# Feasibility Study for the Determination of Arsenic Species in Nutritional Products and Raw Ingredients by HPLC-ICP-MS



# Introduction

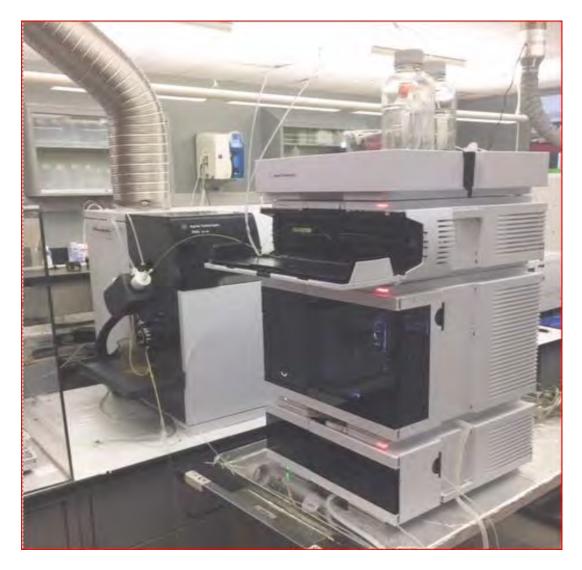
**Overview and Importance**. Hyphenated techniques utilizing high performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) for elemental speciation is one of the fastest growing areas of research in atomic spectroscopy. Elemental speciation plays an important role in food safety. Arsenic is found in the natural environment (soil, water and air) and is a well known human carcinogen. The determination of the total form of arsenic only tells part of the story. For example, the toxicity of arsenic is strongly affected by its chemical form. The inorganic forms of As (arsenite (As (+3)) and arsenate (As(+5)) are generally more toxic than the organic forms of arsenic (dimethylarsinic acid (DMA), and monomethylarsonic acid (MMA)). Other organic forms of arsenic such as arsenocholine (AsC) and arsenobetaine (AsB) are relatively non-toxic in humans. Therefore, their concentrations were not determined in this study.

**Objective**. To demonstrate the applicability of Agilent 7900 ICP-MS combined to the Agilent 1260 HPLC for the determination of arsenic species. In this study, we report the results obtained from Abbott Nutrition (AN) and UC-Davis laboratories for the determination of four arsenic species (arsenite (As+3), arsenate (As+5), dimethylarsinic acid (DMA), and monomethylarsonic acid (MMA)) in raw ingredients and milk based products by using HPLC-ICP-MS

# Experimental

#### Instrumentation and chromatographic conditions

Figure 1. HPLC-ICP-MS: Agilent 7900 ICP-MS and 1260 HPLC at AN



• At UC-Davis an Agilent Triple Quadrupole ICP-MS (run in single quad mode) was employed

#### Table 1. Agilent 7900 ICP-MS operating parameters

Plasma mode	Kinetic Energy Discrimination
Radio Frequency Power	1550 W
Radio Frequency Matching	1.8 V
Sample Depth	10.0 mm
Nebulizer Gas	1.08 L/min
Nebulizer Pump	0.1 rps
Auxiliary Gas	0.90 L/min
Cooled Spray Chamber	2 °C
Collision Reaction Cell Gas	He (≥ 99.9999 %)
He Flow	4.3 mL/min
Plasma Gas	Argon

Analytical Column							
Column Temperature							
Injection Volume							
Total Acquisition time							
Draw Speed							
Eject Speed							
Flow rate							

### Table 3. Gradient settings

u							
-		Mobile Pl					
5	Time	0.5 mM	15 mM	Flow	Max. Pressure		
	(min)	ammonium	ammonium	Rate	Limit (bar)		
		citrate dibasic	citrate dibasic	(mL/min)			
		(pH=4.5)	(pH=8)				
-	0	100	0	1.0	400		
	2	100	0	0.50	400		
	2.01	100	0	0.50	400		
	3	0	100	0.50	400		
	3.01	0	100	0.50	400		
	10	0	100	0.50	400		
	10.01	100	0	0.5	400		
_	12	100	0	0.50	400		

