Authors

Lee Davidowski, Ph.D.

Praveen Sarojam, Ph.D.

PerkinElmer, Inc.
Shelton, CT 06484 USA

Determination of Arsenic in Baby Foods and Fruit Juices by GFAAS

Introduction

The United States does not have specific regulations specifying the allowable levels of toxic elements in foods, but many other countries do. For example, Canada has a specific tolerance level for arsenic of 0.1 ppm in ready to serve fruit juices, nectars, and beverages[1]. The toxic nature of arsenic is such that chronic exposure to the element can lead to internal cancers of the bladder and kidney, skin cancer, neurological effects, and cardiovascular disease.

Arsenic can find its way into food through a variety of paths. In the recent past, various organic arsenicals were used as herbicides and antimicrobial agents in growth fields as well as applied directly on fruits and fruit trees. Prior to 2003, arsenic was commonly used as a wood preservative. Sawing and/or sanding of this wood would yield arsenic contaminated sawdust. In some areas, arsenic is naturally found in rock formations and can enter soil and water which is used in the growth of food products. Foods can also be contaminated during manufacturing, processing, packaging and transport processes.

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There are a few specific analytical challenges that an analyst must consider in the determination of arsenic in foods by GFAAS. Toxic elements, such as arsenic, which may be present in foods are biologically important at very low concentrations. The U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR) defines a minimal risk level for chronic inorganic arsenic exposure to be 0.0003 mg As/kg/day. For a 45 lb. child drinking a liter of fruit juice a day, the minimal risk level for that juice would then be about 6 µg/L. Therefore, the analytical technique employed for this application must have the capability to accurately measure arsenic in sample digestates at the sub-ppb concentration level.

A complete method has been developed for the determination of arsenic (As) in baby foods and baby fruit juices by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). This method includes sample preparation steps using microwave assisted closed vessel digestion. Foods come in a wide variety of complex sample types and matrices, but their fundamental major components are water and various carbohydrates. In this work, the samples were totally digested in a microwave oven so that the samples' various carbohydrate matrices were completely destroyed prior to instrumental analysis. Microwave digestion has several analytical advantages for this type of analysis. Because the sample is placed in a sealed PTFE polymer digestion vessel, contamination is minimized and there is no loss of volatile elements during the digestion procedure. In a sealed vessel, higher temperatures of digestion are reached thereby quickly yielding complete matrix decomposition. With the microwave system used here, each sample's digestion process is thoroughly documented as to time, pressure and temperature. This gives an analytically repeatable and transferable digestion process.

Figure 1. Examples of samples used in this work.

Experimental

A Multiwave™ 3000 Microwave Oven (PerkinElmer®, Shelton, CT USA) was used for the microwave-assisted digestion. This is an industrial-type oven which can be equipped with various accessories to optimize the sample digestion. In this case, the foods were digested in the Rotor 8XF100 which is a rotor with 8 high pressure vessels made of PTFE-TFM and surrounded by a ceramic jacket. TFM is chemically modified PTFE that has enhanced mechanical properties at high temperatures compared to conventional PTFE. This vessel has a "working" pressure of 60 bar (580 psi) and can operate at temperatures up to 260 ˚C with an internal volume of 100 mL. All vessels' temperatures were monitored with the IR Temperature Sensor Accessory. This device gives thermal protection to the reactions in all of the vessels by measuring the temperature remotely on the bottom surface of each vessel liner during the digestion process. Pressure is continuously monitored in all vessels using load-cell technology in the upper rotor plate.

Figure 2. The Multiwave Rotor.

Samples of fruit juices and solid fruit purees were weighed directly into the PTFE-TFM digestion vessel liners (Figure 2). Sample weights were approximately 2 grams for the liquid juices and 1 gram for the fruit purees. To each sample, 6 mL of concentrated nitric acid and 0.5 mL of concentrated hydrochloric acid were added. A pre-digestion spike of arsenic was added to some of the samples to measure analyte recovery through the digestion process. Some vessels contained only the acids with no sample to act as analytical reagent blanks. The vessels were sealed and placed into the rotor for the microwave digestion. The acids used were high purity GFS Chemical™ (Columbus, OH, USA) which are packaged in PTFE containers. After the digestion process, the digestates were transferred to polypropylene 50-mL autosampler vials (PerkinElmer part number B0193234) and laboratory ASTM type I water was added to a final total weight of 25 grams.

Table 1. Microwave Digestion Program.

