Automated laser ablation- and liquid chromatography-ICP-MS sample introduction systems for food safety analysis

C. Derrick Quarles Jr., Ph.D.\textsuperscript{1,2}
Sr. Scientist & LC Automation Product Manager
\textsuperscript{1} - Elemental Scientific, Inc. - Atlanta (ESI HQ are located in Omaha, NE)
\textsuperscript{2} - Elemental Scientific Lasers
Outline

**Liquid Sample Introduction**

- Sample Introduction Technology (*FAST* & *prepFAST*)
- *prepFAST* IC - Automated Total Metals & Elemental Speciation
- Arsenic Speciation
- Selenium Speciation

**Solid Sample Introduction**

- LA-ICP-MS
- Elemental Imaging
- Bulk Analysis Using Automation
What is FAST?
Faster Analysis = More Productive

Traditional Autosampler = 5 min per sample
ICP-MS Method = 50 s
4 min 10 s = sample flush, read delay, wash

Traditional Autosampler = 288 samples in 24 h

FAST Autosampler = 1 min 30 sec per sample
ICP-MS Method = 50 s
40 s = sample flush, read delay, wash

Reduction of 200 s per sample

FAST Autosampler = 1200 samples in 24 h

Assuming you run samples 24 h straight
1200 vs 288 = 417% More Productive with FAST
prepFAST – Inline Dilution

**Manual Dilution** 3\%HNO₃

- Digested Sample
- 10mL Diluted Sample
- 10mL Mixed Sample

400μL/min

**In-valve Autodilution** 3\%HNO₃

- 10x Dilution
- Sample Flow Rate 400μL/min
- Diluent 3\%HNO₃
- No Mixing Required

Digested Sample

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prepFAST – Inline Dilution

1. Fill Loop
   - Sample
   - Waste
   - S4: Internal Standard
   - S2: Carrier
   - S3: Diluent
   - Vacuum

2. Dilute Sample
   - Sample
   - Waste
   - S4: Internal Standard
   - S2: Carrier
   - S3: Diluent
   - Vacuum
   - To ICPMS

3. Inject Sample
   - Rinse
   - Carrier
   - To ICPMS
   - S2: Carrier
   - S4: Internal Standard
   - S3: Diluent
   - Waste

4. Clean V1
   - Sample
   - S1: Carrier
   - Carrier
   - Waste
   - S3: Diluent
   - S2: Carrier
   - To ICPMS
   - Vacuum
Conventional Calibration vs prepFAST Autocalibration

Conventional Calibration (seven points)
Offline Prep: 1 Blank + 7 Standards

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<thead>
<tr>
<th>STD Position</th>
<th>Concentration</th>
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<tbody>
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<tr>
<td>1</td>
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<td>2</td>
<td>5</td>
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<td>3</td>
<td>12.5</td>
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<tr>
<td>4</td>
<td>50</td>
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<td>5</td>
<td>100</td>
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<td>6</td>
<td>200</td>
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<td>7</td>
<td>500</td>
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prepFAST Autocalibration (seven points)
Inline Prep: 1 Blank + 1 Standard

<table>
<thead>
<tr>
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<th>Inline Dilution Factor</th>
<th>Std Dilution</th>
<th>Diluent Dilution</th>
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<td>10000</td>
<td>0</td>
<td>10000</td>
<td>500</td>
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prepFAST Calibration: Blank can be analyzed diluted or undiluted.
## prepFAST Saves Time

<table>
<thead>
<tr>
<th></th>
<th>Traditional Analysis</th>
<th>prepFAST Analysis</th>
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<tbody>
<tr>
<td>Sample Preparation (per sample)</td>
<td>1 min</td>
<td>0 min</td>
</tr>
<tr>
<td>100 samples (preparation time)</td>
<td>1 h 40 min</td>
<td>5 min</td>
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<tr>
<td>Calibration and QC prep</td>
<td>20 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Re-run of failed samples (10%)</td>
<td>20 min</td>
<td>0 min</td>
</tr>
<tr>
<td>Total Preparation Time</td>
<td>2 h 20 min</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time Saved per Day</td>
<td>2 h 10 min</td>
<td></td>
</tr>
<tr>
<td>Time Saved per Week</td>
<td>10 h 50 min</td>
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</tr>
<tr>
<td>Time Saved per Year</td>
<td>563 h 20 min</td>
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% Time Saved per year ~ 27%