#### Table 4. Microwave extraction operating parameters

Parameters	
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- 100 % power, W
- Ramp to temperature,
- Hold time, min
- Temperature, °C

Cool down, min

### **Calibration Solutions**

- solutions

### Sample Material Used

- 1. NIST SRM 1568b Ric
- 2. NIST SRM 1549 Non
- 3. NIST SRM 1849a Infa
- 4. NIST SRM 1643e Tra
- 5. Whey Protein Concent
- 6. EV4H2R Infant Formula RTI

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# Experimental

#### 60 HPLC operating parameters

PRP-X 100 10µm 250x4.6 mm
20 °C
100 µL
20 min
100 µL/min
400 µL/min
0.5 mL/min

### Calculation of LOD and LOQ

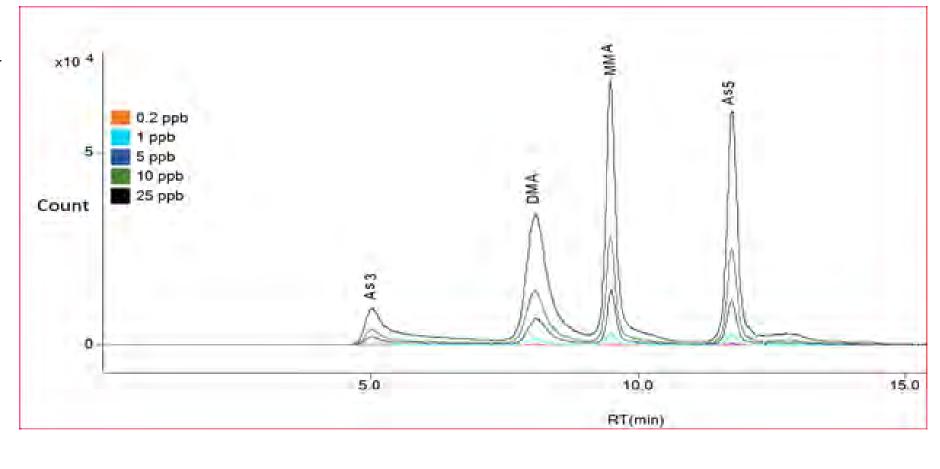
	Value	
	1600	
min	10	
	60	
	90	
	20	

 Working standards (UC Davis) - 0 μg/kg, 0.4 μg/kg, 0.5 μg/kg, 1 μg/kg, 5 μg/kg, 10 μg/kg, 20 μg/kg; prepared from intermediate

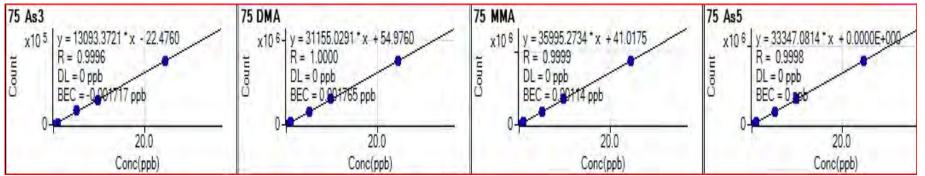
• Working standards (AN) - 0 μg/kg, 0.2 μg/kg, 1 μg/kg, 5 μg/kg,10 µg/kg, 25 µg/kg; prepared from intermediate solutions

ce Flour	7. Acid Casein
n-Fat Milk Pwd	8. Maltodextrin
fant formula Pwd	9. Milk Protein
ace Element in Water	10. Rice Syrup
trate	11. Cocoa Pwd
nula RTF	

