Analytical Challenges for Food Safety in the Global Competitive Market

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Laboratory Manager
About OMIC

- Overseas Merchandise Inspection Company
  A Japanese Company

- Established in 1954

- Core Businesses:
  - Inspection, testing, and appraisal of the quality, quantity, and weight of cargo
  - Food Safety Inspection
  - Price evaluation for imported and exported products
  - Certification of Organic Products
Laboratory Network supports Overseas Merchandise Inspection Company

- Portland, OR
- Tokyo
- Bangkok
- Melbourne

June 2012
OMIC USA laboratory

Located in Portland, Oregon
ca. 30 employees
ca. 10,500 sample per year
OMIC USA’s purpose is...

**Exporting**
- Food and Feed Grains, Beans and Pellets
- Fruits and Vegetable
- Tea and Coffee
- Food supplements

**Importing**
- FDA – DWPE Program

**Analytical Services**
- FDA Nutrition Label
- Pesticides Residue
- Pathogen Testing
- Mycotoxins
- Food Additives
- GMO Testing

**Soil Pesticides Testing**
- rotating crops
- Drift problem

**GLP Projects**

**FSMA (future work/accreditation)**
Export Testing Service

Through increased interaction with government offices in foreign countries (MHLW Japan and KFDA in Korea) we are able to assist clients to meet import requirements.

Our chemists received necessary analytical training in foreign government laboratory for their approved methods.
Testing the limits

June 2012

Focus on Food Safety

Increasing volume and diversity of food

Increasing population and good demand

Greater public demand for health protection

Changing agricultural practice and climate

Changing human behavior and ecology

More sophisticated instrumentation and lower detection limit

Political Map of the World
Food Safety Testing

- Pesticides
- Natural Toxicants – mycotoxins
- Additives – colors
- Packing migration
- Environmental contaminants – PCB’s, PAH’s, metals
- Authenticity and traceability
- Deliberate adulteration
Food Safety Analytical Challenges

Methodology

Complexities

✓ multi- residue / multi elements
✓ matrix complexity (dry, high fat, spices)
✓ lower Maximum Residue Limits (MRL)
✓ not uniform MRL => more method validation

Challenges

✓ development of analytical method for analysis of multi residues pesticides in complex matrix
✓ need expensive equipment, MSMS, HRMS, TOF
Food Safety Analytical Challenges

Method Validation

Complexities

✓ suitable for given range
✓ sensitivity: LOD = 3 x S/N, LOQ = 3 x LOD
✓ specificity/selectivity
✓ repeatability/precision
✓ recovery (usually 70 – 120 %)
✓ matrix standard vs solvent made standard

Challenges

✓ validated method for various parameters
Food Safety Analytical Challenges

Sampling

Complexities

✓ homogeneous sample
✓ sample taking for testing must represent the entire lot
✓ multi portions sampling for different tests
  ▪ GMO, mycotoxins, micro testing, pesticides
✓ statistical sampling determination

Challenges

✓ Representative sample for the complete lot
Food Safety Analytical Challenges

Sample Extraction

Complexities

✓ chemical nature of analytes
✓ chemical type of matrix
✓ co-extractants problem
✓ adsorption of analyte on the matrix

Challenges

✓ selection of the right solvent
✓ optimize the extraction condition
Food Safety Analytical Challenges

Clean up

Complexities
✓ number of compounds
✓ matrix interference
✓ adsorption of the analytes onto the SPE powder

Challenges
✓ selection of the appropriate technique
✓ adsorbant powder selection
✓ solvent elution
Food Safety Analytical Challenges

Sample Concentration

Complexities

✓ type of analyte
✓ selection of technique (roto-evaporator, N\textsubscript{2}-evaporator)

Challenges

✓ LOD /LOQ meet the MRL value
✓ acceptable % recovery
Food Safety Analytical Challenges

Analytical Instrumentation

Complexities

✓ instrument noise level (LOD)
✓ interference
✓ false negative / false positive
✓ instrument cost / operation cost
✓ expiration date for reference standards

Challenges

✓ confirmation method (MSMS, TOF, HRMS)
✓ availability of reference standard (second source)
✓ data result interpretation
Food Safety Analytical Challenges

Analyst

Complexities

✓ training and experience
✓ skill, attitude, problem solving worker
✓ judgment, making the right decision

Challenges

✓ long–term employment employee
We did all the testing

Building consumer trust

From: Fear

To: Confidence
Challenges – Screening for 750 Pesticides

Complexities

✓ increase number
✓ difficult matrices
✓ multi residue method or single analysis
✓ lower sensitivity (as low as 0.3 ppb)
✓ diversity of pesticide structure (organochlorine, organophosphates, carbamates, pyrethrum, etc.)
✓ no history of pesticide usage in foreign country
Challenges – Screening for 750 Pesticides