### Comparison:

<table>
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<tr>
<td>Sample Preparation (per sample)</td>
<td>2 min</td>
<td>0 min</td>
</tr>
<tr>
<td>100 samples (preparation time)</td>
<td>3 h 20 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Calibration and QC prep</td>
<td>20 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Re-run of failed samples (10%)</td>
<td>20 min</td>
<td>0 min</td>
</tr>
<tr>
<td>Total Preparation Time</td>
<td>4 h 00 min</td>
<td>10 min</td>
</tr>
<tr>
<td></td>
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<tr>
<td>Time Saved per Day</td>
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<td>Time Saved per Week</td>
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<td>Time Saved per Year</td>
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</table>

% Time Saved per year ~ 48%

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prepFAST IC - “Automated Total Metals and Elemental Speciation”
prepFAST IC Features

- Completely metal-free liquid and sample flow path from pump to nebulizer.
- Compatible with acids and organic solvents.
- Inline autodilution and autocalibration functions.
- Ability to operate in total metals or chromatography mode with a single instrument.
- Syringe-driven, post-column standard addition, dilution, or derivatization.
prepFAST IC – Total Metals and Speciation

**Speciation Mode**

Intensity @ m/z = 75 (cps)

- ~ 25 uL Injection

**Total Metals Mode**

- 1.5 mL Dilution Loop

Time (s)

Intensity (a.u.)
Sample Uptake - Total Metals

- Biological Sample
- Stirred Sample
- Sample Taken Up
- Sample Loop
- Dilution Loop
- Chromatographic Column
- Carrier, Sample, Internal Standard Total Flow 400 µL/min
- Carrier 300 µL/min
- Internal Standard 100 µL/min
- To ICPMS
Sample Uptake - Speciation
## prepFAST IC – Total Metals and Speciation

### Autosampler Location

<table>
<thead>
<tr>
<th>Autosampler Location</th>
<th>Dilution Factor</th>
<th>Sample</th>
<th>Action</th>
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<tbody>
<tr>
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<td>1</td>
<td>Blank - Total Metals</td>
<td>Total Metals</td>
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<tr>
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<td>50</td>
<td>Standard 1</td>
<td>Total Metals</td>
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<td>Total Metals</td>
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<td>10</td>
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<td>2</td>
<td>5</td>
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<td>Total Metals</td>
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<td>2</td>
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<td>101</td>
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<td>240</td>
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<td>Sample 100</td>
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<tr>
<td>10</td>
<td>1</td>
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### Speciation

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<td>Dummy Sample</td>
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### prepFAST IC – Total Metals and Speciation

#### Autosampler Location

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<tr>
<td>9</td>
<td>1</td>
<td>Dummy Sample</td>
<td>Prime for Total Metals</td>
</tr>
</tbody>
</table>

- **Samples of Total Metals**: Blue dots
- **Samples of Speciation**: Pink dots
- **Speciation Stock Standard**: Green dots
- **Speciation Blank**: Green dots
- **Total Metals Stock Standard**: Orange dots
- **Total Metals Blank**: Orange dots

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Use of an inline dilution method to eliminate species interconversion for LC-ICP-MS based applications: focus on arsenic in urine†

C. Derrick Quarles, Jr, O * Patrick Sullivan, M. Paul Field, Scott Smith and Daniel R. Wiederin

Measuring arsenic in urine provides important information for clinical and epidemiological studies. While many researchers have studied ways to improve sample storage and understand why arsenic species undergo species interconversion, none have investigated inline dilution as a solution for arsenic speciation sample stability. A fast inline dilution method for AsB, DMA, MMA, As (III), and As (V) was demonstrated in this work. Inline dilution calibrations from a single stock standard were shown to have good linearity and resulted in LCDs in the single digit ppt range. Inline dilutions of 3DX, 50X, and 100X resulted in 0.1 s to 1.1 s variation in retention time. Manual sample preparation resulted in poor recovery (61%) for As (III) over a 24 h time period, which was a direct result of As (III) converting to As (V). Inline dilution of urine spiked with As (III) resulted in good recovery (101%) and reduced the species interconversion of As (III) to As (V) to ~1%. Accuracy to NIST SRM 2569 arsenic in frozen urine) was found to be within reported values for the five arsenic species tested for in this method.

