Veterinary Drug in Food
8:15am – 9:45am	Santa Barbara	Symposium: PDES Inhibitors in Dietary Supplements – the USP Expert Panel Experience

9:45am – 10:15am	San Bernardino	Exhibitor Presentation: LGC Standards
10:00am – 10:30am	CA Ballroom	Refreshment Break
10:00am – 12:00pm	Beaudry A	AOAC Research Institute Board of Directors Meeting
10:00am – 5:00pm	CA Ballroom	Poster Presentations: Analysis of Non-Foodborne Contaminants and Residues, Botanicals and Dietary Supplements, Performance Tested Methods SM , and Water and Wastewater Analysis
10:15am – 11:45am	Santa Barbara	Symposium: Analytical Assessment of Food Sensory Quality: Bridging Two Disciplines
10:15am – 11:45am	San Gabriel	Analytical Roundtable for Regulators and the Regulated: Analytical Laboratories and the Dietary Supplements cGMP Challenge
10:15am – 11:45am	Santa Anita	Symposium: SPICES in the Focus – Fraud and Allergens. Why Spices Will Remain a Truly Hot Issue
11:45am – 1:00pm	Beaudry B	Technical Programming Council Meeting
12:00pm – 12:30pm	San Bernardino	Exhibitor Presentation: Wyatt Technology Corp.
12:00pm – 1:00pm	CA Ballroom	Poster Author Presentations
1:00pm – 2:30pm	Santa Barbara	Symposium: Analyses of Carbohydrates and Dietary Fiber
1:00pm – 2:30pm	San Gabriel	Symposium: Ten Years of the Food Emergency Response Network (FERN) – Integration of Federal, State and Local Laboratories to Improve the National Food Defense and Food Safety System
1:00pm – 2:30pm	Santa Anita	Symposium: Understanding Cannabis and the Challenges of Cannabis Testing Laboratories
2:30pm – 3:00pm	CA Ballroom	Refreshment Break
2:30pm – 3:30pm	Huntington Suite 316B	Meet Your Board of Directors
3:00pm – 4:30pm	San Gabriel	Symposium: Analytical Challenges and Reporting Framework of Results in Perspective of Sound Method Performance Requirements
3:00pm – 4:30pm	Santa Barbara	Roundtable: Progress and Remaining Challenges in the Control of Marine Biotoxins
3:00pm – 4:30pm	Santa Anita	Symposium: AOAC INTERNATIONAL Stakeholder Panels Update – ISPAM, SPADA, SPOS, SPIFAN, and SPSFAM
4:30pm – 6:00pm	Palos Verdes	AOAC INTERNATIONAL Business Meeting
8:00pm – 11:00pm	Hollywood Ballroom	Annual Meeting Closing Reception

THURSDAY, OCTOBER 1, 2015

8:30am – 12:00pm	Santa Anita C	Food Industry Analytical Chemists Share Group Meeting
10:00am – 6:00pm	San Fernando	Official Methods Board Meeting
1:00pm – 5:00pm	Santa Anita C	Juice and Juice Products Meeting

Detection of Diethyl Yellow Dye Used Illegally in Processed Soy milk Curd by Coupled LC-Photodiode Array Detection and High Resolution Orbitrap MS



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INTRODUCTION

When we started to make clear of the adulteration of dimethyl yellow in processed soy milk curd (tofu), an unexpected unknown dye was discovered additionally.

METHODS

In order to find the unknown dye, we coupled an HPLC-PDA and an HRMS to locate the unknown dye peak in the mass chromatograms.

PDA monitored in the visible light range efficiently indicated the unknown dye peak out of near one hundred peaks with two mass chromatograms. This technique pointed out the peak at RT=12.46 [Fig. 1 b] was the unknown dye.

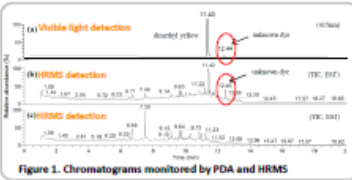


Figure 1. Chromatograms monitored by PDA and HRMS

RESULTS

The accurate mass of the unknown dye was found to be 254.16512 in [M+H]⁺ form. The possible element composition was listed in the following Table.

number	formula	DBE	delta mDa
1	C ₁₂ H ₁₀ N ₂	8.5	-0.1
2	C ₁₂ H ₁₀ ON	9.0	-29.8
3	C ₁₂ H ₁₀ O ₂ N	9.5	-59.0
4	C ₁₂ H ₁₀ ON	8.5	44.0
5	C ₁₂ H ₁₀ O ₂ N	9.5	47.6
6	C ₁₂ H ₁₀ N ₂	8.0	-49.5

The unknown may be elucidated by the relative isotopic abundance (RIA) as shown in following figure.