Challenges
✓ increased monitoring program (more samples)
✓ client demands low cost
✓ faster turnaround time (7 w. days or less)
✓ quick extraction
OMIC USA trends in Multi pesticide screen method

1993: 30 compounds
- LL Extraction
- GC-ECD
- GC-FPD
- GC-NPD

1996: 60 compounds
- SPE Cleanup

1997: 156 compounds
- GC-AED
- GCMS
- LCMS

2001: 240 compounds
- Mixed-mode SPE
- GCMS
- MSMS

2004: 400 compounds
- Dispersive SPE (QuEChERS)
- HPLC
- MSMS

2006: 520 compounds
- UPLC
- MSMS
- MSMS

2009: 520 compounds

2011: Total analysis capability: 740+ compounds
- GCMS
- MSMS
Multi Residue Method Strategies

SPEED
SAMPLE REP.

{ Extraction

Cleanup

COST - EFFICIENCY

LIMS

EFFICIENCY
ROBUSTNESS

Detection

SENSITIVITY
SELECTIVITY

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Extraction Procedures

MASE – Microwave-Assisted Solvent Extraction

A process of heating solid sample and solvent in a sealed (closed) vessel with microwave energy and temperature controlled conditions.

PFL – Pressurized Fluid Extraction

A process similar to Soxhlet extraction except that the solvents are used near their supercritical region where they have high extraction properties.
Extraction Procedures

SBSE – Stir Bar Sorptive Extraction
Extraction is performed using a special glass coated magnetic stir bar which is coated with polydimethylsiloxane (PDMS).

SPE – Solid Phase Extraction
Well established procedure used for isolating and concentrating analytes at low detection levels because it eliminates the interferences that contribute to signal suppression.
Extraction Procedures

LLE – Liquid–Liquid Extraction

A mass transfer operation in which a liquid solution (the feed) is contacted with an immiscible or nearly immiscible liquid (solvent) that exhibits selectivity toward one or more of the components in the feed.

SPME – Solid Phase Micro Extraction

A solvent–less extraction procedure that involves exposure of a probe (coated fused silica fiber) to a gaseous or liquid sample or the headspace above a liquid or solid sample.
Extraction Procedures

SFE – Supercritical Fluid Extraction

A supercritical carbon dioxide is used as solvent. This solvent has penetration and transport properties similar to a gas but acts as a liquid when dissolving analytes from matrix.

QuEChERS–Quick Easy Cheap Effective Effective Rugged Safe

An extraction method using dispersive SPE clean –up.

SBSE – Stir Bar Sorptive Extraction

- A PolyDimethylSiloxane (PDMS) coated stir bar is placed in a liquid (water sample or sample extract) and stirred for several minutes.
- The analytes of interest are extracted from matrix into the PDMS phase.
- The analytes are thermally desorbed from the stir bar in a GC Thermo Desorption Unit (TDU) made by GERSTEL and transferred to a GC capillary column.
- Gerstel’s Twister SBSE is an effective extraction and rapid extraction technique.
SBSE – Stir Bar Sorptive Extraction

Sample size: 15 g (vegetable, fruit)

Methanol 30 ml

Ultraturrax: 5 min + Ultrasonic bath: 15 min

1 ml extract + 10 ml Water

SBSE (Twister 10 mm L x 0.5 mm d) for 60 min

TDU – Inject to GC (MSD, MSMS, etc)
SBSE – Stir Bar Sorptive Instrument Injection

GERSTEL Thermal Desorption Unit (TDU) with MPS-2 robot

98 positions
Twisters are put in a clean empty glass liner and capped with special tube head

Auto sampler rack for MPS-2-TDU

MPS-2-TDU on top of GC
Testing the limits

QuEChERS
Anastassiades, S.J. Lehotay, D. Stajnbaher and F.J. Schenck,

- Extraction/Partition
  - Sample + ACN:H$_2$O
  - Citrate (pH=6.4), or Acetate (pH=4.8)

- Dispersive clean-up of ACN extract PSA/C$_{18}$ or GCB
  - Concentration/ solvent exchange (optional)

- Filtration

Berries  Orange  Wheat  Rice
Pesticide residue analysis: ~740 compounds
QuEChERS ~520

QuEChERS
(70 % of all compounds)
GC – Detection Challenges

- GC work common problem
  - Peak tailing or analyte lost due to undesired interaction with active sites in the inlet column.
  - Higher Detection limit for these compounds and difficult to identify and calculate.