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d for each	ch arsenic specie. The S	SD and baseline
   
   |  |   | MMA   |   |  | iAs   
  |  | Spec  
  | iation Total  |  
  |  |   | on)  |
| <ul> <li>Instrument LOD were obtained from 10 microwave extracted blanks.</li> <li>The LOQ was obtained by multiplying the instrument LOD by 3.3 or from the blank mean + 10 sigma.</li> </ul> |  |  |   |  | Lab  | Certified<br>(ng/g)  | Exp.<br>(ng/g)   
   
   | Rec.<br>(%)  | Certified<br>(ng/g)   | Exp.<br>(ng/g)  | Rec.<br>(%)   |  | Exp.<br>(ng/g)  
  | Rec.<br>(%)  | Certified<br>(ng/g)   
  | Exp.<br>(ng/g)  | Rec.<br>(%)  
  | Certified<br>(ng/g)  | Exp.<br>(ng/g)  | Rec.<br>(%)  |
|  | 0  | J by the dilution  | factor for liquid   | '  |  |  |  
   
   |  |   |   |   |  |   
  |  |   
  |   |  
  |  |   |  |
| •  |  | / /•   |   | 1568b  | UC Davis   | 180 <u>+</u> 12  | 173.0 <u>+</u> 1.3   
   
   | 96   | 11.6 <u>+</u> 3.5   | 14.9 <u>+</u> 0.03  | 129   | 92 <u>+</u> 10   | 98.1 <u>+</u> 1   
  | 107  | 285 <u>+</u> 14   
  | 286.1 <u>+</u> 0.7  | 100  
  | 285 <u>+</u> 14  | 278.9 <u>+</u> 5.9  | 98   |
|  |  |  |   |  | AN   |  | 178.1 ±4.9   
   
   | 99   | 11.6 <u>+</u> 3.5   | 10.1 ± 0.3  | 87  | 92 <u>+</u> 10   | 92.3 ± 2.5  
  | 100  | 285 <u>+</u> 14   
  | 280 ± 1   | 98   
  | 285 <u>+</u> 14  | 277.9 ± 4.1   | 98   |
| -5)), wer  | e obtained for liquid an   | id powder samp   | JIES, respectively.   |  |  |  |  
   
   |  |   |   |   |  |   
  |  |   
  |   |  
  |  |   |  |
| etention   | times and recovery f   | or four arsenic  | ; species   | 1549   | UC Davis   | NR   | NR   
   
   |  | NR  | NR  |   | NR   | NR  
  |  | 1.9*  
  | NR  |  
  | NR   | Diluted too   |  |
|  |  | Measured   |   | '  |  |  |  
   
   |  |   |   |   |  |   
  |  | 4.0*  
  |   | '  
  |  | /   | 407  |
| RT   | Theoretical Conc.  | Conc.  | Recovery  | /  | AN   | NK   |  
   
   |  |   |   |   | 1.9"   | $2.04 \pm 0.05$   
  |  | 1.9"  
  | $2.04 \pm 0.05$   |  
  | 1.9"   | $2.04 \pm 0.05$   | 107  |
| (min)  | (ng/g)   | (ng/g)   | (%)   |  |  |  |  
   
   |  |   |   |   |  |   
  |  |   
  |   |  
  |  | Diluted too   |  |
| 5  | 20.1   | 20.2   | 100.5   | 1849a  | UC Davis   | NR   | NR   
   
   |  | NR  | NR  |   | NR   | 25.0 <u>+</u> 0.4   
  |  | NR  
  | 25.0 <u>+</u> 0.4   |  
  | NR   | high<br>(~400x)   |  |
| 8.1  | 20   | 18.9   | 94.5  | · · · · · · · · · · · · · · · · · · ·  | AN   | NR   | NR   
   
   |  | NR  | NR  |   | NR   | 26.7 ± 1.0  
  |  | NR  
  | 26.7 ± 1.0  |  
  | NR   | 24.8 ± 2.1  | 92.9   |
| 9.5  | 19.9   | 19.6   | 98.5  |  |  |  |  
   
   |  |   |   |   |  |   
  |  |   
  |   |  
  |  |   |  |
|  |  |  |   | 1643e  | UC Davis   | NR   | NR   
   
   |  | NR  | NR  |   | 58.98 ± 0.70   | 57.7 <u>+</u> 1.0   
  | 98   | 58.98 ± 0.70  
  | 57.7 <u>+</u> 1.0   | 98   
  | 58.98 ± 0.70   | ) NR  | NR   |
| <u> </u>   | 20.1   |  |   | 1  | NR- Not repr   | reported SRM 1549 - NonFat milk Powder *Information value only- not certified by NIST  |  
   
