An Examination of Arsenic Content in American and European Hard Ciders

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INTRODUCTION

Hard cider or alcoholic cider is an alcohol-fermented beverage produced primarily from apples. Hard ciders have a long history around the world but have only become readily available in the United States over the past two decades. Over the last several years, several studies have been conducted showing the presence of arsenic in apple juices and wine.

The historical and continued use of arsenic based pesticides around the world and the exposure of crops to arsenic from potentially arsenic laden fertilizers can expose agricultural products to arsenic contamination. Arsenic based pesticides, particularly lead arsenic, were in widespread and common use in the United States up until the 1970's until their final ban in 1988. Despite arsenic residue being recognized as a potential problem from the turn of the 20th century, lead arsenate was one of the most widely used pesticides in the nation and was applied to millions of acres of crops through the 1940's when it was replaced by DDT.

Lead arsenate was the most commonly applied pesticide in apple orchards since it was effective against the codling moth, which, to this day, is one of the most persistent apple harvest pests. Many of the historical apple orchards around the world still operate producing apples and apple products, but the potential for the persistent arsenic compounds remain. Heavy metal pesticides were designed to be persistent and this issue can cause environmental and health problems decades after the pesticides were banned.

In this study, samples were obtained of popular American and European hard ciders. Modern hard ciders are produced from either fresh apples or apple concentrates. American ciders are required to be at least 50% apples or concentrate, while UK ciders are required to be at least 35% apples. Samples were digested using microwave digestion and testing by ICP-MS for total arsenic concentration and LC-ICP-MS to determine potential content of the arsenic species.

METHOD & MATERIALS

Samples

Alcoholic ciders were purchased from a New Jersey liquor store and represented thirteen ciders, seen in Table 1, originating from the United States and Europe.

Table 1. Cider Sample Profiles Used In This Study.

ID	Country of Origin	% Alcohol	Carbs (g)	Approximate % Apples
WDR	United States	6.9%	NR	> 50%
EAP	United States	5.2%	6	> 50%
SSO	England	5%	8	> 35%
OSR	United States	6%	10	> 50%
AOD	United States	5.5%	11	> 50%
MIO	Ireland	4.5%	14	> 35%
RAA	United States	5%	17	Unknown
DEU	United States	5.1%	17	> 50%
SBA	England	6%	17	> 35%
SBG	England	5%	19	> 35%
SAC	Belgium	4.5%	22	Unknown
LPL	Belgium	3.5%	37	Unknown
IBC	United States	5.2%	42	> 50%

Materials

- SPEX CertiPrep Standards
  - CLMS-1, CLMS-2, CLMS-3, CLMS-4: Multi-Element Solution Standards 1-4
  - Single-Element Speciation Standards:
    - SPEC-AS-DMA
    - SPEC-AS-MMA
    - SPEC-AS3
    - SPEC-AS5
- Reagents
  - High Purity Nitric Acid

Sample Preparation

Initial Sample Preparation:

Ciders were dispensed into 50 mL centrifuge tubes and were vigorously shaken and vented to remove excess of carbon dioxide present in the beverages. The samples were allowed to sit to dissipate any foaming prior to further preparation.

METHOD & MATERIALS (cont'd)

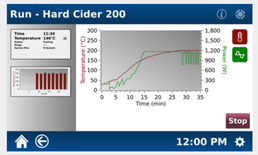
Samples were prepared in two different methods for analysis. In the first experiment, 5 mL of each cider were weighed into a microwave vessel. 10 mL of nitric acid were added to each sample and the samples were allowed to fume partially open while sonicating for 15 minutes prior to digestion. Before digestion the samples were spiked with 1 mL of mixed standards of the four arsenic species: DMA, MMA, As III & As V at10 µg/mL.

In the second preparation, 50 mL of cider were decanted into centrifuge tubes and reduced in volume down to 10 mL using a thermovap under nitrogen and gentle heat under 90 °C. 5 mL of the reduced sample were weighed into a microwave vessel. 10 mL of high purity nitric acid were added to the vessel and allowed to fume partially open while sonicating for 15 minutes prior to digestion.

Microwave Digestion:

Samples were digested using a CEM MARS 6 microwave with iWave temperature control.

- Microwave Conditions
  - MARSXpress Plus Vessels
  - 5 mL of sample
  - 10 mL of HNO_3
    - 20 minute ramp to 200 °C
    - 15 minute hold



Instrumentation

- PerkinElmer ICP-OES
- Agilent ICP-MS 7900
  - Meinhard nebulizer
  - Cyclonic spray chamber
  - Analysis performed
    - No gas mode
    - Collision mode: Helium
      - As line 75 with helium gas

RESULTS & DISCUSSION

Study of Potential Arsenic Loss Through Sample Processing

Prior to the digestion and analysis of all of the cider samples, a small study was conducted to determine potential losses of arsenic from sample processing. One cider sample and a nitric acid blank solution were spiked with 1 mL of the mixed arsenic species standards at three different points in sample process: before sonication, immediately prior to microwave digestion and post-digestion prior to sample dilution and analysis. The arsenic recoveries for samples and blanks spiked prior to sonication was 96% while the samples and blanks spiked prior to digestion had 97%. Samples that were spiked just prior to dilution and testing had a 98% recovery. The similar recoveries for the standard spike in all of the samples and blanks showed that any potential arsenic in the samples would not be lost during any of the preparation steps including digestion.