Step	Power (Watts)	Ramp (min)	Hold (min)	Fan Speed
1	750	10	10	1
2	1200	10	10	1
3	0 (cool-down)	0	15	3

Table 1 shows the power/time program used for the sample digestions. To ensure a safe digestion, the Multiwave 3000's IR sensor measures the temperature of each vessel. If a vessel nears its maximum operating temperature of 260 ℃, then the Multiwave oven will automatically decrease the applied power. Also, the pressure sensor sends data to the Multiwave oven controller during the digestion. The Multiwave oven will automatically reduce power if the maximum pressure of 60 bar is approached.

An AAnalyst™ 800 Atomic Absorption Spectrometer (PerkinElmer) was used for the GFAAS measurements of arsenic in the digested samples. The AAnalyst 800 features longitudinal Zeeman-effect background correction[2] and a solid-state detector which is highly efficient at low wave-lengths (arsenics's primary AA wavelength is 193.7 nm). The AAnalyst 800 uses a transversely heated graphite atomizer (THGA) which provides uniform temperature distribution across the entire length of the graphite tube. The THGA features an integrated L'vov platform[3] which is useful in overcoming potential chemical interference effects common to the GFAAS technique.

For instrument calibration, a 10 µg/L As standard was prepared from serial dilutions of a 1000 mg/L stock standard (PE Pure, PerkinElmer Part Number N9300102). The AAnalyst 800 autosampler then prepared a calibration curve of 2.5, 5.0 and 10.0 µg/L from that 10 µg/L arsenic standard. A QC standard was also measured by this method, High Purity Standards TM-A, (Charleston, SC 29423) and is certified to be 10 µg/L arsenic. A mixed matrix modifier of palladium and magnesium nitrate was prepared by diluting and combining individual stock matrix modifier solutions. The mixed modifier solution is prepared by combining 5 mL of the stock palladium modifier (1% solution, PerkinElmer Part Number B0190635) and 0.5 mL of the magnesium nitrate stock modifier (PerkinElmer Part Number B0190634) and diluting to 50 mL with ASTM Type I water. Other instrumental parameters are given in Tables 2 and 3.

A typical calibration curve is shown in Figure 3 and calibration standard profiles are shown in Figure 4. The curve has good linearity and the sensitivity is good at low concentrations.

Table 2. AAnalyst 800 Instrumental Parameters.

Wavelength (nm)	193.7
Source Lamp (mA)	EDL 380
Slit Width (nm)	0.7
Background Correction	Zeeman-effect
Measurement Mode	Peak Area, 3 replicates
Calibration Algorithm	Linear thru Zero
Integration Time	5.0
Sample Volume	24
Matrix Modifier Volume	6
THGA	Standard THGA Tube

Table 3. THGA Heating Program.

Step	Temperature (℃)	Ramp Time (sec)	Hold Time (sec)	Argon Gas (mL/min)
1*	120	1	30	250
2	140	5	15	250
3	1100	10	15	250
4**	1900	0	5	0
5	2450	1	3	250

* = Injection Temperature = 100 ˚C.
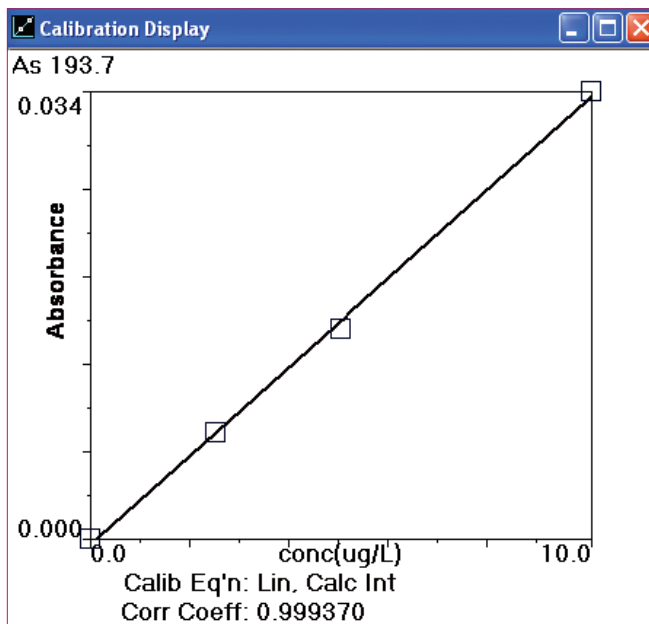**= Atomization Step
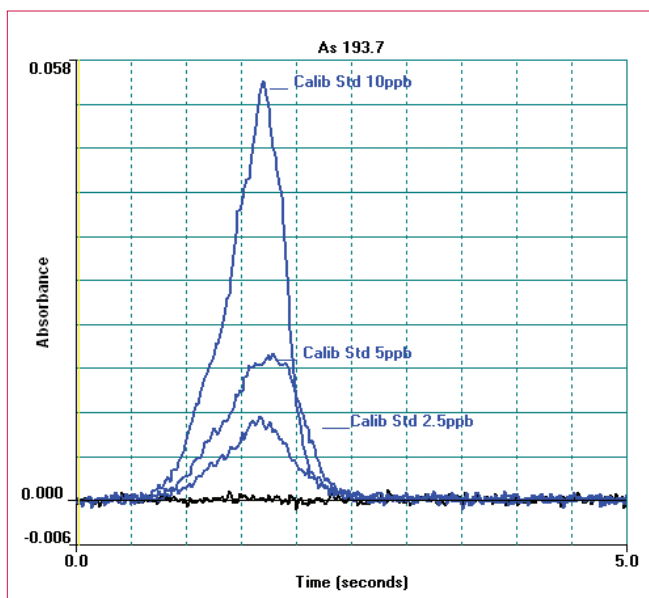