   |  |   |   |   | J by NIST  |   
  |  |   
  |   |  
  |  |   |  |
| Separat <sup>7</sup>   | ion of the four arseni   | c species in w   | orking standards  | SRM  | VI 1849a - In  | fant Formu   | la Powder  
   
   | SRN  | / 1643e -Tra  | ce Element i  | n Wat   | er   |   
  |  | iAs = As(+  
  | +3) + As(+5)  |  
  |  |   |  |
| d ອິດ<br>ການ<br>(+ <b>ອ</b>  | d for each<br>ent LOD v<br>Q was ob<br>k mean +<br>Q numbe<br>nd powde<br>alues of a<br>+5)), were<br>etention f<br>RT<br>(min)<br>5<br>8.1<br>9.5<br>11.7 | d for each arsenic specie. The S<br>ent LOD were obtained from 10<br>Q was obtained by multiplying the<br>k mean + 10 sigma.<br>Q numbers were then multiplied<br>and powder (~50) samples.<br>alues of approximately 2.5 ng/g at<br>+5)), were obtained for liquid an<br>etention times and recovery for<br>RT Theoretical Conc.<br>(min) (ng/g)<br>5 20.1<br>8.1 20<br>9.5 19.9<br>11.7 20.1 | d for each arsenic specie. The SD and baseline<br>ent LOD were obtained from 10 microwave extr<br>Q was obtained by multiplying the instrument Lo<br>ak mean + 10 sigma.<br>Q numbers were then multiplied by the dilution<br>and powder (~50) samples.<br>alues of approximately 2.5 ng/g and 5 ng/g (As(<br>+5)), were obtained for liquid and powder samp<br>etention times and recovery for four arsenic<br>RT Theoretical Conc. Measured<br>RT Theoretical Conc. Conc.<br>(min) (ng/g) (ng/g)<br>5 20.1 20.2<br>8.1 20 18.9<br>9.5 19.9 19.6<br>11.7 20.1 21.1 | Ak mean + 10 sigma.Q numbers were then multiplied by the dilution factor for liquid<br>and powder (~50) samples.alues of approximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA,<br>+5)), were obtained for liquid and powder samples, respectively.Measured<br>Conc.RecoveryRTTheoretical Conc.Conc.Recovery(min)(ng/g)(%)520.120.2100.58.12018.994.59.519.919.698.5 | d for each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks.       NIST         Q was obtained by multiplying the instrument LOD by 3.3 or from ik mean + 10 sigma.       NIST         Q numbers were then multiplied by the dilution factor for liquid nod powder (~50) samples.       1568b         alues of approximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       1568b         etention times and recovery for four arsenic species       1549         RT       Theoretical Conc.       Conc.       Recovery         (min)       (ng/g)       (%)       1849a         8.1       20       18.9       94.5         9.5       19.9       19.6       98.5         11.7       20.1       21.1       105.0 | d for each arsenic specie. The SD and baseline for the<br>ent LOD were obtained from 10 microwave extracted blanks.<br>Q was obtained by multiplying the instrument LOD by 3.3 or from<br>ik mean + 10 sigma.<br>Q numbers were then multiplied by the dilution factor for liquid<br>and powder (~50) samples.<br>alues of approximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA,<br>+5)), were obtained for liquid and powder samples, respectively.<br>etention times and recovery for four arsenic species<br>RT Theoretical Conc. Conc. Recovery<br>(min) (ng/g) (ng/g) (%)<br>5 20.1 20.2 100.5<br>8.1 20 18.9 94.5<br>9.5 19.9 19.6 98.5<br>11.7 20.1 21.1 105.0<br>NR- Not report | d for each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks.       NIST         Q was obtained by multiplying the instrument LOD by 3.3 or from ik mean + 10 sigma.       NIST       Lab       Certified (ng/g)         Q numbers were then multiplied by the dilution factor for liquid nd powder (~50) samples.       Isome 125       Isome 125       Isome 125         alues of approximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       Isome 125       Isome 125         etention times and recovery for four arsenic species       Measured       Isome 125       Isome 125         Manne       Isome 120       NR       Isome 125       Isome 125         Measured       Conc.       