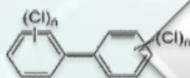


Develop, validate, and transfer multiclass, multiresidue methods for pesticides, environmental, and emerging contaminants in FSIS-regulated foods, and conduct a survey of food samples for the contaminants

Simultaneous analysis method for diverse pesticides, legacy and emerging environmental contaminants in meats and poultry



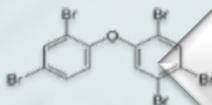
Pesticides (EPA list) 200 total



Polychlorinated biphenyls (PCBs)



Polycyclic aromatic hydrocarbons (PAHs)



Polybrominated diphenyl ethers (PBDEs)



Other flame retardants (FRs)

265
total

2 g of
homogenized
sample + Internal
standards

- Add 2 mL MeCN + 0.8 g MgSO₄ & 0.2 g NaCl

Extraction

- shake 10 min on vortex shaker at 80% setting with max. pulsing
- centrifuge 3 min at 4150 rpm

Cleanup

- Automated mini-SPE cleanup

0.2 µm PVDF



LC-MS/MS

GC-MS/MS

Automated SPE cleanup

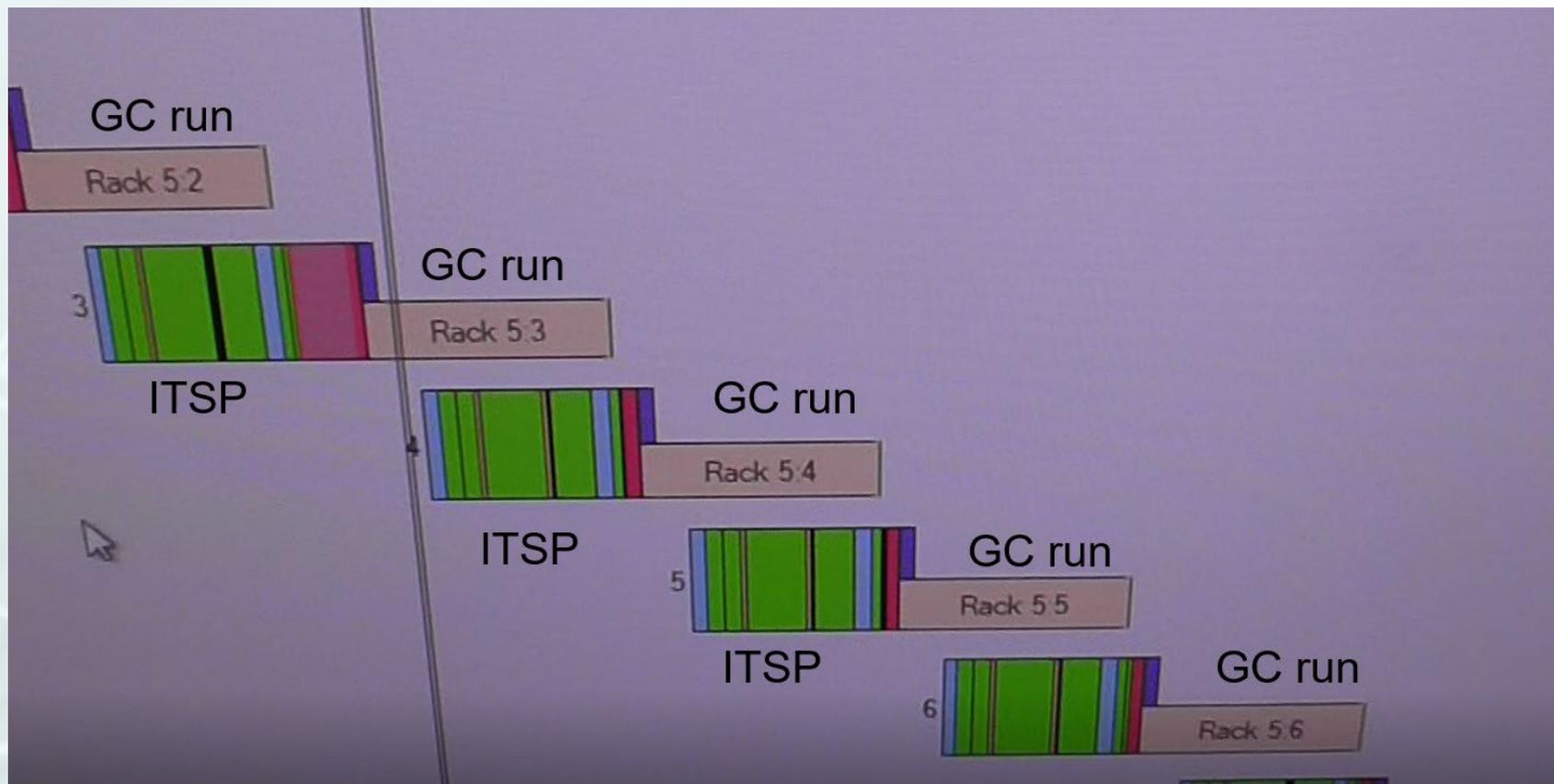


Robotic liquid handler:

- Pass 300 μL extract at 2 $\mu\text{L}/\text{s}$ through 45 mg mini-cartridge with anh. MgSO_4 , PSA/C18/Carbon X
- 3 min cleanup step
5 min washing/switching syringes
- 8 min per sample**

