

Multiresidue Analysis of Pesticides in Fresh Produce using QuEChERS concepts, GC, and GC-MS/SIM



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Reasons for monitoring pesticides at FDA

- Food safety
- Food defense (pesticides are potential chemical weapons)
- Pesticides are used on other items beside food, i.e., herbal supplements
- Public, Industry, and Government agencies rely on FDA for pesticide monitoring

Current Objectives

- Develop and apply **efficient, fast, easy, and inexpensive methods** for **multiresidue** pesticide analysis
- Develop methods for various pesticide classes
- **Validate multiresidue methods** for a variety of pesticides in fresh produce
- Methods developed for regulatory work

Multiresidue Procedure based on Canadian Method and QuEChERS

J AOAC Int. 2000, 83 (3): 698-713	Proposed Method	J AOAC Int. 2003, 86(2):412-31
50 g sample 100 mL ACN Blend and add 10 g NaCl	15 g sample + 15 mL 1% AcOH/ACN Blend	10 g sample + 10 mL ACN Vortex or shake
15 mL ACN extract C-18 SPE cartridge	6 g MgSO ₄ , 2.5 g NaOAc Blend + Centrifuge	4 g MgSO ₄ + 1 g NaCl Vortex (or shake), add I.S., Centrifuge
Add Na ₂ SO ₄ , Centrifuge, and Evaporate 13 mL ACN extract to ~0.5 mL	Quant. Transfer ~15 mL 0.5 g C-18, 1.2 g MgSO ₄ Shake and centrifuge	Transfer 1 mL ACN extract 0.025 g PSA + 0.15 g MgSO ₄ Shake
Load extract for GCB/PSA Solid phase extraction	Quant. Transfer ~12 mL 0.4 g PSA + 0.2 g GCB + 1.2 g MgSO ₄ Vortex	Transfer to ALS vials
Elute with 20 mL 3:1 ACN:toluene	Add 4 mL toluene Shake and centrifuge	GC-MS Analysis
Evaporate, add I.S., and bring to Volume Transfer to ALS vials	Quant. Transfer ~12 mL Evaporate and bring to volume Add I.S.	
GC-MS or HPLC Analysis	Add MgSO ₄ , Vortex and centrifuge Transfer to ALS vials	
	GC and GC-MS Analysis	

Features of Proposed Procedure

- Optimization-based procedure (based on QuEChERS concepts)
- **Sample cleanup** (using cleanup concepts such as C-18, PSA, and graphitized carbon based on Canadian, Florida, California pesticide procedures)
- **Robust** (tested on a variety of produce commodities)
- **Inexpensive** (use of solid-phase dispersive techniques rather than solid-phase extraction)
- **Easy** (no esoteric equipment required, i.e., typical equipment usually found in a pesticide lab- requires teflon tubes, homogenizer, centrifuge)
- Procedure adopts "**Green Chemistry**" concepts: less sample, less solvent, less waste (no SPE cartridges), and solvent is collected in a solvent trap

1. Prepare sample and weigh 15 g in centrifuge tube



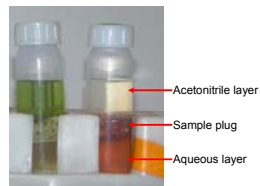
2. Add solvent and blend 2 minutes



3. Add salts and blend for ~1 min



4. Centrifuge



5. C-18 cleanup

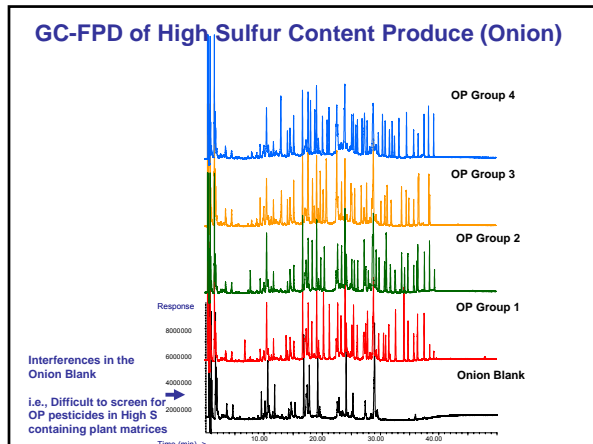


6. PSA/GCB Cleanup (add toluene and shake)



7. Centrifuge, aliquot extract, and remove solvent





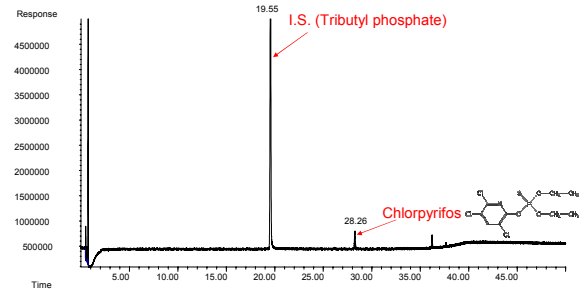
Summary of Pesticide Analysis in Fresh Produce