AsB = Arsenobetaine
DMA = Dimethylarsinic acid
AsC = Arsenocholine
MMA = Monomethylarsonic acid
Inline Dilution Eliminates Species Interconversion

Manual Dilution
30X Manual DF
1 (Urine Spiked with 10 ppb As III): 29 (DI H₂O)

Inline Dilution
30X Inline DF
Urine Spiked with 10 ppb As III

Inline Dilution Eliminates Species Interconversion

Manual Dilution
30X Manual DF
1 (Urine Spiked with 10 ppb As III): 29 (DI H$_2$O)

Inline Dilution
30X Inline DF
Urine Spiked with 10 ppb As III

Inline Dilution Eliminates Species Interconversion

**Manual Dilution**
30X Manual DF
1 (Urine Spiked with 10 ppb As III): 29 (DI H$_2$O)

**Inline Dilution**
30X Inline DF
Urine Spiked with 10 ppb As III

Inline Dilution Eliminates Species Interconversion

**Manual Dilution**
30X Manual DF
1 (Urine Spiked with 10 ppb As III): 29 (DI H₂O)

**Inline Dilution**
30X Inline DF
Urine Spiked with 10 ppb As III

Comparison to Historical Data

Manual Prep vs prepFAST Inline Dilutions

HPLC vs prepFAST IC

$y = 0.9777x + 99.251$
$R^2 = 0.9773$

$y = 0.9844x + 0.2043$
$R^2 = 0.9846$

Total Metals & Arsenic Speciation
Food Application - Apple and Grape Juice

prepFAST IC + ICP-MS
Arsenic Speciation – Method A

Ammonium Phosphate Method

[Graph showing data analysis with peaks identified as 75As (As III), 75As (As V), 75As (EMMA), and 75As (EMMA)].

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Arsenic Speciation – Method B

Ammonium Carbonate Method
# Apple Juice – Total Metals

<table>
<thead>
<tr>
<th></th>
<th>$^{23}$Na (ppm)</th>
<th>$^{24}$Mg (ppm)</th>
<th>$^{39}$K (ppm)</th>
<th>$^{43}$Ca (ppm)</th>
<th>$^{52}$Cr (ppb)</th>
<th>$^{55}$Mn (ppb)</th>
<th>$^{57}$Fe (ppb)</th>
<th>$^{60}$Ni (ppb)</th>
<th>$^{63}$Cu (ppb)</th>
<th>$^{65}$Zn (ppb)</th>
<th>$^{75}$As (ppb)</th>
<th>$^{111}$Cd (ppb)</th>
<th>sum Pb (ppb)</th>
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<tbody>
<tr>
<td>Mott's 100% Apple Juice</td>
<td>27</td>
<td>55</td>
<td>1132</td>
<td>68</td>
<td>60</td>
<td>212</td>
<td>265</td>
<td>5</td>
<td>197</td>
<td>132</td>
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<tr>
<td>Juicy Juice 100% Apple Juice</td>
<td>21</td>
<td>37</td>
<td>1013</td>
<td>30</td>
<td>58</td>
<td>334</td>
<td>324</td>
<td>5</td>
<td>45</td>
<td>80</td>
<td>2.6</td>
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<td>White House 100% Apple Juice</td>
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<td>1241</td>
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<td>69</td>
<td>402</td>
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<td>23</td>
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<td>Apple &amp; Eve Organics Apple Juice</td>
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<td>932</td>
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<td>66</td>
<td>487</td>
<td>430</td>
<td>12</td>
<td>195</td>
<td>409</td>
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<tr>
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<td>92</td>
<td>84</td>
<td>363</td>
<td>91</td>
<td>78</td>
<td>827</td>
<td>818</td>
<td>16</td>
<td>73</td>
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<td>3.4</td>
<td>7.1</td>
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<tr>
<td>Publix 100% Grape Juice</td>
<td>22</td>
<td>84</td>
<td>275</td>
<td>92</td>
<td>73</td>
<td>2829</td>
<td>1045</td>
<td>21</td>
<td>190</td>
<td>614</td>
<td>2.1</td>
<td>26.3</td>
<td>3.4</td>
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<tr>
<td>Welch’s Refreshingly Simple Concord Grape Juice</td>
<td>13</td>
<td>37</td>
<td>454</td>
<td>54</td>
<td>49</td>
<td>1201</td>
<td>170</td>
<td>8</td>
<td>82</td>
<td>255</td>
<td>1.4</td>
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<td>1.6</td>
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<tr>
<td>Welch’s 100% Concord Grape Juice</td>
<td>36</td>
<td>109</td>
<td>944</td>
<td>117</td>
<td>95</td>
<td>2906</td>
<td>677</td>
<td>23</td>
<td>219</td>
<td>794</td>
<td>10.4</td>
<td>26.4</td>
<td>7.8</td>
</tr>
</tbody>
</table>
# Apple Juice – Arsenic Speciation