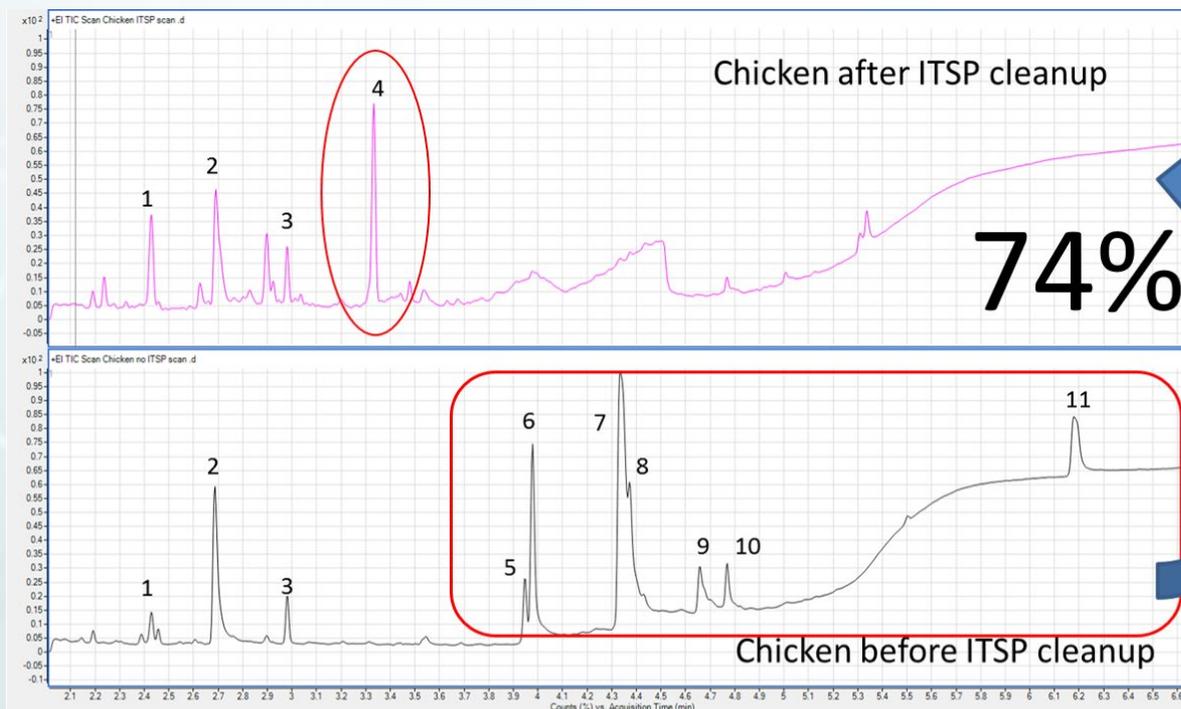
Instrument Top Sample Preparation (ITSP)





ITSP

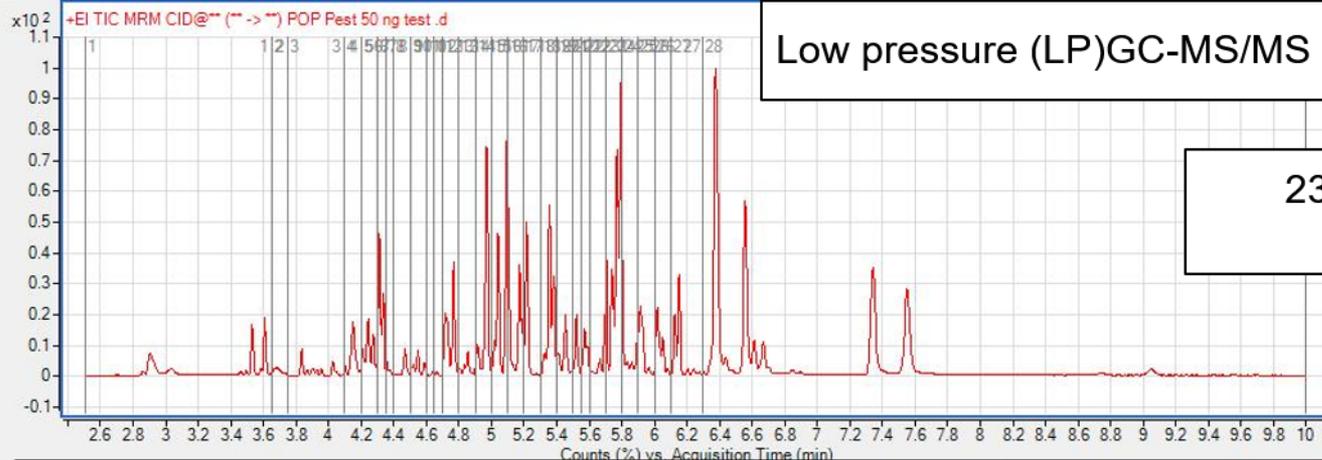
Chicken Before and
After ITSP Cleanup



1. Cyclohexasiloxane, dodecamethyl-
2. Niacinamide
3. Phenol, 2,4-bis(1,1-dimethylethyl)-
4. Benzophenone
5. 9-Hexadecenoic acid