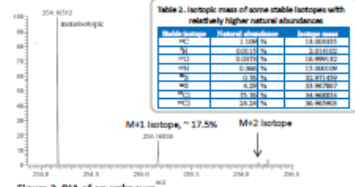


Figure 2. RIA of an unknown

The M+1 isotope was mostly contributed by ¹³C due to its higher natural abundance. The M+2 isotope may be contributed by ³⁷Cl and ³⁵S. The M+2 isotope in the unknown is too low, hence there is no Cl or S element in its structure. The natural abundance of ¹³C is 1.109%, the number of carbon in the unknown can be obtained by computing 17.5 / 1.1 = 16. Therefore, only two candidates (C₁₆H₁₀N₂ and C₁₆H₁₀ON) were left.

The molecular ion m/z = 254.2 was further fragmented and its production mass spectrum was shown in the following figure. The structure elucidation from the fragments suggested the unknown dye was diethyl yellow.

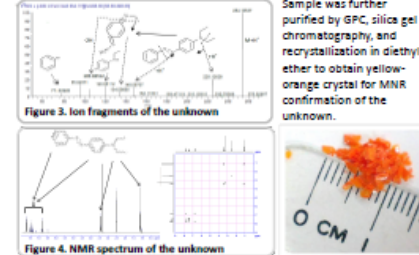


Figure 3. Ion fragments of the unknown

Figure 4. NMR spectrum of the unknown

CONCLUSIONS

Diethyl Yellow was found in the ingredient of processed tofu. This is the first time that diethyl yellow has reported in foods. Food manufacturing demands a reliable source of ingredients. Therefore, food safety and sanitation checks may be required for an ingredient before being used in food.

REFERENCES

Food Additives and Contaminants: Part A. 2015
DOI: 10.1080/19440049.2015.1055830



Open Access Journal
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Quantification of 143 Pesticides in Foods of Animal Origin Using a Modified QuEChERS Method Combined with LC-MS/MS and GC-MS/MS

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²Taiwan Agricultural Chemicals and Toxic Substances Research Institute, Council of Agriculture, Taichung, Taiwan

Abstract

In this method, foods of animal origin were extracted by acetonitrile containing 1% of acetic acid and salting out with anhydrous magnesium sulfate and sodium acetate. After centrifugation, the buffered acetonitrile extract was cleaned up via clean-up powder containing primary secondary amine, C18, graphitized carbon and anhydrous magnesium sulfate before analysis. Totally 75 and 68 pesticide compounds could be analyzed by LC-MS/MS and GC-MS/MS respectively in a 20-30 min single run. The recovery tests were conducted at the concentrations of 0.01 and 0.05 µg/g in four matrices. The validation results showed good precision, accuracy and sensitivity with recoveries between 60 to 140%, coefficient of variation below 20% and LOQ of 0.01 ppm for most pesticide compounds. The proficiency test was also conducted in Taiwan in 2014 using this method. Most results of all the 11 participated laboratories were satisfactory. Therefore, this reliable and efficient method is suitable to be used in the routine analysis of pesticides in foods of animal origin.

Material and Method

Sample preparation

1. Weigh 10 g frozen homogenized sample into 50 mL centrifuge tubes
2. Add 10 mL acetonitrile containing 1% acetic acid and 15 µL of 75 µg/mL ISTD (TPP)
3. Add extraction powder (4 g MgSO₄ anhydrous + 1 g sodium acetate)
 1. Shake vigorously for 1min
 2. Shake for 1min at 1,000 rpm
 3. Centrifuge for 1min at 4,000 x g and 15°C
4. Transfer 5 mL supernatant transfer to 15 mL centrifuge tube containing PSA 375 mg + C18 EC 250 mg + anh. MgSO₄ 750 mg + GBC 45 mg
 1. Shake for 1 min at 1,000 rpm
 2. Centrifuge for 5 min at 4,000 x g and 15°C
5. Transfer 1 mL supernatant transfer to 15 mL centrifuge tubes then evaporate to dryness with nitrogen evaporator.
 1. Add 1 mL methanol (PVDF)
 2. Filter by 0.22 µm (PVDF)
 3. LC-MS/MS analysis
 1. Add 1 mL hexane/acetone (1:1,v/v)
 2. Filter by 0.22 µm (PVDF)
 3. GC-MS/MS analysis