<table>
<thead>
<tr>
<th></th>
<th>AsB (ppb)</th>
<th>DMA (ppb)</th>
<th>As III (ppb)</th>
<th>MMA (ppb)</th>
<th>As V (ppb)</th>
<th>Speciation Sum (ppb)</th>
<th>i-As (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mott's 100% Apple Juice</strong></td>
<td>1.2</td>
<td>1.5</td>
<td>5.7</td>
<td>0</td>
<td>0.40</td>
<td>8.8</td>
<td>6.1</td>
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<tr>
<td><strong>Juicy Juice 100% Apple Juice</strong></td>
<td>0.72</td>
<td>0.58</td>
<td>1.7</td>
<td>0</td>
<td>0.11</td>
<td>3.1</td>
<td>1.8</td>
</tr>
<tr>
<td><strong>White House 100% Apple Juice</strong></td>
<td>0.98</td>
<td>0.82</td>
<td>2.5</td>
<td>0</td>
<td>1.1</td>
<td>5.4</td>
<td>3.6</td>
</tr>
<tr>
<td><strong>Publix Premium Apple Juice</strong></td>
<td>0.67</td>
<td>0.74</td>
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<td>0</td>
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<tr>
<td><strong>Mott's Natural Apple Juice</strong></td>
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<td>0.11</td>
<td>0.09</td>
<td>0</td>
<td>0</td>
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<tr>
<td><strong>White House Fresh Pressed 100% Natural Apple Juice</strong></td>
<td>0</td>
<td>0.75</td>
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<td>0</td>
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<tr>
<td><strong>Juicy Juice Organics Apple Juice</strong></td>
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<td>0.54</td>
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<td>0</td>
<td>2.9</td>
<td>1.8</td>
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<tr>
<td><strong>Apple &amp; Eve Organics Apple Juice</strong></td>
<td>0.64</td>
<td>0.68</td>
<td>1.7</td>
<td>0</td>
<td>0</td>
<td>3.0</td>
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<tr>
<td><strong>Lakewood Organic Pure Unfiltered Apple Juice</strong></td>
<td>0</td>
<td>0.35</td>
<td>0.13</td>
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<td>0</td>
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<td>0.1</td>
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<tr>
<td><strong>R.W. Knudsen Family Organic Apple Juice</strong></td>
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<td>0.56</td>
<td>0.92</td>
<td>0</td>
<td>0.09</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Gerber Toddler Apple Juice</strong></td>
<td>0</td>
<td>0.68</td>
<td>5.4</td>
<td>0</td>
<td>0</td>
<td>6.1</td>
<td>5.4</td>
</tr>
<tr>
<td><strong>Mott's For Tots Apple White Grape Juice</strong></td>
<td>0</td>
<td>0.28</td>
<td>1.2</td>
<td>0</td>
<td>0.4</td>
<td>1.9</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>Gerber Toddler White Grape</strong></td>
<td>0</td>
<td>5.5</td>
<td>3.8</td>
<td>0</td>
<td>2.6</td>
<td>11.8</td>
<td>6.4</td>
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<tr>
<td><strong>Gerber Toddler Pear</strong></td>
<td>0.42</td>
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<td>6.5</td>
<td>0</td>
<td>0.57</td>
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<tr>
<td><strong>Publix 100% White Grape Juice</strong></td>
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<td>0.83</td>
<td>4.2</td>
<td>0</td>
<td>0</td>
<td>5.0</td>
<td>4.2</td>
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<tr>
<td><strong>Welch's 100% White Grape Juice</strong></td>
<td>0.23</td>
<td>1.5</td>
<td>6.5</td>
<td>0</td>
<td>5.6</td>
<td>13.8</td>
<td>12.1</td>
</tr>
<tr>
<td><strong>R.W. Knudsen Family Organic Just Concord Grape Juice</strong></td>
<td>0</td>
<td>1.7</td>
<td>3.9</td>
<td>0</td>
<td>1.1</td>
<td>6.7</td>
<td>5.0</td>
</tr>
<tr>
<td><strong>Publix GreenWise Organic Grape Juice</strong></td>
<td>0</td>
<td>2.3</td>
<td>3.0</td>
<td>0</td>
<td>0.39</td>
<td>5.6</td>
<td>3.4</td>
</tr>
<tr>
<td><strong>Publix 100% Grape Juice</strong></td>
<td>0</td>
<td>0.68</td>
<td>2.4</td>
<td>0</td>
<td>0</td>
<td>3.0</td>
<td>2.4</td>
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<tr>
<td><strong>Welch's Refreshingly Simple Concord Grape Juice</strong></td>
<td>0</td>
<td>0.62</td>
<td>0.68</td>
<td>0</td>
<td>0</td>
<td>1.3</td>
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<tr>
<td><strong>Welch's 100% Concord Grape Juice</strong></td>
<td>0</td>
<td>1.4</td>
<td>2.5</td>
<td>0</td>
<td>3.8</td>
<td>7.7</td>
<td>6.3</td>
</tr>
</tbody>
</table>
Total Metals & Arsenic Speciation
Food Application - Fish and Lobster