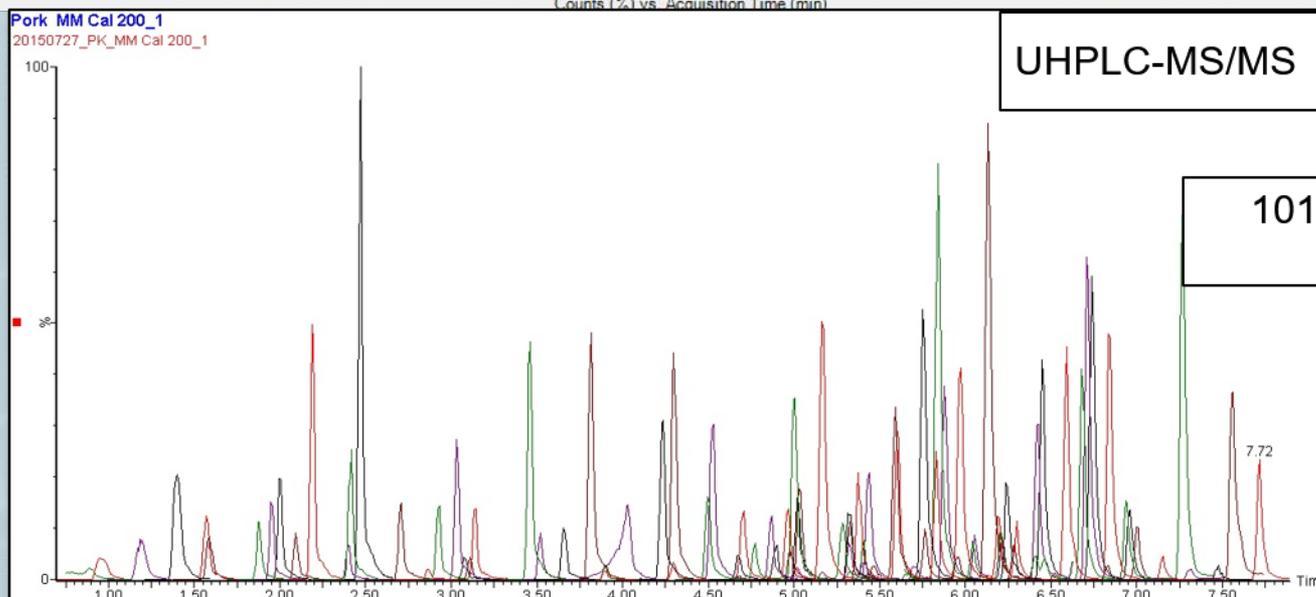
6. n-Hexadecanoic acid
7. 9,12-Octadecadienoic acid (Z,Z)-
8. Oleic acid
9. Docosahexaenoic acid, 1,2,3-propanetriyl ester
10. 9-Octadecenamide
11. Cholesterol