Arsenic in Cider Samples

The first set of cider analyses were performed on the cider samples that were digested using microwave digestion without the concentration step. Arsenic recoveries were very poor for these samples probably due to the highly dilute nature of the samples.

The second set of cider samples was concentrated from 50 mL to 10 mL prior to digestion. One sample of concentrated cider combusted during digestion and therefore was not used in this study (SBG 52). Speciation was not conducted at this time to determine the form of the arsenic found. Further studies will encompass arsenic speciation of targeted cider samples to determine species content.

Six of the twelve ciders (50%) were </= 1 ppb of arsenic. The remaining six ciders ranged from > 1 ppb to under 5 ppb in arsenic concentration (see Table 2). Four of the six ciders which tested over 1 ppb of arsenic were from Europe and two were from the United States. The highest arsenic was found in an English organic cider which contained 4.8 ppb of arsenic.

RESULTS & DISCUSSION

Table 2. Total Arsenic Content (ppb) In Cider Samples From the United States and Europe.

ID	Country of Origin	Approximate % Apples	As (ppb)
WDR	United States	> 50%	2.38
EAD	United States	> 50%	0.81
SSO	England	> 35%	4.79
OSR	United States	> 50%	0.16
AOD	United States	> 50%	1.73
MID	Ireland	> 35%	0.40
RAA	United States	Unknown	0.85
DEU	United States	> 50%	0.77
SBA	England	> 35%	1.70
SAC	Belgium	Unknown	1.53
LPL	Belgium	Unknown	2.48
IBC	United States	> 50%	1.05

Arsenic Content and Exposure

In the past several years, articles and studies have been popularized regarding arsenic in non-alcoholic ciders and juices. In one study by Consumer Reports, the amount of arsenic found was up to 13.2 ppb. The FDA has proposed an action level for inorganic arsenic in juices of 10 ppb and the FDA has a limit of 10 ppb for arsenic in bottled in water. In comparison to these limits, the alcoholic cider's total arsenic concentrations are just below half of what was found in the juices and below the limits. The suggested serving of juice is limited to eight ounces per day (237 mL) which would allow for a maximum exposure of 2.4 µg/day from the juice.

An adult's exposure to arsenic from alcoholic cider could potentially be higher due to the larger serving containers (usually 12 ounces = 355 mL) and the number of servings typically consumed can be anywhere from 3 or more servings (see Table 3).

Table 3. Total Arsenic Exposure (µg) From Typical Alcoholic Cider Servings

ID	As (µg) in 1 serving	As (µg) in 3 servings	As (µg) in 6 servings
WDR	0.8	2.5	5.1
EAD	0.3	0.9	1.7
SSO	1.7	5.1	10.2
OSR	0.1	0.2	0.3
AOD	0.6	1.8	3.7
MID	0.1	0.4	0.9
RAA	0.3	0.9	1.8
DEU	0.3	0.8	1.6
SBA	0.6	1.8	3.6
SAC	0.5	1.6	3.2
LPL	0.9	2.6	5.3
IBC	0.4	1.1	2.2

The total arsenic levels found in some ciders become a concern as the amount of servings increase. The next step in this research will be to examine the species distribution of the arsenic by LC-ICP-MS to determine if the arsenic content is primarily due to organic arsenic species such as MMA and DMA or due to potentially toxic inorganic arsenic species (As III & As V).

CONCLUSION

Cider samples tested in this study contained between 0.16 and 4.8 ppb of total arsenic. Four of the six samples containing the highest concentration of arsenic were manufactured in Europe. Studies of other similar products, such as non-alcoholic ciders and juices, have cited up to 13.2 ppb of arsenic. The FDA has current arsenic limits for bottled water set at 10 ppb of inorganic arsenic and is proposing an action limit in juice for the same. While the alcohol cider samples all had total arsenic concentrations less than half the suggested limits, there is a question of exposure through serving size. Typical juice servings are limited to 8 ounces per day. Most beer and cider servings are a minimum of 12 to 16 ounces per bottle with most adults consuming more than one serving in a day when the beverages are consumed. In the case of multiple servings, the potential exposure can become up to five times more than the potential amount of exposure from a small eight ounces of juice. The question of the impact of that exposure comes down to the type of arsenic in the cider. Follow-up studies are being conducted on these cider samples to determine the arsenic species of these cider samples using LC-ICP-MS. The characterization of the arsenic species will help in understanding the potential impact and exposure to potentially toxic arsenic in alcoholic cider.