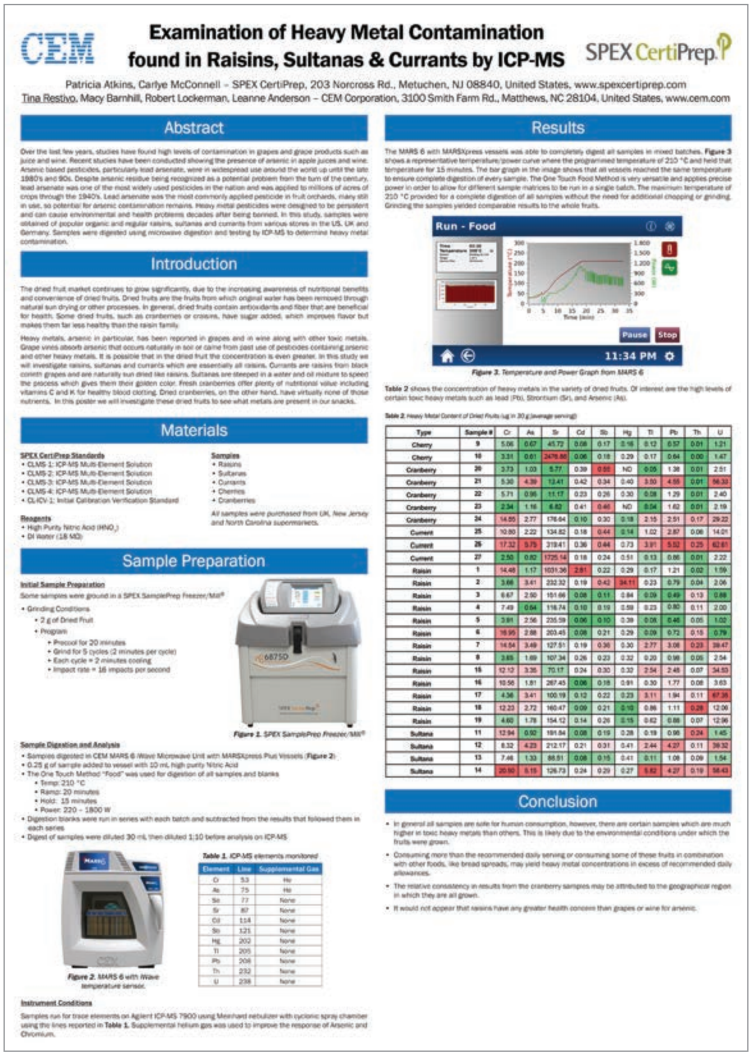
Examination of Heavy Metal Contamination found in Raisins, Sultanas & Currants by ICP-MS



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Poster Content

Abstract

Over the last few years, studies have found high levels of contamination in grapes and grape products such as juice and wine. Recent studies have been conducted showing the presence of arsenic in apple juices and wine. Arsenic based pesticides, particularly lead arsenate, were in widespread use around the world up until the late 1980's and 90s. Despite arsenic residue being recognized as a potential problem from the turn of the 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. Lead arsenate was the most commonly applied pesticide in fruit orchards, many still in use, so potential for arsenic contamination remains. Heavy metal pesticides were designed to be persistent and can cause environmental and health problems decades after being banned. In this study, samples were obtained of popular organic and regular raisins, sultanas and currants from various stores in the US, UK and Germany. Samples were digested using microwave digestion and testing by ICP-MS to determine heavy metal contamination.

Introduction

The dried fruit market continues to grow significantly, due to the increasing awareness of nutritional benefits and convenience of dried fruits. Dried fruits are the fruits from which original water has been removed through natural sun drying or other processes. In general, dried fruits contain antioxidants and fiber that are beneficial for health. Some dried fruits, such as cranberries or craisins, have sugar added, which improves flavor but makes them far less healthy than the raisin family.

Heavy metals, arsenic in particular, has been reported in grapes and in wine along with other toxic metals. Grape vines absorb arsenic that occurs naturally in soil or came from past use of pesticides containing arsenic and other heavy metals. It is possible that in the dried fruit the concentration is even greater. In this study we will investigate raisins, sultanas and currants which are essentially all raisins. Currants are raisins from black corinth grapes and are naturally sun dried like raisins. Sultanas are steeped in a water and oil mixture to speed the process which gives them their golden color. Fresh cranberries offer plenty of nutritional value including vitamins C and K for healthy blood clotting. Dried cranberries, on the other hand, have virtually none of those nutrients. In this poster we will investigate these dried fruits to see what metals are present in our snacks.

Materials

SPEX CertiPrep Standards

- CLMS-1: ICP-MS Multi-Element Solution
- CLMS-2: ICP-MS Multi-Element Solution
- CLMS-3: ICP-MS Multi-Element Solution
- CLMS-4: ICP-MS Multi-Element Solution
- CL-ICV-1: Initial Calibration Verification Standard

Samples

- Raisins
- Sultanas
- Currants
- Cherries
- Cranberries

All samples were purchased from UK, New Jersey and North Carolina supermarkets.