Overlapping
Analytes



232 targeted analytes & 15
internal/QC standards

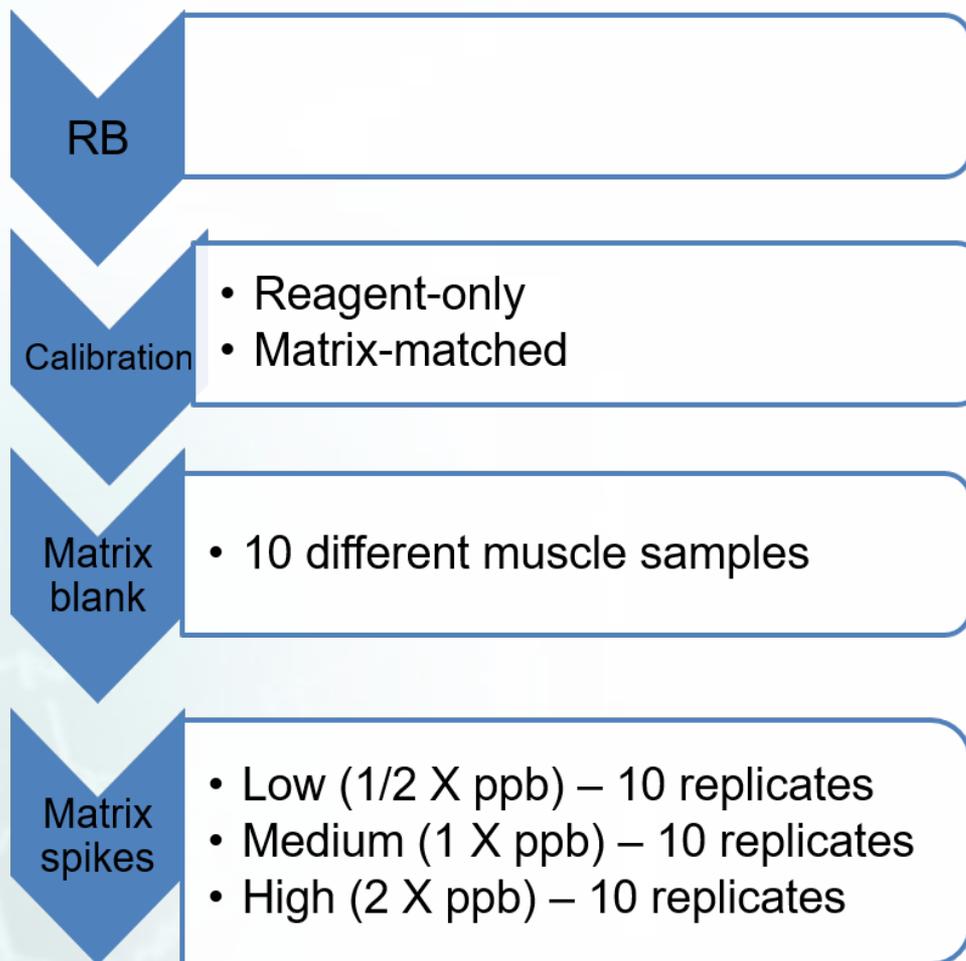
53 overlapping
analytes



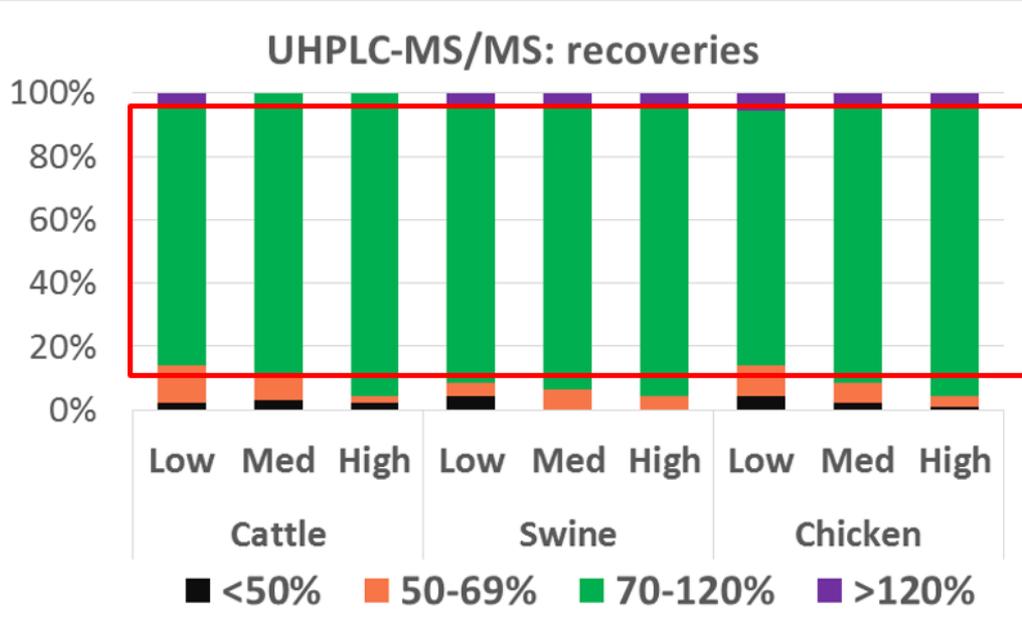
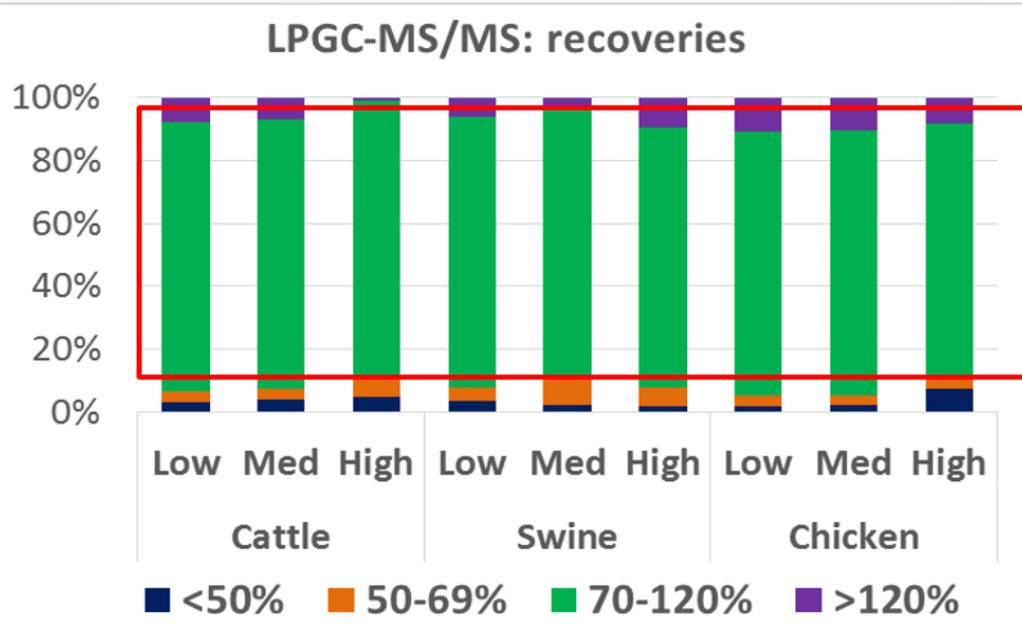
101 pesticides & 3 internal/ QC
standards

