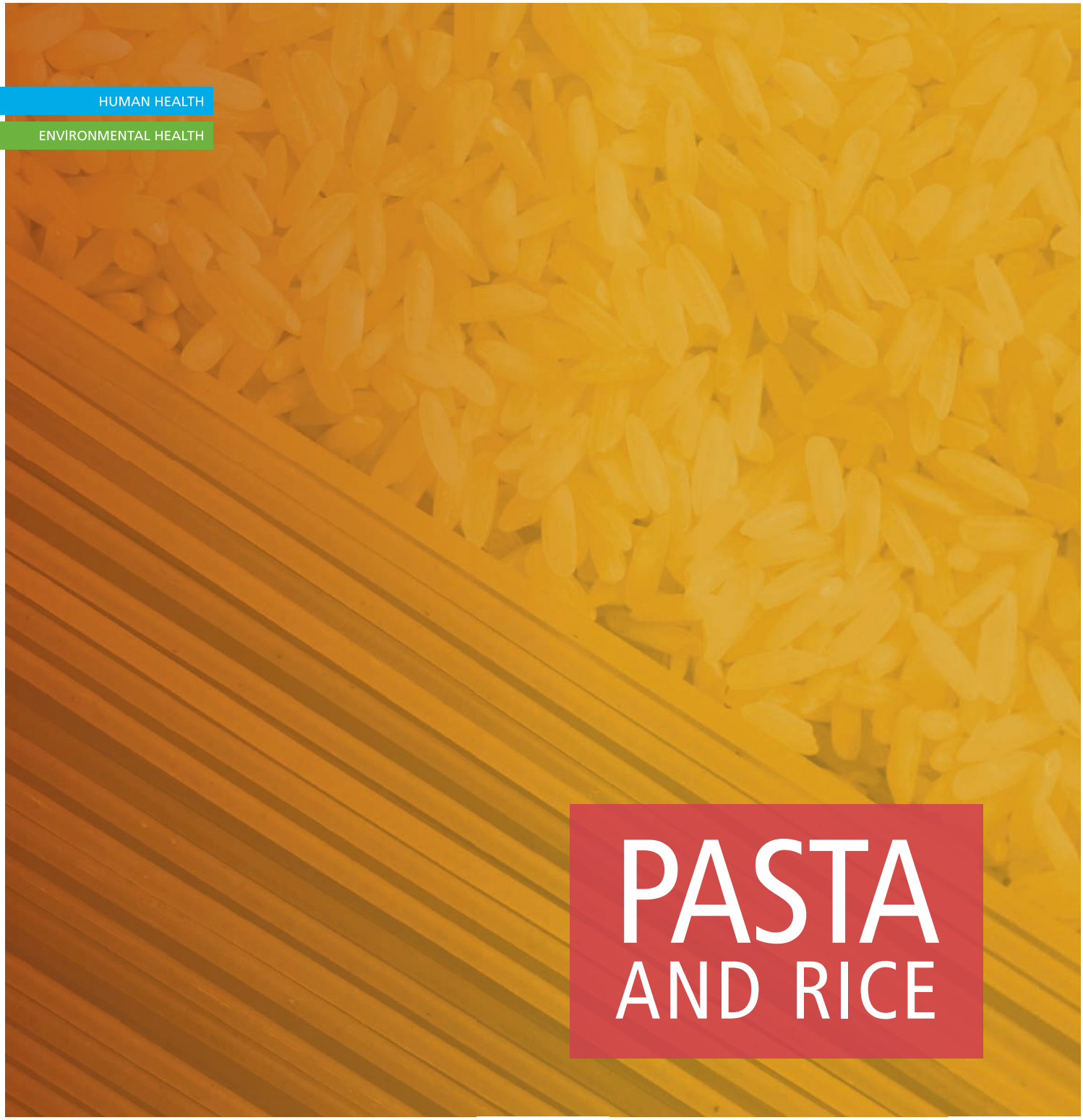
HUMAN HEALTH

ENVIRONMENTAL HEALTH



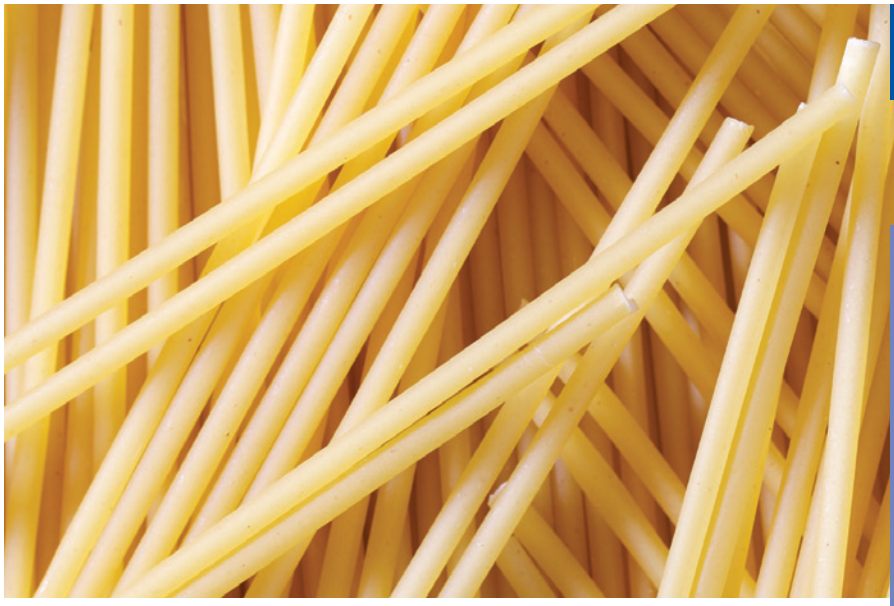
PASTA AND RICE

Pasta and Rice Compendium

PerkinElmer®
For the Better

PASTA AND RICE

Table of Contents



APPLICATION NOTE

Thermal Analysis

Effect of Humidity on Mechanical Properties of Pasta

Summary

The mechanical properties of pasta are very important. In its dried form, it is very brittle and quite stiff. If introduced into a humid environment and heated, the properties of the pasta change dramatically. This application note will investigate the effect of humidity on pasta under isothermal and temperature scanning conditions.

Introduction

Dynamic Mechanical Analysis (DMA) measures the stiffness of a material. The stiffness of pasta is a good indication as to the stability of the dried product. Dried pasta from the packet is quite stiff and humidity and temperature will decrease the stiffness as the material softens. The modulus gives an indication of the stiffness as it decreases and tan δ indicates when the material becomes more viscous and less elastic.

DMA works by applying an oscillating force to the material and the resultant displacement of the sample is measured. From this, the stiffness can be determined and the modulus and tan δ can be calculated. Tan δ is the ratio of the loss modulus to the storage modulus. By measuring the phase lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. Tan δ is plotted against temperature and a glass transition is normally observed as a peak since the material will absorb energy as it passes through the glass transition.

Dried pasta can be stored for long periods without risk of biological decay. When exposed to water, either by immersion or humidity, the pasta will absorb the water and start to hydrate. The humidity and temperature affect the hydration rate significantly as will be demonstrated.

PerkinElmer®
For the Better

Experimental

1. Isothermal experiement at 50 ˚C and 100% RH.

The sample was mounted in the Single Cantilever Bending clamps of the PerkinElmer® DMA 8000 and the temperature set to 50 °C. The experiment was started when the humidity reached 100%.

2. Temperature scanning experiement at 62% and 100% RH.

The sample was mounted in the Single Cantilever Bending clamps of the DMA 8000 and the RH was allowed to equilibrate. The samples were run from ambient to over 100 °C.