LC-MS/MS conditions

LC-MS/MS (ESI):	ACQUITY UPLC with Xevo TQ-S Mass Spectrometer
LC Column:	ACQUITY UPLC BEH C18 Column (1.6 µm, 2.1 mm x 100 mm)
Mobile phase:	A: 0.1% formic acid and 5 mM ammonium acetate in water B: 0.1% formic acid and 5 mM ammonium acetate in methanol
Gradient:	Time (min) A B
	0.0→2.0 98→50 2→50
	2.0→8.0 50→30 50→70
	8.0→10.0 30→5 70→95
	10.0→13.0 5→5 95→95
	13.0→15.0 5→2 95→98
	15.0→16.0 2→2 98→98
Flow rate:	0.3 mL/min
	inj. volume 10 µL

GC-MS/MS conditions

GC-MS/MS (EI):	Brüker 450-GC with 320-MS
GC Column:	VF-5MS, 30 m x 0.25 mm x 0.25 µm
Carrier gas:	Helium, constant flow 1 mL/min
Temperature program:	1 min at 60°C, 1 st ramp at 40°C/min to 170°C, then 2 nd ramp at 10°C/min to a final temperature of 310°C and hold for 2.25 min.
Transfer-line:	280°C
Source temperature:	250°C
inj. volume:	1 µL

Results

Matrices spiked with pesticides at levels of 0.05 and 0.01 mg/kg (n=5) were used to validate this method. Figure 1 shows the validation results of 143 pesticides at LOQ level in four sorts of animal products. The numbers of pesticides which can be detected by this method are 133 (in pork muscle), 131 (in pork liver and chicken) and 127 (in fish). And there are 11, 9, 9 and 5 items (LOQ=0.05 mg/kg) respectively in four matrices. Figure 2 and 3 show the total ion chromatograms of 75 and 68 pesticides by LC-MS/MS and GC-MS/MS. 76 animal products were surveyed by this method in Taiwan from October to December in 2014. Among them, 17 samples were found to be contaminated with 6 pesticides.

Conclusions

In this study, a QuEChERS (acronym of Quick, Easy, Cheap, Effective, Rugged, and Safe) procedure for quantify multi-class pesticide residues in foods of animal origin by LC-MS/MS and GC-MS/MS was developed. The analytes included 143 pesticide compounds in pork muscle, pork liver, chicken and fish. Therefore, this reliable and efficient method is suitable to be used in the routine analysis of pesticides in foods of animal origin.

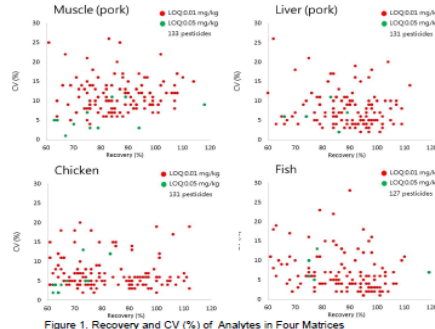


Figure 1. Recovery and CV (%) of Analytes in Four Matrices

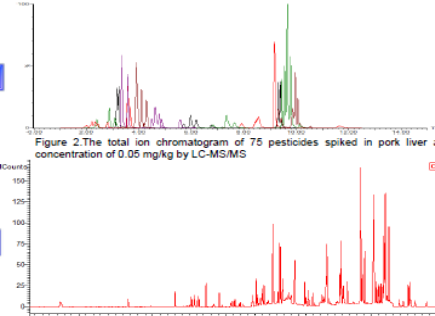



Figure 2. The total ion chromatogram of 75 pesticides spiked in pork liver at concentration of 0.05 mg/kg by LC-MS/MS

Figure 3. The total ion chromatogram of 68 pesticides spiked in pork liver at concentration of 0.05 mg/kg by GC-MS/MS



Development of QuEChERS-Based Extraction and Liquid Chromatography-Tandem Mass Spectrometry Method for Eugenol and Tricaine Methanesulfonate in Fish Muscle

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Abstract

In this study, a QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method was developed to determine 2 common anaesthetics (eugenol and tricaine methanesulfonate) in fish muscle by LC-ESI-MS/MS. Five grams of fish muscle were first extracted by acidified acetonitrile (containing 1% acetic acid) and then salting out with citrate buffer (with magnesium sulfate, sodium chloride, trisodium citrate and disodium citrate sesquihydrate). Through centrifugation step, the supernatant was cleaned up via clean-up powder containing primary secondary amine, C18 and anhydrous magnesium sulfate before analysis. The results indicated recoveries of 89.9-94.7% for tricaine methanesulfonate and 98.3-103.8% for eugenol, with coefficient of variation (CV) less than 5% on both drugs. The limit of quantification of tricaine methanesulfonate and eugenol were 0.002 and 0.01 µg/g, respectively.