Method validation

- Day 1: beef
- Day 2: chicken
- Day 3: pork



$X =$ US tolerance



219 analytes validated successfully

Method application

46 muscle samples:

10 chicken, 16 cattle, 14 swine, 3 goat, 1 turkey

Measured pesticides concentrations, ng/g

Pesticide	Swine	Cattle	Chicken	US tolerance, ng/g	EPA rank
hexachlorobenzene	0.5-7.5	2.4-8.6	0.5-5.9	10	HH
flonicamid	ND	2.4	ND	30-80	L
ethion	0.2-0.8	7.4	0.5	10	H
piperonyl butoxide	1-20	1-4	1-28	100-3000	HH
methoxychlor	0.4-1.4	0.1-0.6	0.3-1.2	10-80	H
p,p-DDE	0.2-1.2	0.4-0.6	0.4-0.5	10	H
p,p-DDE	0.1	ND	0.4	10	HH
mirex	0.1-1.1	ND	0.4-0.6	10	H

Measured concentrations of environmental contaminants, ng/g

Analyte	Swine	Cattle	Chicken	US tolerance, ng/g
acenaphthene	0.6-1.0	ND	ND	
benzo(c)fluorene	0.1-1.8	ND	0.6-1.0	
fluorene	ND	2.5	ND	
phenanthrene	0.3-1.5	1.2-1.7	ND	
PBDE 47	3	ND	ND	

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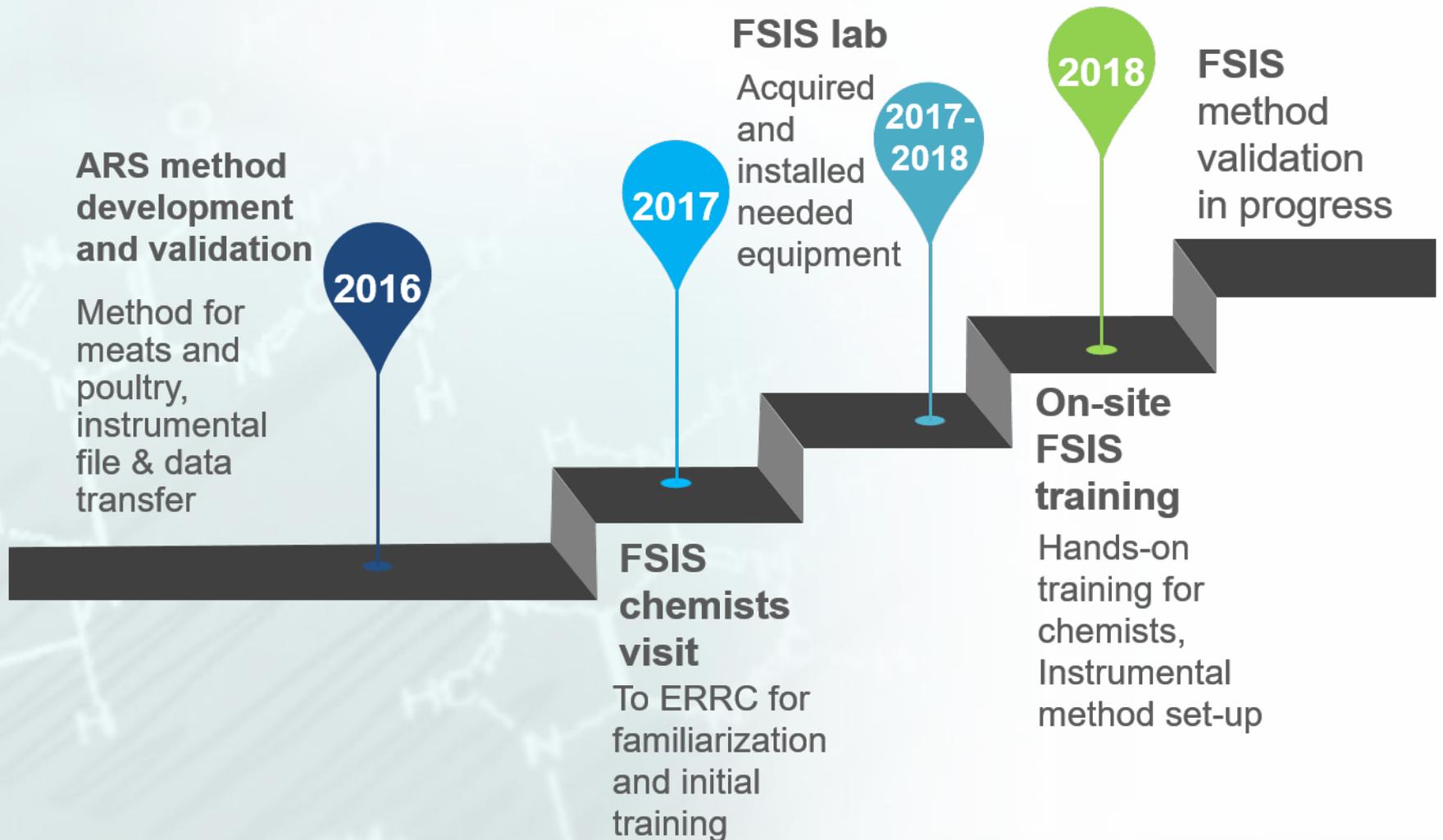
High-throughput analytical method for 265 pesticides and environmental contaminants in meats and poultry by fast low pressure gas chromatography and ultrahigh-performance liquid chromatography tandem mass spectrometry