Recovery       Isome 125       NR         Manne       Isome 120       Isome 125       NR         9.5       20.1       20.2       100.5       NR         9.5       19.9       19.6       98.5       Isome 125       NR         11.7       20.1       21.1       105.0       NR       Isome 126       Isome 126         NR       Isome 12.5       Isome 12.5 </td <td>DMADMADMAMathematical form 10 microwave extracted blanks.Q was obtained by multiplying the instrument LOD by 3.3 or from<br/>ik mean + 10 sigma.Q numbers were then multiplied by the dilution factor for liquid<br/>and powder (~50) samples.<br/>alues of approximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA,<br/>+5)), were obtained for liquid and powder samples, respectively.Measured<br/>RT Theoretical Conc.Conc.RecoveryMeasured<br/>(min)NRNRNRNR8.12018.994.59.519.919.698.511.720.121.1105.0NR- Not reported</td> <td>d for each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks.       Image: Constant of the ent LOD by 3.3 or from ik mean + 10 sigma.         Q numbers were then multiplied by the dilution factor for liquid and powder (~50) samples.       Image: Constant of the ent log of a proximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       Image: Constant of the ent log of a proximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       Image: Constant of the ent log of a proximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       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The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks.       Imma       Imma         Q was obtained by multiplying the instrument LOD by 3.3 or from k mean + 10 sigma.       Imma       Rec. Certified (ng/g)       Exp. (ng/g)       Rec. Certified (ng/g)       Exp. (ng/g)       Rec. Certified (ng/g)       Exp. (ng/g)       Imma         Q numbers were then multiplied by the dilution factor for liquid and powder (~50) samples.       alues of approximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       Imma       Imma       Imma       Imma       Imma       Imma         etention times and recovery for four arsenic species       Measured       NR       NR</td> <td>MMA         MMA         MMA         NIST<br/>sem       Certified<br/>(ng/g)       Kec.<br/>(ng/g)       Certified<br/>(ng/g)       Kec.<br/>(ng/g)       Certified<br/>(ng/g)       Kec.<br/>(ng/g)       Kec.<br/>(ng/g</td> <td>Image: constraint of the set of the ent LOD were obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. Q was obtained for multiplying the instrument LOD by 3.3 or from k mean +10 sigma.       NIST SRM       Lab       Certified (ng/g)       Rec. (ng/g)       Rec. (ng/g)       Rec. (ng/g)       Rec. (ng/g)</td> <td>Image: bit of the service specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. Q was obtained by multiplying the instrument LOD by 3.3 or from k mean + 10 sigma.       Image: bit of the service servi</td> <td>Image: difference of the ent LOD were obtained from 10 microwave extracted blanks. Q numbers were then multiplying the instrument LOD by 3.3 or from is mean + 10 sigma.       Image: difference of the ent LOD were obtained from 10 microwave extracted blanks. Q numbers were then multiplied by the dilution factor for liquid and powder (~50) samples.       NIST SRM       Lab       Certified (ng/g)       Exp. (ng/g)       Rec. (ng/g)       Certified (%)       Exp. (ng/g)       Rec. (ng/g)       Rec. (ng/g)       Certified (%)       Exp. (ng/g)       Rec. (ng/g)<td>Image: display baseline for the ent LOD were obtained from 10 microwave extracted blanks. Quas obtained by multiplying the instrument LOD by 3.3 or from is mean + 10 sigma.       