prepFAST IC + ICP-MS
**Issue:** Some CRMs or real samples have very large concentrations of species that overload the column.

- **Current solution for HPLC** – off-line dilution, which is susceptible to species interconversion and time consuming.

- **prepFAST IC solution** – inline dilution, just seconds before injection onto the column which eliminates potential species interconversion.
  
  - TORT-3 has ~ 55 ppm AsB, at this level and a large injection volume – no inline dilution will correct for overloading of the column.

- **Potential Solution** – software controlled injection volume (no hardware change) to reduce amount of material loaded onto the column. This work will explore the minimum injection volume needed to accurately measure As in DORM and TORT CRMs and determine the performance characteristics for small injection volumes using the prepFAST IC.
Comparison of Standard 4 and TORT-3 (2X dilution factor)

Comparison of Standard 4 and TORT-3 (2X, 5X, 10X, 20X, 50X, and 100X dilution factor)
Swarcly controlled injection volumes with a 100 µL dilution loop:
0.1 µL injection @ 500 µL/min
1.0 µL injection @ 500 µL/min
100 µL injection @ 500 µL/min
As Speciation - TORT-3 & DORM-4 CRMs

CRMs: TORT-3 & DORM-4
1. ~0.5 g weighed into 50 mL polypropylene centrifuge tube
2. 20 mL of 0.28 M HNO₃ added
3. Vortex for 30 seconds
4. Heat @ 70ºC for 30 minutes
5. Centrifuge for 3 minutes
6. Collect supernatant
7. Add 20 mL of 0.28 M HNO₃ to residue
8. Vortex for 30 seconds
9. Heat @ 70ºC for 30 minutes
10. Centrifuge for 3 minutes
11. Collect supernatant
12. Combine the collected supernatant, record volume.
13. Use prepFAST IC to analyze sample utilizing inline dilutions (e.g. 50X, 100X, and 150X)
TORT-3 & DORM-4 CRMs (0.5 µL Injection)

AsB
As III
DMA
MMA
AsC
As V

10 ppb Standard
DORM-4 50X
TORT-3 50X

DORM-4 50X DF
TORT-3 50X DF

Intensity @ m/z = 75 (cps)
Time (s)
As Speciation - TORT-3 & DORM-4 CRMs (0.5 µL Injection)