Equipment	Experimental Conditions	
DMA 8000	Sample:	Pasta
Fluid Bath	Geometry:	Single Cantilever Bending
Humidity Generator	Dimensions:	2.75 (l) x 4.50 (w) x 0.83 (t) mm
Circulator	Frequency:	1 Hz

Results and conclusion

Figure 1 shows the modulus and tan δ response from a sample of pasta at 50 °C and 100% RH. The modulus starts decreasing almost immediately on exposure to the RH and loses all integrity by about 1.5 hours. The tan δ increases steadily over the experiment indicating that the sample is getting more viscous and less elastic until after 1.5 hours, the sample collapses totally. The shoulder seen at 40 minutes indicates the "al dente" point where although fully hydrated, it still has some firm texture.

The responses from the two temperature scanning experiments are show in Figure 2. The black lines correspond to the experiment at 62% RH and the red lines to the experiment at 100% RH. The modulus in both experiments start at approximately the same level, indicating similar material was examined. The higher RH experiment shows a more rapid reduction in modulus as expected. It actually loses structural integrity at about 100 °C. The 62% RH experiment shows a smaller drop in modulus over the temperature range. The 100% RH modulus response clearly shows a similar shoulder at 75 °C, as in the first graph, indicating the pasta reaching "al dente" point.

The tan δ response in the 62% RH experiment shows a gradual increase indicating an increase in viscosity. Like the modulus response, it is not a constant increase, indicating more than one process is involved. It is more obvious, and faster, for the 100% RH sample. Here a peak is observed at about 75 °C which might be a plasticized relaxation event but corresponds to the "al dente" point mentioned earlier. The sample goes on to a very viscous sample as it "cooks" at about 100 °C. This application note has demonstrated the ability of the DMA 8000 to make measurements under a controlled humidity environment. The pasta used in this study showed dramatic mechanical effects when the temperature and humidity of the sample were controlled and changed.

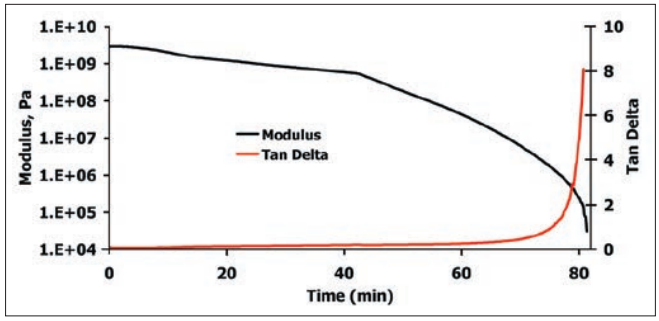


Figure 1. Modulus and tan δ from a sample of pasta at 50 ˚C.

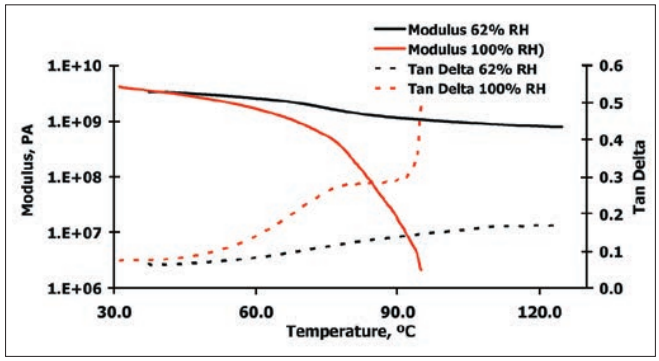


Figure 2. Modulus and tan δ from two temperature scanning experiments.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

007771B_27

APPLICATION NOTE

HPLC/ICP - MS

Authors:
Kyoko Kobayashi, Osamu Shikino
Inorganic Product Specialists
PerkinElmer Japan Co., Ltd.

Arsenic Speciation Analysis in Brown Rice by HPLC/ICP-MS Using the NexION 300D/350D

Introduction

Arsenic (As) is a well-known toxic element which has been highly regulated, especially for drinking water. Although regulatory limits have been for total arsenic, its toxicity varies widely and is dependent on its chemical form. For example, inorganic forms of arsenic are highly toxic and carcinogenic. However, organic forms (such as monomethylarsonic acid, dimethylarsinic acid, and arsenobetaine) are recognized as non-toxic or as having low toxicity.