Image: microwave extracted blanks. Quas obtained by multiplying the instrument LOD by 3.3 or from is mean + 10 sigma.       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(ng/g)       Rec. (ng/g)       Certified (ng/g)       Exp. (ng/g)       Rec. (ng/g)       Rec. (ng/g)       <th< td=""><td>If or each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. Q was obtained by multiplying the instrument LOD by 3.3 or from ik mean + 10 sigma.       Image: milling transmit is instrument LOD by 3.3 or from ik mean + 10 sigma.       Nist SRM       Lab       Certified (ng/g)       Rep. (ng/g)</td><td>Image: constraint of the constraint</td><td>I or each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Qwas obtained by multiplying the instrument LOD by 3 3 or from int mean + 10 sigma.       Image: Control of the ent int of t</td></th<></td></td> | DMADMADMAMathematical form 10 microwave extracted blanks.Q was obtained by multiplying the instrument LOD by 3.3 or from<br>ik mean + 10 sigma.Q numbers were then multiplied by the dilution factor for liquid<br>and powder (~50) samples.<br>alues of approximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA,<br>+5)), were obtained for liquid and powder samples, respectively.Measured<br>RT Theoretical Conc.Conc.RecoveryMeasured<br>(min)NRNRNRNR8.12018.994.59.519.919.698.511.720.121.1105.0NR- Not reported | d for each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks.       Image: Constant of the ent LOD by 3.3 or from ik mean + 10 sigma.         Q numbers were then multiplied by the dilution factor for liquid and powder (~50) samples.       Image: Constant of the ent log of a proximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       Image: Constant of the ent log of a proximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       Image: Constant of the ent log of a proximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.       Image: Constant of the ent log of a proximately 2.5 ng/g and 5 ng/g (As(+3), DMA, MMA, +5)), were obtained for liquid and powder samples, respectively.         etention times and recovery for four arsenic species       Image: Constant of the ent log of a proximately 2.5 ng/g (ng/g) (%)       Image: Constant of the ent log of a proximately 2.5 ng/g (ng/g) (%)         5       20.1       20.2       100.5       Image: Constant of the ent log of a proximately 2.5 ng/g (Ng/g) (%)         5       20.1       20.2       100.5       Image: Constant of the ent log of a proximately 2.5 ng/g (Ng/g) (%)       Image: Constant of the ent log of a proximately 2.5 ng/g (Ng/g) (%)       Image: Constant of the ent log of a proximately 2.5 ng/g (Ng/g) (%)         5       20.1       20.2       100.5       Image: Constant of the ent log of a proximately 2.5 ng/g (Ng/g) (%)       Image: Constant of the ent log of a proximately (Ng/g) | JMAJMANIST<br>LabCertified<br>(ng/g)Exp.<br>(ng/g)Rec.<br>(ng/g)Certified<br>(ng/g)NIST<br>LabCertified<br>(ng/g)Exp.<br>(ng/g)Rec.<br>(ng/g)Certified<br>(ng/g)NIST<br>LabCertified<br>(ng/g)Exp.<br>(ng/g)Rec.<br>(ng/g)Certified<br>(ng/g)NIST<br>LabCertified<br>(ng/g)Exp.<br>(ng/g)Rec.<br>(ng/g)Certified<br>(ng/g)NIST<br>LabCertified<br>(ng/g)Exp.<br>(ng/g)Rec.<br>(ng/g)Certified<br>(ng/g)NIST<br>LabCertified<br>(ng/g)Exp.<br>(ng/g)Rec.<br>(ng/g)Certified<br>(ng/g)NIST<br>LabCertified<br>(ng/g)Exp.<br>(ng/g)Rec.<br>(ng/g)Certified<br>(ng/g)NIST<br>LabCertified<br>(ng/g)Exp.<br>(ng/g)Exp.<br>(ng/g)Exp.<br>(ng/g)Exp.<br>(ng/g)Exp.<br>(ng/g)Exp.<br>(ng/g)NIST<br>LabUC DavisNRNRNRNRMeasured<br>Conc.<br>Conc.<br>Conc.<br>RecoveryUC DavisNRNRNRNR1549UC DavisNRNRNRNRNR9.519.919.698.51643eUC DavisNRNRNR1643eUC DavisNRNRNRNRNR1643eUC DavisNRNRNRNR10.1021.1105.0NRNRNR | d for each arsenic specie. 