<table>
<thead>
<tr>
<th></th>
<th>Mass (g)</th>
<th>Volume (L)</th>
<th>Target (µg/L)</th>
<th>Target SD</th>
<th>AsB (µg/L)</th>
<th>AsB (as As) (µg/L)</th>
<th>SD (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dorm-4 (A)</td>
<td>0.5513</td>
<td>0.04</td>
<td>94.7</td>
<td>8.6</td>
<td>213.3</td>
<td>89.8</td>
<td>6.6</td>
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<tr>
<td>Dorm-4 (B)</td>
<td>0.4873</td>
<td>0.04</td>
<td>83.7</td>
<td>7.6</td>
<td>168.7</td>
<td>71.0</td>
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<tr>
<td>Tort-3 (A)</td>
<td>0.5975</td>
<td>0.04</td>
<td>888.8</td>
<td>40.5</td>
<td>2113.9</td>
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<tr>
<td>Tort-3 (B)</td>
<td>0.5511</td>
<td>0.04</td>
<td>819.8</td>
<td>37.3</td>
<td>1985.1</td>
<td>835.9</td>
<td>48.3</td>
</tr>
</tbody>
</table>

**TORT-3 - Lobster Hepatopancreas**  
AsB (as As) = 54.9 ± 2.5 mg/kg

**DORM-4 - Fish Protein**  
AsB (as As) = 3.95 ± 0.36 mg/kg
Selenium Speciation
Food

prepFAST IC + ICP-MS
Se Speciation - LGC/ESI Collaboration

![Graphs showing Se speciation and intensity at m/z = 94 (\(^{78}\text{Se}^{16}\text{O}\))](image)

- **Cal Blank**
- **1 ppb**
- **5 ppb**
- **10 ppb**
- **20 ppb**
- **50 ppb**
- **100 ppb**
- **500 ppb**

**Equations and R\(^2\) Values:**

- \(y = 1521.8x + 389.31\)
- \(R^2 = 0.9999\)

- \(y = 1208.8x + 1518.9\)
- \(R^2 = 0.9999\)

- \(y = 1561.5x + 1439.3\)
- \(R^2 = 0.9999\)

**Concentration (µg/L)**

- **Se Met**
- **Se IV**
- **Se VI**
Se Speciation - LGC/ESI Collaboration

Initial results for various Se containing samples:

<table>
<thead>
<tr>
<th>Sample</th>
<th>SeMet</th>
<th>Se IV</th>
<th>Se VI</th>
<th>% I-Se</th>
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<tbody>
<tr>
<td>Pharmaceutical Tablets for Se</td>
<td>65675</td>
<td>1431</td>
<td>-</td>
<td>2.1</td>
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<tr>
<td>Yeast Supplements</td>
<td></td>
<td></td>
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<tr>
<td>Se Enriched Yeast</td>
<td>392721</td>
<td>29560</td>
<td>214</td>
<td>7.0</td>
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<tr>
<td>Wheat</td>
<td>3723</td>
<td>2109</td>
<td>248</td>
<td>38.8</td>
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<tr>
<td>Feed</td>
<td>7.6</td>
<td>174</td>
<td>-</td>
<td>95.8</td>
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<tr>
<td>Mushroom</td>
<td>2041</td>
<td>140</td>
<td>5.8</td>
<td>6.7</td>
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</tbody>
</table>
Pharmaceutical Tablets for Se Yeast Supplements

<table>
<thead>
<tr>
<th></th>
<th>SeMet</th>
<th>Se IV</th>
<th>Se VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>6514</td>
<td>205</td>
<td>-</td>
</tr>
<tr>
<td>Se IV Spike 1</td>
<td>6630</td>
<td>404</td>
<td>-</td>
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<tr>
<td>Se IV Spike 2</td>
<td>6115</td>
<td>465</td>
<td>-</td>
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<tr>
<td>Se VI Spike 1</td>
<td>7187</td>
<td>215</td>
<td>366</td>
</tr>
<tr>
<td>Blank Extraction</td>
<td>10</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>Blank Extraction</td>
<td>7.8</td>
<td>11</td>
<td>-</td>
</tr>
</tbody>
</table>
Se Speciation - LGC/ESI Collaboration