Material and Method

Apparatus

High-speed shaker is a 2010 Geno/Grinder, SPEX SamplePrep (Metuchen, NJ, USA). The homogenizer is a Polytron PT-MR 3100 (Kinematic AG, Littau, CH). LC system comprised an Eksigent ultraLC system (AB SCIEX, Redwood City, CA) equipped with a quaternary pump, an autosampler, a degasser, and a column oven. An Poroshell HPH C18 (2.7 µm, 3 mm x 100 mm, Agilent Technologies, Santa Clara, CA, USA) was used to separate the analytes. Mass spectrometry was performed using a QTRAP 5500 (AB SCIEX, Framingham, MS, USA) hybrid triple quadrupole mass spectrometer equipped with a Turbo V ion source and TIS (Turbolon Spray) probe operating in ESI-MS-MS positive ion mode.

Sample preparation

Weigh 5g frozen homogenized fish muscle

↓

Add 10 mL cooling distilled water and 10 mL acetonitrile containing 1% acetic acid and then vortex

↓

Add extraction powder (4 g MgSO₄ anhydrous + 1 g NaCl + 1 g NaCitrate + 0.5 g Disodium citrate sesquihydrate)

1. Shake vigorously for 1min
2. Shake for 1min at 1000 rpm
3. Centrifuge for 1min at 5000 rpm

Mass Conditions

Compound	Precursor ion (m/z) > Product ion (m/z)	DP* (V)	CE** (eV)
Eugenol	183 > 148***	-55	-19
	183 > 121	-55	-36
	183 > 93	-55	-40
Tricaine methanesulfonate	166 > 138***	171	23
	166 > 94	171	30

* DP : Declustering potential
** CE : Collision energy
*** Quantification transition

LC Conditions

LC Column Poroshell HPH C18 Column (2.7 µm, 3 mm x 100 mm, Agilent Technology)

Mobile phase A: 0.05% ammonium solution(NH₃)
B: 0.05% NH₃ in Methanol

Gradient Time (min)	A	B
0.0	50	50
8.0	0	100
11.0	0	100
12.0	50	50
15	50	50

Flow rate 0.25 mL/min

Injection volume 20 µL

Analytical time 15 min

Results

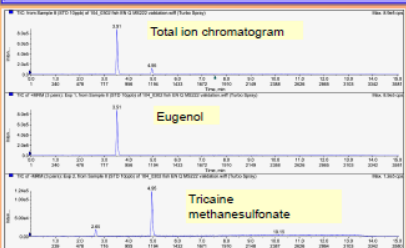


Figure 1. MRM chromatograms of eugenol and tricaine methanesulfonate at concentration of 10 ng/mL.

Table 1. Recovery and CV of eugenol and tricaine methanesulfonate spiked in fish muscle at different levels

Compound	Intra-day trial*			Inter-day trial**	LOQ (ppm)
	0.01 µg/g	0.05 µg/g	0.1 µg/g	0.05 µg/g	
Eugenol	Recovery% (CV%)			CV%	0.01
	98.3 (2.9)	103.8 (2.8)	102.4 (2.5)	3.9	
Tricaine methanesulfonate	Recovery% (CV%)			CV%	0.002
	89.9 (4.1)	90.2 (3.0)	94.7 (4.0)	6.8	

* N=5
** N=15

Conclusion

Anaesthetics can be used in fish when capturing, handling and transportation from harbor to market. However, little attention was paid on these drugs analysis in fish as well as their residue. This is the first research regarding QuEChERS procedure on eugenol and tricaine methanesulfonate analysis in fish muscle. In Taiwan, maximum residue level of eugenol and tricaine methanesulfonate were 0.05 µg/g and 0.01 µg/g respectively. The method we provided shows good recoveries, low variance and high sensitivity when analyzing the drugs. The full analysis time (including sample preparation) is less than 30 min for a batch of sample. The limit of quantification of tricaine methanesulfonate and eugenol were 0.002 and 0.01 µg/g, respectively.