The Joint Expert Committee on Food and Additives (JECFA) recognizes the importance of monitoring inorganic arsenic intake. In 1988, they established a provisional tolerable weekly intake (PTWI) of 0.015 mg/kg body weight inorganic arsenic. However, this recommendation was withdrawn in 2010.

In Japan, the average total arsenic intake/person/day is divided between seafood (53.6%), vegetables and seaweed (35.4%), rice (7.1%), and other sources.[1] It is known that the majority of arsenic in marine organisms is in the form of arsenobetaine, which is non-toxic. However, because of the large quantities of rice consumed in Japan, it is important to know what forms of arsenic are present in rice.

PerkinElmer®
For the Better

In recent years, it has become common to measure different forms of arsenic using HPLC/ICP-MS: HPLC separates the forms and ICP-MS detects them as they elute from the column. The advantage of ICP-MS as an HPLC detector is that it is very sensitive and can measure trace levels, as demonstrated by its use to measure impurities in a wide range of electronic materials and environmental samples.

This work focuses on the use of HPLC/ICP-MS to measure various arsenic compounds in brown rice.

Experimental

Calibration and Sample Preparation

As part of an inter-laboratory study, brown rice samples with known arsenic concentrations were distributed to eight labs. The sample preparation, HPLC conditions, and analysis scheme were defined by the institution coordinating the study.

Sample preparation consisted of adding 10 mL ultrapure water to 0.1 g rice powder and heating for 4 hours at 90 °C. After cooling to room temperature, the samples were centrifuged and filtered with a 0.45 µm syringe filter.

Standards were prepared by mixing DMA, MMA, As(III), and As(V); AsB was also added as an internal standard. Calibration curves, established with 0.5, 1, 2, 5, 10, 20, and 30 ppb standards, had correlation coefficients > 0.999 for all compounds.

Instrumental Conditions

All analyses were done using a PerkinElmer Flexar™ HPLC system coupled to a PerkinElmer NexION® 300D ICP-MS. When performing elemental analyses with ICP-MS, polyatomic interferences are a concern. For example, if a sample contains chloride, $ArCl^+$ and $CaCl^+$ may interfere with arsenic measurements since they all exist at m/z 75. The NexION 300 series ICP-MS is equipped with a Universal Cell, which allows the effects of polyatomic interferences to be removed either through chemical reactions or collisions. Although collisions with helium as a cell gas remove the interferences, there is also a significant decrease in analyte sensitivity. In this work, methane was used in the Universal Cell to remove any $ArCl^+$ or $CaCl^+$ polyatomic interferences on As^+ through chemical reactions without significantly reducing As^+ sensitivity. Both the HPLC and ICP-MS conditions used in this work are shown in Tables 1 and 2, respectively.

Table 1. HPLC Conditions

Parameter	Condition
Instrument	Flexar HPLC
Column	4.6 mm × 250 mm, 5 µm particles
Mobile phase	10 mmol/L 1-butanesulfonic acid (sodium salt)⁄4 mmol/L tetramethyl ammonium hydroxide, 4 mmol/L malonic acid, 0.05 % methanol, 0.03% nitric acid
Flow	0.8 mL/min
Column temperature	Room temperature
Injection volume	10 µL

Table 2. ICP-MS Conditions

Parameter	Condition
Instrument	NexION 300D ICP-MS
RF power	1600W
Analyte	m/z ^{75}As
Cell conditions	Methane, 0.3 mL/min

Results

The concentrations of each compound were determined by measuring peak area; Chromera HPLC software was used for instrument control, sample analyses, and data processing. Figure 1 shows the chromatograms of two brown rice samples; each contained As(V), As(III), and DMA, with AsB added as the internal standard. Each sample measurement required 7 minutes.