- Development of a validated procedure for the analysis of organohalogen pesticides using GC-ELCD, GC-XSD, and GC-MS
- Development of a validated procedure for the analysis of organophosphorus pesticides using GC-FPD and GC-MS
- Method is straight-forward, inexpensive, robust, and easy to implement
- GC with element selective detection and GC-MS/SIM complement each other for analyzing pesticides for most types of produce
- Quantitation and screening of high-sulfur content produce is a problem by GC-FPD

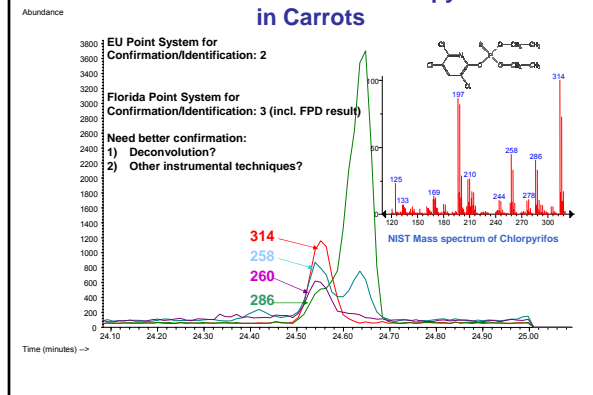
Current and Future Studies

- Develop sample prep procedures for different types and forms of foods and dietary supplements
- New techniques to detect and identify pesticides
- Integrate procedures to screen for pesticides in food and herbal supplements using GC, GC-MS and LC-MS/MS
- Validation of GC-MS and LC-MS/MS procedures

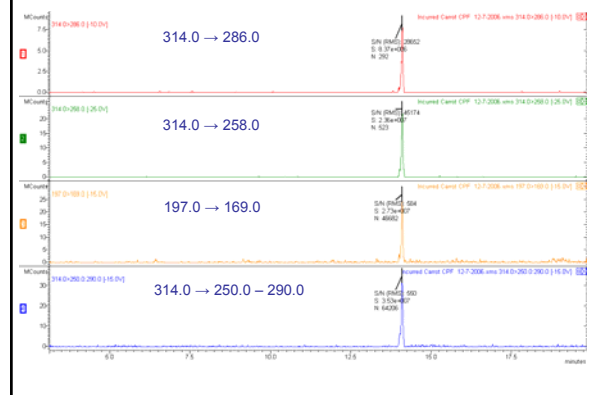
GC-FPD of Carrot Extract containing Chlorpyrifos