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Imma       Imma       Imma       Imma       Imma       Imma         etention times and recovery for four arsenic species       Measured       NR       NR | MMA         MMA         MMA         NIST<br>sem       Certified<br>(ng/g)       Kec.<br>(ng/g)       Certified<br>(ng/g)       Kec.<br>(ng/g)       Certified<br>(ng/g)       Kec.<br>(ng/g)       Kec.<br>(ng/g | Image: constraint of the set of the ent LOD were obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. Q was obtained for multiplying the instrument LOD by 3.3 or from k mean +10 sigma.       NIST SRM       Lab       Certified (ng/g)       Rec. (ng/g)       Rec. (ng/g)       Rec. (ng/g)       Rec. (ng/g) | Image: bit of the service specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. 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(ng/g)       Rec. (ng/g)       Certified (ng/g)       Exp. (ng/g)       Rec. (ng/g)       Rec. (ng/g)       <th< td=""><td>If or each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. Q was obtained by multiplying the instrument LOD by 3.3 or from ik mean + 10 sigma.       Image: milling transmit is instrument LOD by 3.3 or from ik mean + 10 sigma.       Nist SRM       Lab       Certified (ng/g)       Rep. (ng/g)</td><td>Image: constraint of the constraint</td><td>I or each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Qwas obtained by multiplying the instrument LOD by 3 3 or from int mean + 10 sigma.       Image: Control of the ent int of t</td></th<></td> | Image: display baseline for the ent LOD were obtained from 10 microwave extracted blanks. 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Quas obtained for liquid and powder samples, respectively.       Image: microwave extracted blanks. Quas obtained for liquid and powder samples, respectively.       Image: microwave extracted blanks. Quas obtained for liquid and powder samples, respectively.       Image: microwave extracted blanks. Quas obtained for liquid and powder samples, respectively.       Image: microwave extracted blanks. Quas obtained for liquid and powder samples, respectively.       Image: microwave extracted blanks. Quas obtained for liquid and powder samples, respectively.       Image: microwave extracted blanks. Quas obtained for liquid and powder samples, respectively.       Image: microwave extracted blanks. Quas obtained for liquid and powder samples, respectively.       Image: | Id for each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Q was obtained by multipling the instrument LOD by 3.3 or from k mean + 10 sigma.       NST       Lab       Certified (ng/g)       Rec. (ng/g)       Certified (ng/g)       Exp. (ng/g)       Rec. (ng/g)       Certified (ng/g)       Rec. (ng/g)       Certified (ng/g)       Exp. (ng/g)       Rec. (ng/g)       Rec. (ng/g)       Certified (ng/g)       Exp. (ng/g)       Rec. (ng/g)       Rec. (ng/g) <th< td=""><td>If or each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Q was obtained from 10 microwave extracted blanks. Q was obtained by multiplying the instrument LOD by 3.3 or from ik mean + 10 sigma.       Image: milling transmit is instrument LOD by 3.3 or from ik mean + 10 sigma.       Nist SRM       Lab       Certified (ng/g)       Rep. (ng/g)</td><td>Image: constraint of the constraint</td><td>I or each arsenic specie. The SD and baseline for the ent LOD were obtained from 10 microwave extracted blanks. Qwas obtained by multiplying the instrument LOD by 3 3 or from int mean + 10 sigma.       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### Figure 3. Calibration curves for As(+3), DMA, MMA, and As(+5)