Yelena Sapozhnikova

U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, 600 East Mermaid Lane, Wyndmoor, PA 19038, USA



The method transfer to FSIS Western Laboratory



Catfish

- 308 analytes: 264 pesticides & 44 environmental contaminants
- Pesticides:
 - US Tolerance
 - Food Handling Establishment (FHE) tolerance
 - US FDA Action Level
- 255 analytes were successfully validated

Sample	Compound	ng/g	US tolerance, (ng/g)
catfish	Fluorene	5.3 ± 0.5	-
	Cyhalothrin-lambda	32.3 ± 3.8	-
	Piperonyl butoxide	6.4 ± 0.6 (GC)	-
	Piperonyl butoxide	4.2 ± 0.2 (LC)	-
catfish	Diuron	8.2 ± 0.2	2000
	Diuron	11.5 ± 0.2	2000
	o,p'-DDT + p,p'-DDD	5.3 ± 0.1	5000 (Action level)
catfish	p,p'-DDE	10.9 ± 0.1	5000 (Action level)
	o,p'-DDT + p,p'-DDD	9.3 ± 0.7	5000 (Action level)
catfish	p,p'-DDE	45.4 ± 0.7	5000 (Action level)
catfish	p,p'-DDE	14.3 ± 1.3	5000 (Action level)

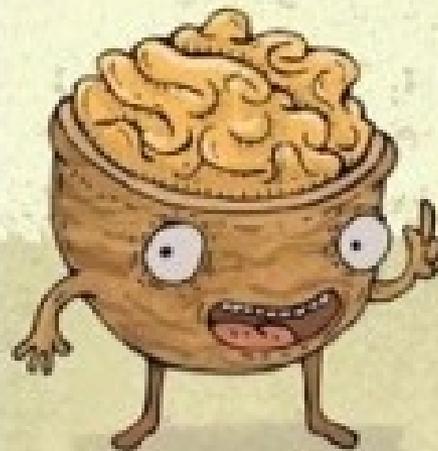
You Are What You Eat?