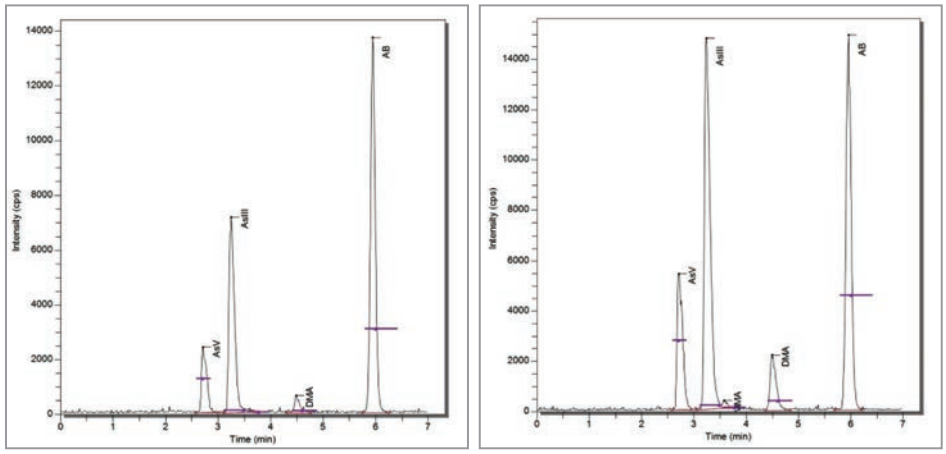


Figure 1. Chromatograms of rice samples A and C.

Table 3 shows the LODs and LOQs for each arsenic compound, along with the results for the five brown rice samples measured. The LODs and LOQs are based on the signal-to-noise ratios (S/N), with the LOD defined as S/N = 3 and the LOQ defined as S/N = 10.

Table 3. Results for Brown Rice Samples, LODs, and LOQs

Species	LOD	LOQ	Sample A	Sample B	Sample C	Sample D	Sample E
As(V)	0.00013	0.00044	0.021	0.043	0.044	0.040	0.053
As(III)	0.00012	0.00039	0.070	0.13	0.13	0.15	0.18
MMA	0.00014	0.00046	ND	ND	0.0013	ND	ND
DMA	0.00022	0.00072	0.0063	0.017	0.020	0.030	0.026

Units: mg-As/kg ND: Not detected

Figure 2 shows the results from the inter-laboratory study for all species in all five samples, as well as the total arsenic results. The error bars represent the range of results from the participating labs, while the red triangles show the average. The green circles represent the results from this work and fall at or near the center of the range for each sample, thus indicating the accuracy of the results.

The last plot in Figure 2 shows the results for total As in each sample. The blue diamonds (◆) represent the results supplied by the institution running the study. These total As values were determined after sample decomposition in a microwave. The green circles (●) show the sum of the individual species in each sample from this work. The red triangles (▲) represent the average of the sum of all species from each of the participating labs. These results demonstrate the accuracy of the analysis and confirm that all of the As in the rice was extracted during the sample preparation for the chromatographic analysis.