Figure 3. Arsenic calibration curve.

Figure 4. Arsenic atomic profile signals for calibration standards and blank.

Results

The Multiwave 3000 Digestion System with the rotor-8 produced clear, fully digested, sample solutions. No filtration was necessary. The AAnalyst 800 gave a characteristic mass (M_o) of 36 pg for arsenic with these conditions which is in good agreement with the manufacturers recommended Mo value of 40 pg. Nine different samples of baby juice and puree foods were analyzed by this method. The fruit juices and one of the puree samples were prepared in duplicate to check the entire method's reproducibility. These samples were also "spiked" prior to digestion with the equivalent in the undiluted sample of approximately 240 ng/g arsenic. The percent recovery of this spike will be used to check for any losses of arsenic during the digestion and to check for the presence of any matrix interferences. All of those data are given in Table 4.

Table 4. Results for the Analyses of Baby Foods by GFAAS.

Sample ID (ng/g)	Mean (ng/g)	SD	%RSD	% DIFF of Spike*	%Recovery
B_Pear Juice	10.2	1.2	12	9.9	93.9
G_Pear Juice	15.1	0.65	4.3	3.3	90.0
B_Grape Juice	27.4	2.2	8.2	0.70	85.0
B_Apple Juice	12.4	0.96	7.8	3.4	92.6
G_Apple Juice	18.2	0.29	1.6	4.7	
B_Cherry Juice	10.3	0.77	7.5	23	
B_Pear Puree	5.00	2.0	35	55	95.7
G_Pear Puree	<3				
B_Apple Sauce	<3				
HP QC TM-A (µg/L)	10.0 (µg/L)	0.051	0.51		99.9

*Predigestion spike of 5 µg/L in the final solution or analysis

Table 4 shows the mean of the three replicate measurements for the food sample corrected for weight used and final volume, the standard deviation of those measurements (SD), and the relative standard deviation of the three replicates (%RSD). Also, the first seven samples shown were digested in duplicate. The difference between the two are shown in the column labeled % Diff. The relatively high percent differences in the pear puree samples is due to the fact that the concentration of arsenic is very low in this sample, near the method detection limit for the puree of 3 ng/g.

For samples that were split and spiked with arsenic prior to digestion, that measure of the spike recovery is shown as the percentage of the recovery in the last column of Table 4. A recovery value of near 100% shows that there is little or no loss of analyte during the digestion process and that there are no unresolved matrix interferences with the analytical method.

Conclusion

It has been shown that this method can be successfully applied to the determination of arsenic in these types of foods. The Multiwave 3000 Digestion System gave completely digested, clear samples with no loss of arsenic during the high temperature, high pressure process. The AAnalyst 800 with longitudinal Zeeman-effect background correction and THGA tube containing the L'vov platform, gave good spike recoveries with no matrix interference. The detection limit estimated to be 3 ng/g was well below the Canadian limit of 100 ng/g in the original juice or puree and offers room for lower regulatory limits that may be established in the future to also be satisfactorily measured.

References

1. Department of Justice Canada, http://laws.justice.gc.ca/en/showdoc/cr/C.R.C.-c.870

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