by D.R. Smith

I ate a broccoli
and feel tall as a tree



I ate a walnut
and feel like a brain



I ate a mushroom
and I hate this game



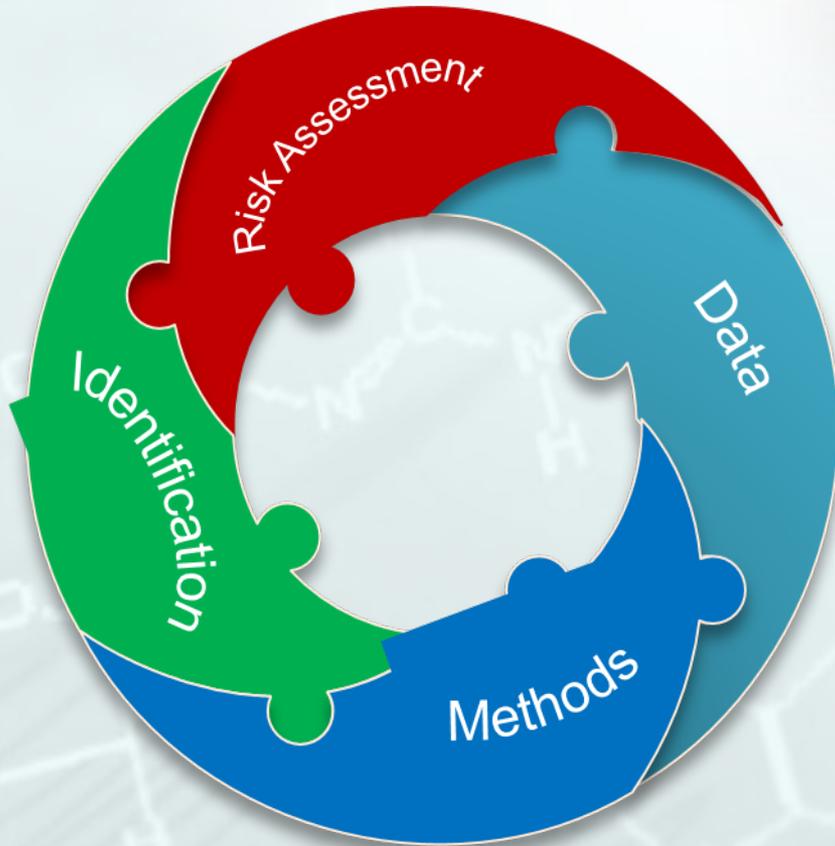
Maritt

Method development for food packaging contaminants in FSIS-regulated foods



Risk assessment

To protect consumer's health



Generated data on occurrence

Market surveys

Analytical methods

Development and validation
of multi-residue methods

Identification and characterization

FP contaminants potentially
migrating into foods

Food packaging types





Extraction

FDA food simulant:
water/ethanol 5%/95%, v/v

Hexane
Ethyl acetate
Acetonitrile

~4 g of film
+ food
simulant/
solvent

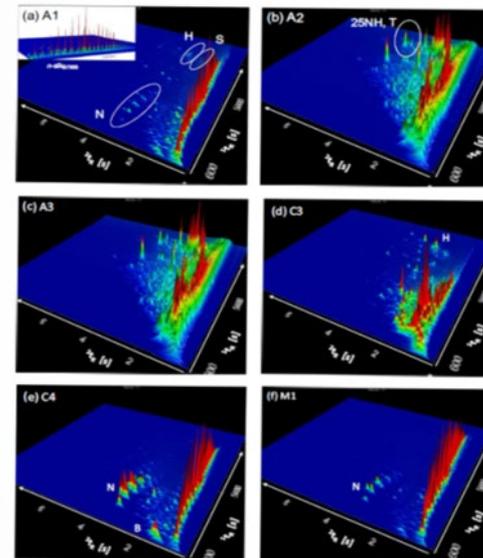
Solvent
rinsed
glass
beaker

Ultrasonic
extraction
30 min

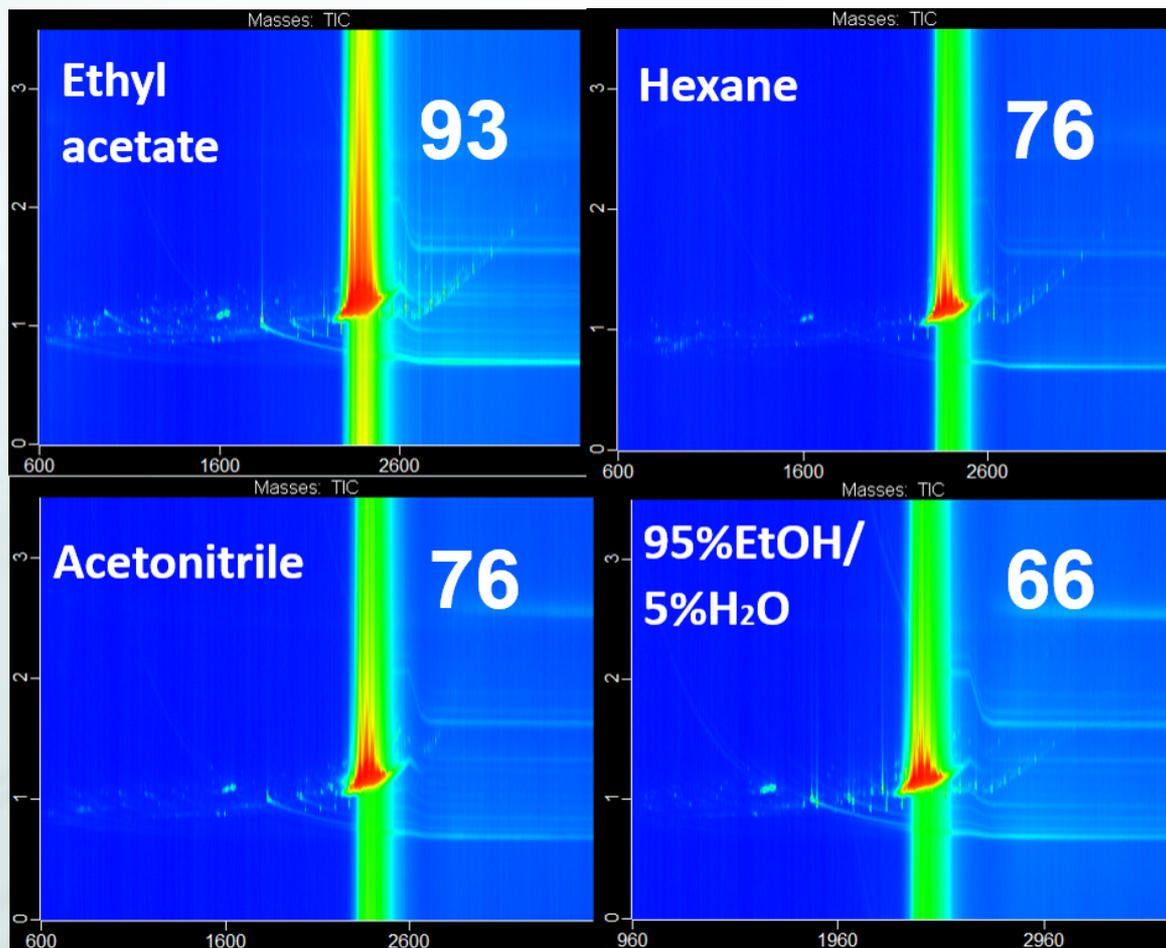
No plastic!