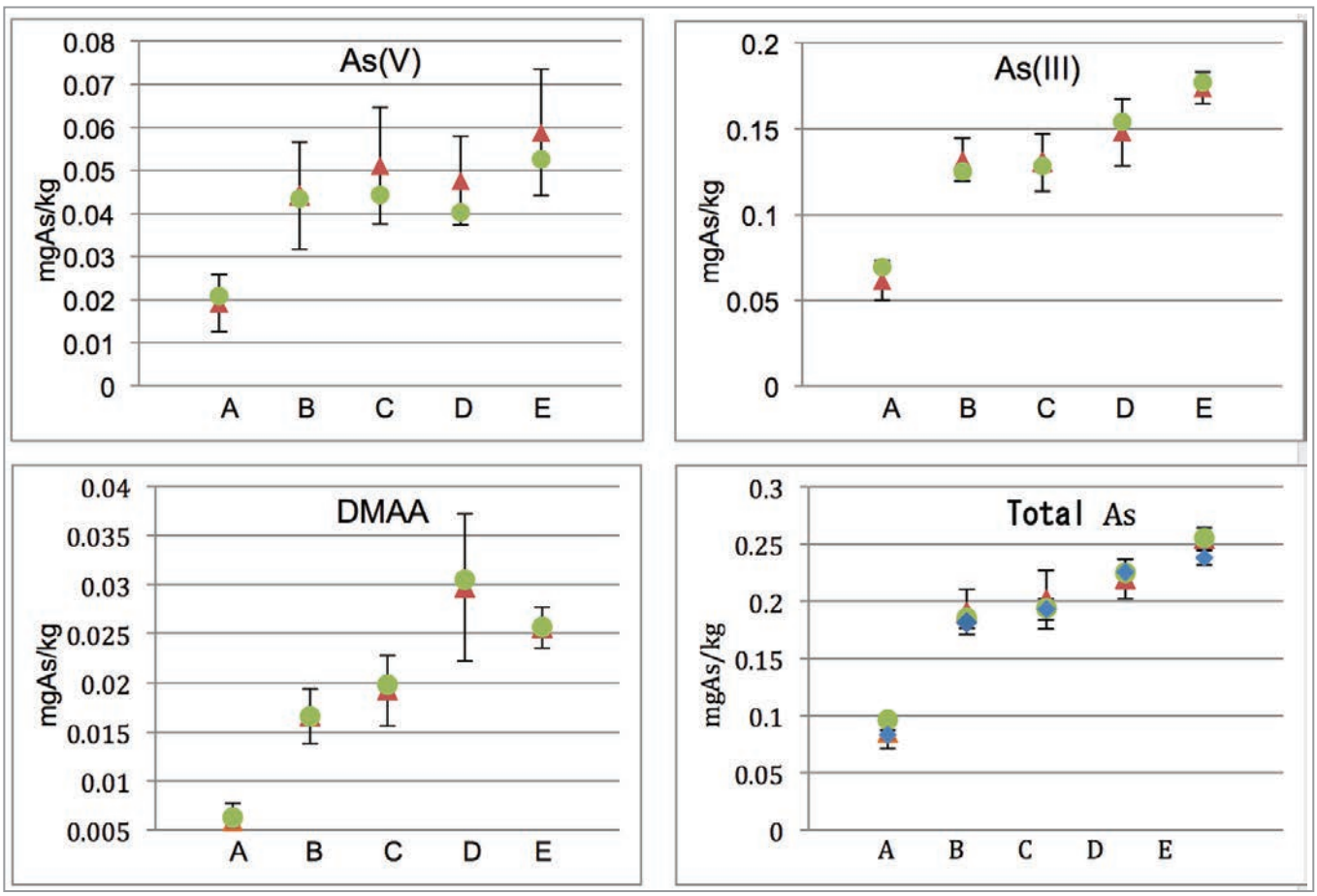


Figure 2. Results for As(V)(upper left), As(III)(upper right), DMAA(lower left), and Total As(lower right) ▲: Average results from the 8 participating labs; ●: Results from this work; ◆: Known concentrations

Summary

This work demonstrates the ability to separate and measure arsenic compounds present in brown rice samples by selection of proper HPLC and ICP-MS conditions. The results of this work correlate very well with those of the other organizations participating in the study. These results prove that the combination of Flexar HPLC and NexION ICP-MS is suitable for the analysis of different forms of arsenic in brown rice.

References

1. Evaluation of Certain Contamination in Food, 72nd Report of the Joint FAO/WHO Expert Committee on Food Additives

2. Survey Report on the Impact Assessment of Arsenic In Food, 1990, International Medical Information Center

3. Determination of Arsenic Speciation in Apple Juice by HPLC/ICP-MS, Ken Neubauer et.al., PerkinElmer Application Note

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

011185A_01

APPLICATION NOTE

HPLC/ICP - MS

Authors:
Jong Min Park, Sang Kwon Ma
Inorganic Product Specialists
PerkinElmer South Korea

Arsenic Speciation Analysis in White Rice by HPLC/ICP-MS Using the NexION 300D/350D

Introduction

There has been a rising concern about the presence of arsenic in rice, especially in societies which consume large quantities of rice. Arsenic can enter rice naturally through the environment or through the application of pesticides. Because not all arsenic species are toxic, the ability to measure the different forms is important.