Se Enriched Yeast

<table>
<thead>
<tr>
<th></th>
<th>SeMet</th>
<th>Se IV</th>
<th>Se VI</th>
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</thead>
<tbody>
<tr>
<td>Neat</td>
<td>50522</td>
<td>3080</td>
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<tr>
<td>Se IV Spike 1</td>
<td>52509</td>
<td>4471</td>
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<tr>
<td>Se IV Spike 2</td>
<td>50972</td>
<td>5923</td>
<td>-</td>
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<tr>
<td>Se VI Spike 1</td>
<td>49181</td>
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<td>300</td>
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<td>15</td>
<td>-</td>
</tr>
<tr>
<td>Blank Extraction</td>
<td>7.8</td>
<td>11</td>
<td>-</td>
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</tbody>
</table>
Se Speciation - LGC/ESI Collaboration

<table>
<thead>
<tr>
<th>Wheat</th>
<th>SeMet</th>
<th>Se IV</th>
<th>Se VI</th>
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</thead>
<tbody>
<tr>
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<td>14</td>
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<td>Se IV Spike 1</td>
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<tr>
<td>Se IV Spike 2</td>
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<td>16</td>
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<tr>
<td>Se IV Spike 3</td>
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<td>Se VI Spike 1</td>
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<td>338</td>
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<td>10</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>Blank Extraction</td>
<td>7.8</td>
<td>11</td>
<td>-</td>
</tr>
</tbody>
</table>

The table shows the concentration of SeMet, Se IV, and Se VI in different samples, with units in µg/L.
Food Application: Rice

NWR193 + ICP-MS
• Laser Conditions:
  ▪ 193 nm nanosecond laser
  ▪ 100 Hz
  ▪ 30 µm spot size
  ▪ 4.8 J/cm²
  ▪ 30 µm spacing
  ▪ 48 µm/s stage speed

• Hardware Additions:
  ▪ TV²
  ▪ DCI

• Agilent 7700 ICP-MS:
  ▪ Elements measured: P, K, Mn, Cu, Zn, and As
  ▪ 1 – 250 ms dwell times

• Iolite – Data Reduction Software
Laser Ablation

UV 266-193nm Pulsed laser

Transmissive window

Particle collection

Sample

He in

To ICP-MS

Drain
Arsenic Pathways in Rice

- Rice husk (20%)
- Rice bran (8%)
  - Pericarp
  - Aleurone layer
- White rice (70%)
- Rice germ (2%)

Husk
Bran layers
Endosperm
Embryo

Silic acid
Arsenite
Phosphate arsenate

https://www.researchgate.net/profile/Norhaizan_Me/publication/324246893/figure/fig1/AS:623813507174400@1525740138574/The-structure-of-a-rice-grain.png
Rice Sample Preparation

Rice

Section Rice

Fix Rice in Epoxy

Top-Down View

Side View
Rice Imaging Example

Zoom into 3 Line Scans

- Cu63
- Zn66
- As75
Rice Imaging Example

Zoom into 3 Line Scans

- Cu63
- Zn66
- As75
Rice Imaging Example

Zoom into 3 Line Scans

- **Cu63**
- **Zn66**
- **As75**

Intensity (cps)

Time (s)
Rice Imaging Example

Full Scan for Rice Grain

- P31
- K39
- Mn55
- Cu63
- Zn66
- As75

Intensity (cps) vs. Time (s)
Rice Imaging Example

Full Scan for Rice Grain

Iolite – Semi-Quant Mode
Cell Space Images

Intensity (cps)

Time (s)
Rice Imaging – Calibration Scheme

Calibration Standards:
- NMIJ - CRM 7533a
- NIST – SRM 1568b

NMIJ – 0.63 ppm As
NIST – 0.285 ppm As
Sprouts Organic Jasmine White Rice
Sprouts Organic Long Grain Brown Rice
Rice Comparison - P (0 – 6000 ppm P)

- Organic Long Grain White Rice
- Organic Jasmine White Rice
- Paraboiled White Rice
- Paraboiled (90 s) White Rice
- Organic Wild Rice
- Organic Long Grain Brown Rice
- Whole Grain Brown Rice
- Paraboiled (90 s) Brown Rice
Rice Comparison - K (0 – 6500 ppm K)

- Organic Long Grain White Rice
- Organic Jasmine White Rice
- Paraboiled White Rice
- Paraboiled (90 s) White Rice
- Organic Wild Rice
- Organic Long Grain Brown Rice
- Whole Grain Brown Rice
- Paraboiled (90 s) Brown Rice
### Rice Comparison - Mn (0 – 50 ppm Mn)