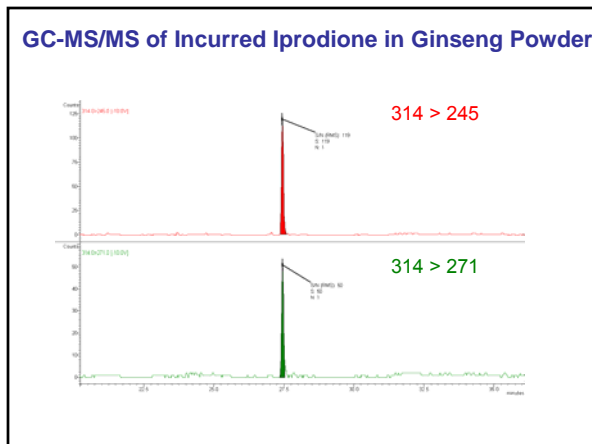
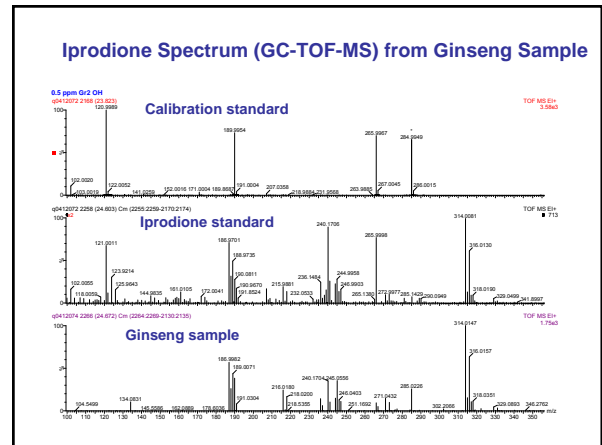
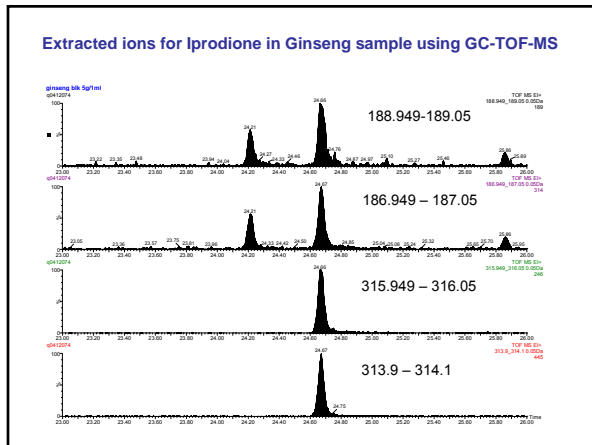
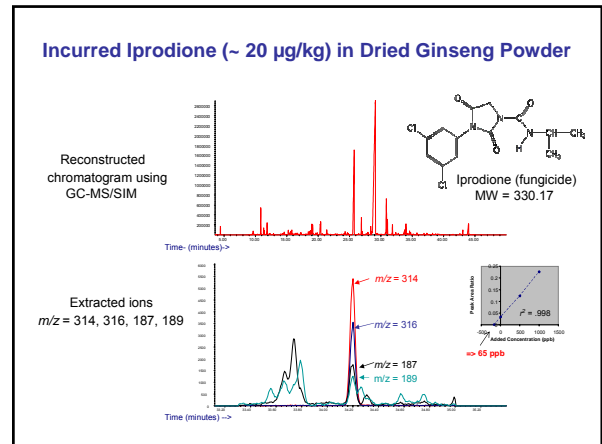
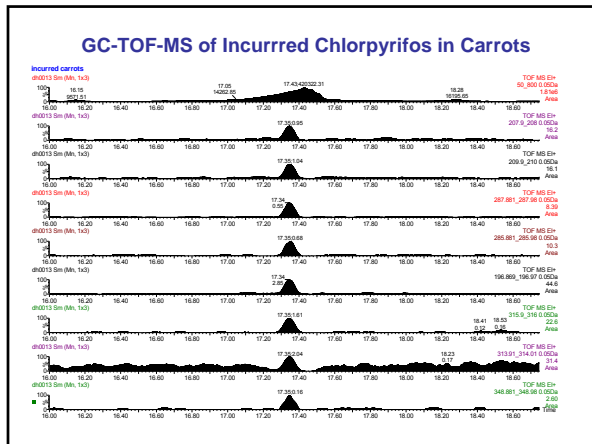


GC-MS/SIM of Incurred Chlorpyrifos in Carrots



GC-MS/MS of Incurred Chlorpyrifos in Carrots (6 point confirmation)





- ### Conclusions
- Multiresidue procedure using GC and GC-MS based on QuChERS principles
 - Validated procedure of > 200 pesticides tested using GC and GC-MS
 - GC-MS/SIM and GC equipped with element selective detection complement each other and are very effective in quantitation and confirmation
 - Techniques (software and instrumentation) will be used for confirmation/identification in current and future studies

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Thank you for your attention



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Please Join Us!

Pesticides Subgroup in Food Community

Currently, the **Chemical Contaminants and Residues in Food Community** is in the process of searching for and identifying potential stakeholders in several areas, such as pesticides.

From the government agency to the private sector or industry, stakeholders help AOAC to understand their analytical needs. This, in turn, helps the Association to better focus its efforts on the areas of greatest interest (priority methods).

Pesticides continue to be an important topic and we seek members including global representatives from **governments, academia, producers, processors, distributors, importers, exporters, private laboratories, equipment/instrument vendors, and consumer groups** working together to develop analytical standards of excellence in the area of pesticides.

The **Pesticide subgroup** will address these needs.

To participate, contact Jon Wong, jon.wong@fda.hhs.gov

and visit the web at:
http://www.aoac.org/chem_contam/cc_homepage.html