Non-targeted analysis by GCxCG-TOF-MS

- Collaboration with San Diego State University
- GCxCG-TOF-MS Pegasus 4D

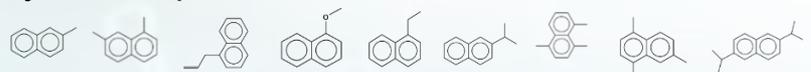
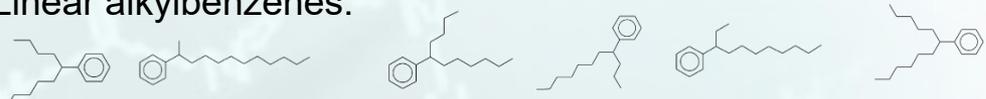
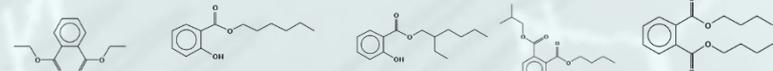
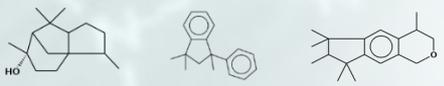


Number of identified migrating compounds



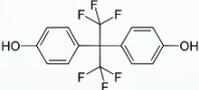
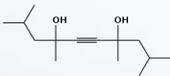
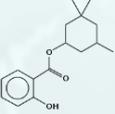
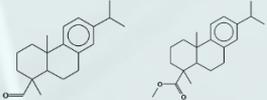
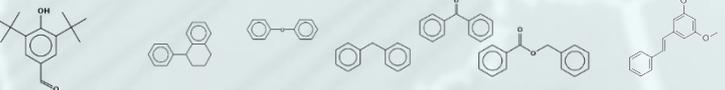
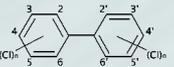
Compounds tentatively identified in food simulants

(with >80% match similarity to the standard NIST mass spectral library)

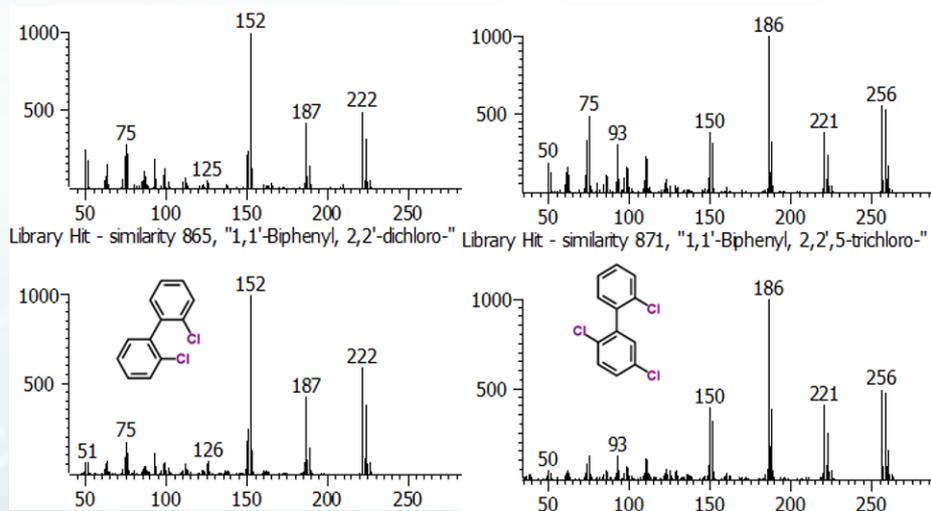
Chemical Class	Uses/Sources
Alkylated naphthalenes: 	lubricant additive
Polycyclic aromatic hydrocarbons (PAHs): 	combustion, biogenic, petroleum
Linear alkylbenzenes: 	precursor of biodegradable detergents
Adipates (DEHA, DOA, and five other adipic acids): 	plasticizers
Phthalates and salicylates: 	plasticizers
Cedrol, 1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-, and Galaxolide (musks) 	fragrance

Compounds tentatively identified in food simulants

(with >80% match similarity to the standard NIST mass spectral library) (2)

Chemical Class	Uses/Sources
Hexafluorobisphenol A Bisphenol AF 	Plastic polymer additive
2,4,7,9-Tetramethyl-5-decyn-4,7-diol 	adhesive, surfactant, plastic additive
Homosalate 	UV filter
13-Isopropylpodocarpa-8,11,13-trien-19-al, 10,18-Bisnorabieta-8,11,13-triene, and Methyl dehydroabietate 	thermal degradation
Phenyl/Biphenyl/diphenyl compounds (miscellaneous) 	
PCBs (two isomers of di-chloro and three isomers of tri-chloro) 	

Unexpected discovery



Mass spectra identified as PCBs: the left shows a 86.5% match with 2,2'-dichlorobiphenyl and the right shows a 87.1% match with 2,2',5-trichlorobiphenyl from the NIST library. The right spectrum was further confirmed by match to an authentic standard, 2,2',5-trichlorobiphenyl.

Examples of tentatively identified chemicals

Identified compound	Use	Concern
Benzyl chloride	Manufacturing of plasticizers	Probable human carcinogen
Benzyl benzoate	Flavor and fragrance agent	Endocrine disruptor
Furan, 2-pentyl	Flavoring agent	Suspected genotoxicity
Benzophenone	UV blocker	Endocrine disruptor
2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB)	Low-viscosity plasticizer	Reproductive/developmental toxicity
2-ethylhexyl methyl isophthalate	Commonly used plasticizer	Genetic mutation, reproduction toxicity

Acknowledgements

- USDA/ARS:
 - Tawana Simons
 - Robyn Moten
 - Alan Lightfield
 - Limei Yun
- USDA/FSIS:
 - John Jarosh
 - Catalina Yee
 - Zoe Samer