<table>
<thead>
<tr>
<th>Organic Long Grain White Rice</th>
<th>Organic Jasmine White Rice</th>
<th>Paraboiled White Rice</th>
<th>Paraboiled (90 s) White Rice</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organic Wild Rice</th>
<th>Organic Long Grain Brown Rice</th>
<th>Whole Grain Brown Rice</th>
<th>Paraboiled (90 s) Brown Rice</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Rice Comparison - Cu (0 – 15 ppm Cu)

- Organic Long Grain White Rice
- Organic Jasmine White Rice
- Paraboiled White Rice
- Paraboiled (90 s) White Rice
- Organic Wild Rice
- Organic Long Grain Brown Rice
- Whole Grain Brown Rice
- Paraboiled (90 s) Brown Rice
<table>
<thead>
<tr>
<th>Organic Long Grain White Rice</th>
<th>Organic Jasmine White Rice</th>
<th>Paraboiled White Rice</th>
<th>Paraboiled (90 s) White Rice</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Organic Wild Rice</th>
<th>Organic Long Grain Brown Rice</th>
<th>Whole Grain Brown Rice</th>
<th>Paraboiled (90 s) Brown Rice</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Rice Comparison - As (0 – 1 ppm As)

- Organic Long Grain White Rice
- Organic Jasmine White Rice
- Paraboiled White Rice
- Paraboiled (90 s) White Rice
- Organic Wild Rice
- Organic Long Grain Brown Rice
- Whole Grain Brown Rice
- Paraboiled (90 s) Brown Rice
Imaging Method

- Laser Conditions:
  - 193 nm nanosecond laser
  - 100 Hz
  - 30 µm spot size
  - 4.8 J/cm²
  - 30 µm spacing
  - 48 µm/s stage speed

- Hardware Additions:
  - TV²
  - DCI

- Time = 45 minutes

- ICP-MS = 6 elements

High Resolution Imaging Method

- Laser Conditions:
  - 193 nm nanosecond laser
  - 100 Hz
  - 10 x 10 µm XYR spot
  - 3.0 J/cm²
  - 10 µm spacing
  - 100 µm/s stage speed

- Hardware Additions:
  - TV²
  - DCI

- Time = 78 minutes

- ICP-MS = 2 elements
Whole Grain Brown Rice

Max Conc. = 1500 ppm P
Whole Grain Brown Rice

Max Conc. = 100 ppm Zn
Food Application: Rice

NWRauto + ICP-MS
Laser Ablation Chamber

- Current LA chambers on the market meet the requirements for academia and R&D projects.
- Chamber can accommodate many samples.
- Chamber size limits the number of samples.
- Chamber size ranges from 100 x 100 mm up to 200 x 200 mm.
Laser Ablation Chamber

Approach 1: larger sample volume means more purge time

Approach 2: smaller sample size means more difficult scan placement and an extra step in the process (cutting).

Problem: Not many samples fit in the chamber at once. Some positions must be used by standards or QC materials in each batch.
Sequential analysis can enhance the throughput, efficiency and reduce human intervention when combined with automation.

Applications implemented so far:
- Industrial (e.g. geological, materials production)
- Medical (e.g. devices, clinical)
NWRauto – SRM Results

NIST SRM 1568b

Reference Value (mg/kg) vs Measured Results

- Mg
- P
- S
- K
- Mn
- Cu
- Zn
- As
- Se
- Mo
- Cd
- Hg

* Reference value below LOD for Cd
NWRauto – Sample Results

Rice Cereal

Concentration (ppm)

- Mg
- P
- S
- K
- Mn
- Cu
- Zn
- As
- Se
- Mo
- Cd
- Hg

Whole Grain 1
Whole Grain 2
Whole Grain 3
Whole Grain 4
Whole Grain 5
Whole Grain 6
Rice Cereal 1
Rice Cereal 2
Rice Cereal 3
Rice Cereal 4
Rice Cereal 5
Rice Cereal 6
NWRauto – Sample Results

Wholegrain & Rice Cereal

- **As**
  - DL = 0.09 ppm

- **Se**
  - DL = 0.02 ppm

- **Mo**
  - DL = 0.2 ppm

- **Cd**
  - DL = 0.03 ppm

- **Hg**
  - DL = 0.004 ppm
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