#### Table 6. Average spike recovery of 5 $\mu$ g/kg As(+3), DMA, MMA, and As(+5) in NIST SRM 1849a

	As+3	DMA	MMA	As+5	-
Average (n=3)	100 %	104 %	105%	101 %	-
Range	97-102 %	103-105 %	104 -105 %	93-109 %	

# Acknowledgements

The authors are grateful to Agilent Technologies for support in this collaborative work.

# Results

#### Table 7. Results from analysis of NIST SRMs for As species obtained at AN and UC Davis laboratories

#### Table 8. Quantitative results for the seven samples analyzed at UC Davis and AN. Average $\pm 1\sigma$ , n=2 for the individual species

	•			-	•	
Laboratory	Sample	iAs	DMA	MMA	Sum of Species	
UC Davis	Whey Protein Conc.	26.57 ± 0.61	<lod< td=""><td><lod< td=""><td>26.57 ± 0.61</td></lod<></td></lod<>	<lod< td=""><td>26.57 ± 0.61</td></lod<>	26.57 ± 0.61	
AN		$25.93 \pm 0.49$	<lod< td=""><td><lod< td=""><td colspan="2"><math display="block">25.93 \pm 0.49</math></td></lod<></td></lod<>	<lod< td=""><td colspan="2"><math display="block">25.93 \pm 0.49</math></td></lod<>	$25.93 \pm 0.49$	
UC Davis	Cocoa Powder	$31.88 \pm 4.25$	<lod< td=""><td><lod< td=""><td><math display="block">34.06 \pm 4.23</math></td></lod<></td></lod<>	<lod< td=""><td><math display="block">34.06 \pm 4.23</math></td></lod<>	$34.06 \pm 4.23$	
AN		32.92 ± 1.28	LOD	<lod< td=""><td><math display="block">32.92 \pm 1.28</math></td></lod<>	$32.92 \pm 1.28$	
UC Davis	Acid Casein	$20.29 \pm 1.09$	<lod< td=""><td><lod< td=""><td><math display="block">20.29 \pm 1.09</math></td></lod<></td></lod<>	<lod< td=""><td><math display="block">20.29 \pm 1.09</math></td></lod<>	$20.29 \pm 1.09$	
AN		22.35 ± 1.17	<lod< td=""><td><lod< td=""><td>22.35 ± 1.17</td></lod<></td></lod<>	<lod< td=""><td>22.35 ± 1.17</td></lod<>	22.35 ± 1.17	
UC Davis	Maltodextrin	27.87 ± 5.77	<lod< td=""><td><lod< td=""><td><math display="block">28.00\pm5.75</math></td></lod<></td></lod<>	<lod< td=""><td><math display="block">28.00\pm5.75</math></td></lod<>	$28.00\pm5.75$	
AN		$28.56\pm0.76$	<lod< td=""><td><lod< td=""><td><math display="block">28.56\pm0.76</math></td></lod<></td></lod<>	<lod< td=""><td><math display="block">28.56\pm0.76</math></td></lod<>	$28.56\pm0.76$	
UC Davis	Milk Protein	18.02 ± 1.25	<lod< td=""><td><lod< td=""><td>18.02 ± 1.25</td></lod<></td></lod<>	<lod< td=""><td>18.02 ± 1.25</td></lod<>	18.02 ± 1.25	
AN		$62.26\pm5.20$	<lod< td=""><td><lod< td=""><td><math display="block">62.26\pm5.20</math></td></lod<></td></lod<>	<lod< td=""><td><math display="block">62.26\pm5.20</math></td></lod<>	$62.26\pm5.20$	
UC Davis	Rice Syrup	28.94 ± 0.73	13.88 ± 0.99	<lod< td=""><td>42.83 ± 1.23</td></lod<>	42.83 ± 1.23	
AN		27.76 ± 1.50	14.53 ± 1.13	<lod< td=""><td>42.29 ±1.88</td></lod<>	42.29 ±1.88	
UC Davis	EV4H2R	15.62 ± 0.32	<lod< td=""><td><lod< td=""><td>15.62 ± 0.32</td></lod<></td></lod<>	<lod< td=""><td>15.62 ± 0.32</td></lod<>	15.62 ± 0.32	
AN		15.79 ± 0.41	<lod< td=""><td><lod< td=""><td>15.79 ± 0.41</td></lod<></td></lod<>	<lod< td=""><td>15.79 ± 0.41</td></lod<>	15.79 ± 0.41	

# Conclusions

Based on these results the Agilent 1260 HPLC combined with an Agilent 7900 ICP-MS is well suited for arsenic speciation in raw ingredients and nutritional products.

• Adequate sensitivity was demonstrated to meet regulatory requirements. • Good accuracy, precision, and comparable results were obtained within and between AN and UC Davis laboratories.

• The next step will be to develop a validated method for all four Arsenic species.

- Inorganic arsenic (As(+3) and As(+5) species were the predominant species found in the raw ingredients and milk based samples