- **Analyte Protectants** provide an effective solution to the problem.
  - They are added to extracts and matrix free standards to enhance the chromatography effect for analytes in a very dirty GC system.
Improved analysis with analyte protectants

225 ppb of o-phenylphenol in:

- matrix + analyte protectants
- solvent + analyte protectants

- **matrix**
- **solvent**

↓ matrix enhancement effect
↑ analyte response
↓ peak tailing
↓ GC system maintenance
↑ ruggedness

matrix = mixed fruit extract (1 g/mL in acetonitrile)
prepared by QuEChERS method

Slide adapted from Steven Lehotay, USDA-ARS
LC–MSMS Detection Challenges

Ion suppression on LC/MS/MS

- Commodity
- Impacts accuracy:
  - S/N and LOQ for screening
  - Quantitation for positive samples
Strawberry Profile
LC–MSMS Chromatogram

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**Cyprodinyl Chromatogram**

Insecticide

Trade name: Vangard WP

Matrix std (berry juice) 0.02 ppm

Matrix blank (berry juice)

Sample, 10 x dil. (strawberry)
Fungicide
Trade name:
Elevate 50 WDG

Fenhexamid Chromatogram

Matrix std (berry juice) 0.02 ppm
Matrix blank (berry juice)
Sample, 10 x dil. (strawberry)
Fludioxonil Chromatogram

Fungicide
Trade name: Maxim, Switch

Matrix std (berry juice) 0.02 ppm

Matrix blank (berry juice)

Sample, 10 x dil. (strawberry)
## Reporting Pesticides

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Result</th>
<th>LOQ</th>
<th>Unit</th>
<th>EPA CFR #</th>
<th>Tolerance USA</th>
<th>Tolerance Canada</th>
<th>Tolerance Japan</th>
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<tbody>
<tr>
<td>Abamectin</td>
<td>0.01</td>
<td>0.01</td>
<td>ppm</td>
<td>180.476</td>
<td>0.02</td>
<td>0.02</td>
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<td>Bifenazate</td>
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<td>0.05</td>
<td>ppm</td>
<td>180.572</td>
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<td>1.5</td>
<td>5</td>
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<tr>
<td>Captan**</td>
<td>10.2</td>
<td>0.01</td>
<td>ppm</td>
<td>180.103</td>
<td>20</td>
<td>5</td>
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<tr>
<td>Cyprodinyl</td>
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<td>0.01</td>
<td>ppm</td>
<td>180.532</td>
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<td>3.5</td>
<td>1</td>
</tr>
<tr>
<td>Fenhexamid</td>
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<td>0.01</td>
<td>ppm</td>
<td>180.553</td>
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<td>3</td>
<td>10</td>
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<tr>
<td>Fludioxonil</td>
<td>0.22</td>
<td>0.01</td>
<td>ppm</td>
<td>180.516</td>
<td>2</td>
<td>2</td>
<td>5</td>
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<tr>
<td>Myclobutanil</td>
<td>0.07</td>
<td>0.01</td>
<td>ppm</td>
<td>180.443</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>
Testing the limits

Strawberry Detected Pesticides (ppm)

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Strawberry Detected Heavy Metals (ppb)
Export Wheat Profile

- Total Number Compounds: 177
- Number of Methods per sample: 23
- TurnAround Time (TAT): 7 w. days
- Equipment use:
  - Gas Chromatograph – MS and MSMS detectors (5)
  - Ultra Precision Liquid Chromatograph – MSMS (5)
Wheat Profile

- Multi Pesticide Screen GC / LC (122)
- Phenoxy Herbicides (21)
- Individual Test (13)
- Multi Pesticide Screen SU (8)
- Premier LC MSMS (3)
- Glyphosate / Glufosinate (2)
- Mycotoxins (2)
- OrganoTin (2)
- Quaternary Ammine (2)
- Volatiles (2)
Export Testing Service
Wheat Profile – Quality Assurance

- Internal Quality Data (minimum 20 spike recoveries) submitted to MAFF on annually basis
- Annually Internal and External audit
- Re-validation method data
  - Ten replicates at MRL level and LOQ level
Testing the limits

Wheat Detected Pesticides (ppm)

Low Detection (ppm)
High Detection (ppm)

Chlormequat
Chlorpyrifos
Cypermethrin
Deltam / Tralom
Dichlorvos
Fenitrothion
Glyphosate
Inorganic Bromide
Malathion
Methoprene
Phosphine
Piperonyl Butox
Pirimiphos M
Vomitoxin
Food Safety Requires . . .

THE POWER OF COLLABORATION...
Food Safety Testing Requires . . .

- One accreditation standard
  - ISO 17025
  - KFDA
  - NELAC / ORELAP
  - MHLW
  - FSMA

- Uniform MRL
- Uniform analytical methods
Thank you for your attention