In recent years, it has become common to measure different forms of arsenic using HPLC/ICP-MS: HPLC separates the forms and ICP-MS detects them as they elute from the column. The advantage of ICP-MS as an HPLC detector is that it is very sensitive and can measure trace levels, as demonstrated by its use to measure impurities in a wide range of electronic materials and environmental samples.

This work demonstrates the ability to measure various arsenic forms in white rice, building upon previous work.[1,2]

PerkinElmer
For the Better

Experimental

Sample Preparation

Rice samples included: NIST 1568a Rice Flour; three samples of rice purchased in a local grocery store, each from a different region of Korea; and two instant rice products, also purchased from a local grocery store.

Uncooked rice was ground into a fine powder, and 0.5 g was transferred to a 15 mL sample tube. Next, 4.5 g of 0.2% HNO_3 (v/v) was added to the tube, which was then mixed with a vortex mixer for 10 seconds. The tube was place in a hot block at 120 °C for four hours and then allowed to cool. The cooled solution was centrifuged at 4000 rpm for 30 minutes and then filtered through a 0.45 µm PTFE membrane. For final analysis, 0.1 mL of the filtered solution was combined with 0.9 mL of deionized water in a 1.5 mL HPLC autosampler vial and mixed for 10 seconds with a vortex mixer.

For comparison, an analysis for total As was also performed in the same samples. Sample preparation involved adding 0.5 g of ground rice powder to a 50 mL tube, to which 4 mL of concentrated nitric acid and 1 mL concentrated hydrogen peroxide were added; the contents were mixed with a vortex mixer for 10 seconds. The tube was then placed in a hot block at 120 °C for 30 minutes, cooled, and brought to a final volume of 50 mL with deionized water.

Instrumental Conditions

All analyses were done using a PerkinElmer Flexar™ HPLC system coupled to a PerkinElmer NexION® 300D ICP-MS. Tables 1 and 2 show the HPLC and ICP-MS conditions used for this work. Separation is accomplished with a reversed-phase column in four minutes using an isocratic chromatographic method. The same ICP-MS conditions were used for both speciation and total analyses, with iridium (Ir) being used as an internal standard for total analysis. All measurements were made against external calibration standards.

Results

Figure 1 shows the separation of a 5 ppb standard containing five common arsenic species: As3+, As5+, monomethyl arsenic (MMA), dimethyl arsenic (DMA), and arsenobetaine (AsB). All peaks are baseline resolved and elute in less than four minutes. The chromatogram in Figure 1 is actually an overlay of five consecutive injections of the same standard, with Table 3 showing the statistics of this analysis. With retention times having RSDs < 0.5% and recoveries within 100 +/- 2%, the reproducibility of the methodology is demonstrated.

Table 1. HPLC Conditions

Parameter	Condition
Instrument	Flexar HPLC System
Separation scheme	Isocratic
Flow rate (mL/min)	1.5
Injection volume (µL)	50
Column	C18
Column temperature	Room temperature

Table 2. ICP-MS Conditions

Parameter	Condition
Instrument	NexION 300D ICP-MS
Spray chamber	Glass cyclonic
Nebulizer	Glass concentric
Analyte monitored	AsO+ (m/z 91)
Cell gas	O_2 = 0.5 mL/min
RPq	0.45
Dwell time (ms)	500

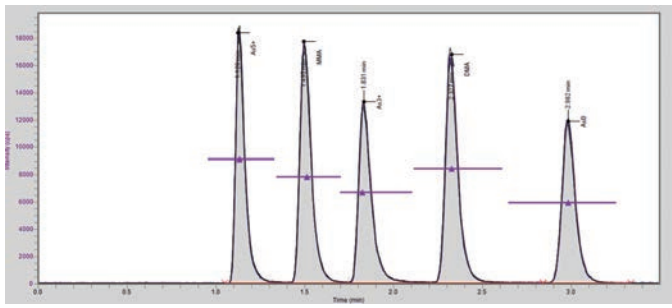


Figure 1. Five consecutive injections of a 5 ppb mixed standard.

Table 3. Results from Five Consecutive Injections of a 5 ppb Mixed Standard

Species	Retention Time #1	Retention Time #2	Retention Time #3	Retention Time #4	Retention Time #5	AVG	SD	%RSD
As5+	1.126	1.126	1.134	1.134	1.134	1.131	0.004	0.387
MMA	1.495	1.495	1.504	1.495	1.504	1.499	0.005	0.329
As3+	1.831	1.831	1.823	1.831	1.831	1.829	0.004	0.196
DMA	2.318	2.327	2.318	2.327	2.318	2.322	0.005	0.212

Species	Results #1	Results #2	Results #3	Results #4	Results #5	AVG	SD	%RSD	% Recovery
As5+	4.928	4.931	4.899	5.008	4.913	4.936	0.042	0.858	98.716
MMA	4.91	4.924	4.913	4.912	4.916	4.915	0.005	0.111	98.3
As3+	4.974	4.96	4.927	5.01	5.021	4.978	0.038	0.766	99.568
DMA	5.007	4.998	4.96	4.931	4.973	4.974	0.03	0.612	99.476
AsB	5.032	5.075	5.081	5.108	5.1	5.079	0.03	0.583	101.584

To examine the effect of the rice matrix on the separation, chromatograms of the three rice samples from different regions of Korea were overlaid with the calibration standards, as shown in Figure 2. Since the retention times of the samples match those of the standards, the rice matrix does not affect the chromatography.

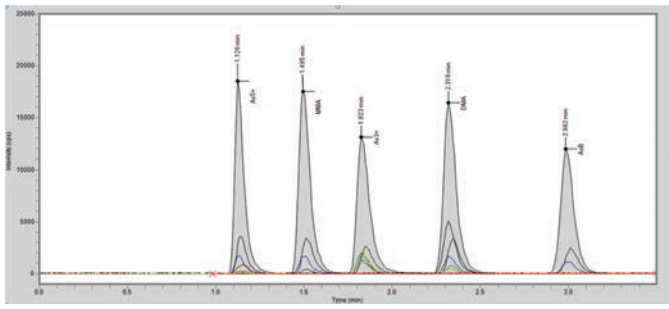


Figure 2. Chromatograms of three rice samples and three calibration standards.

Table 4 shows the quantitative results from both speciation and total analysis. For all samples, the sum of the species is within 10% of the total As content, demonstrating the accuracy of the method. Further validation is seen with the NIST SRM, where both total and the sum of the species are within 10% of the certified value.

Table 4. Quantitative Results

#	Name	Acid Digestion AsO 91 (ppb)	Speciation AsO 91 (ppb)	Speciation/Digestion Matching Rate (%)	NIST SRM Recovery (%) Acid Digestion	NIST SRM Recovery (%) Speciation
1	NIST SRM	287.36	265.60	92.43	99.09	91.59
2	Cooked Rice #1	68.03	73.40	107.89	N/A	N/A
3	Cooked Rice #2	84.66	81.80	96.62		
6	Market Rice #1	106.11	116.80	110.07		
5	Market Rice #2	95.46	91.00	95.33		
4	Market Rice #3	95.91	90.10	93.94		

Conclusion

This work has demonstrated the ability to separate and measure arsenic compounds present in rice. Sample preparation involves a non-aggressive extraction procedure to preserve the species as much as possible. The chromatography separates all species in less than four minutes using an isocratic method and is unaffected by the rice matrix. The results of the separation were validated by comparing the speciated and total results. These results prove that the combination of Flexar HPLC and NexION ICP-MS is suitable for the analysis of different forms of arsenic in white rice.

References

1. "Determination of Arsenic Species in Apple Juice by HPLC/ICP-MS," K. Neubauer, P. Perrone, W. Reuter, PerkinElmer Application Note

2. "As Speciation Analysis in Brown Rice Using HPLC/ICP-MS," K. Kobayashi, O. Shikino, PerkinElmer Application Note

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

011186A_01

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

012258_01 PKI