Reagents

- High Purity Nitric Acid (HNO_3)
- DI Water (18 MΩ)

Sample Preparation

Initial Sample Preparation

Some samples were ground in an SPEX SamplePrep Freezer/Mill®

- Grinding conditions
  - 2 g of dried fruit
  - Program
    - Precool for 20 minutes
    - Grind for 5 cycles (2 minutes per cycle)
    - Each cycle = 20 minutes cooling
    - Impact rate = 16 impacts per second

Figure 2*. SPEX SamplePrep Freezer/Mill®*

Sample Digestion and Analysis

- Samples digested in CEM MARS 6 iWave Microwave Unit with MARSXpress Plus Vessels (**Figure 2**)
- 0.25 g of sample added to vessel with 10 mL high purity nitric acid
- The One Touch Method "Food" was used for digestion of all samples and blanks
  - Temperature: 210 °C
  - Ramp: 20 minutes
  - Hold: 15 minutes
  - Power: 220 – 1800 W
- Digestion blanks were run in series with each batch and subtracted from the results that followed them in each series
- Digest of samples were diluted 30 mL then diluted 1:10 before analysis on ICP-MS

Figure 2. *MARS 6 with iWave temperature sensor.*

Element	Line	Supplemental Gas
Cr	53	He
As	75	He
Se	77	None
Sr	87	None
Cd	114	None
Sb	121	None
Hg	202	None
Tl	205	None
Pb	208	None
Th	232	None
U	238	None

Table 1. *ICP-MS elements monitored*

Instrument Conditions

Samples run for trace elements on Agilent ICP-MS 7900 using Meinhard nebulizer with cyclonic spray chamber using the lines reported in **Table 1**. Supplemental helium gas was used to improve the response of Arsenic and Chromium.

Results

The MARS 6 with MARSXpress vessels was able to completely digest all samples in mixed batches. **Figure 3** shows a representative temperature/power curve where the programmed temperature of 210 °C and held that temperature for 15 minutes. The bar graph in the image shows that all vessels reached the same temperature to ensure complete digestion of every sample. The One Touch Food Method is very versatile and applies precise power in order to allow for different sample matrices to be run in a single batch. The maximum temperature of 210 °C provided for a complete digestion of all samples without the need for additional chopping or grinding. Grinding the samples yielded comparable results to the whole fruits.

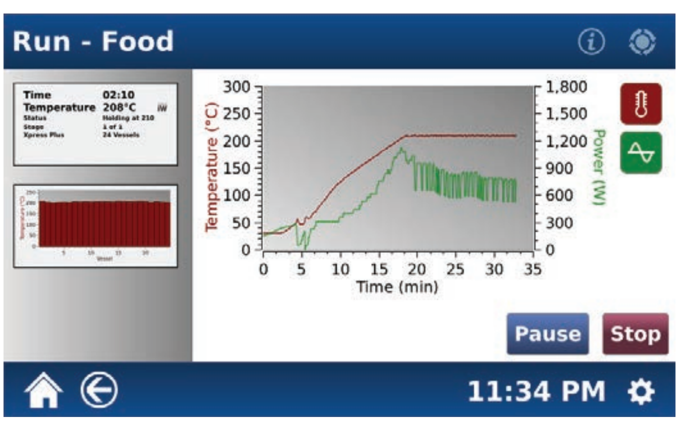

Figure 3. *Temperature and power graph from MARS 6*

Table 2 shows the concentration of heavy metals in the variety of dried fruits. Of interest are the high levels of certain toxic heavy metals such as lead (Pb), Strontium (Sr), and Arsenic (As).

Table 2. *Heavy metals content of dried fruits (ug in 30 g [average serving])*

Type	Sample #	Cr	As	Sr	Cd	Sb	Hg	Tl	Pb	Th	U
Cherry	9	5.06	0.67	45.72	0.08	0.17	0.16	0.12	0.57	0.01	1.21
Cherry	10	3.31	0.61	2476.86	0.06	0.18	0.29	0.17	0.64	0.00	1.47
Cranberry	20	3.73	1.03	5.77	0.39	0.55	ND	0.05	1.38	0.01	2.51
Cranberry	21	5.30	4.39	13.41	0.42	0.34	0.40	3.50	4.55	0.01	56.33
Cranberry	22	5.71	0.95	11.17	0.23	0.26	0.30	0.08	1.29	0.01	2.40
Cranberry	23	2.34	1.16	6.82	0.41	0.46	ND	0.04	1.62	0.01	2.19
Cranberry	24	14.85	2.77	176.64	0.10	0.30	0.18	2.15	2.51	0.17	29.22
Current	25	10.80	2.22	134.82	0.18	0.44	0.14	1.02	2.87	0.06	14.01
Current	26	17.32	5.75	319.41	0.36	0.44	0.73	3.91	5.52	0.25	62.61
Current	27	2.50	0.82	1725.14	0.18	0.24	0.51	0.13	0.86	0.01	2.22
Raisin	1	14.48	1.17	1031.36	2.81	0.22	0.29	0.17	1.21	0.02	1.59
Raisin	2	3.66	3.41	232.32	0.19	0.42	34.11	0.23	0.79	0.04	2.06
Raisin	3	6.67	2.50	151.66	0.08	0.11	0.84	0.09	0.49	0.13	0.88
Raisin	4	7.49	0.64	116.74	0.10	0.19	0.59	0.23	0.80	0.11	2.00
Raisin	5	3.91	2.56	235.59	0.06	0.10	0.39	0.08	0.46	0.05	1.02
Raisin	6	16.95	2.88	203.45	0.08	0.21	0.29	0.09	0.72	0.15	0.79
Raisin	7	14.54	3.49	127.51	0.19	0.36	0.30	2.77	3.08	0.23	39.47
Raisin	8	3.65	1.69	107.34	0.26	0.23	0.32	0.20	0.98	0.05	2.54
Raisin	15	12.12	3.35	70.17	0.24	0.30	0.32	2.54	2.48	0.07	34.53
Raisin	16	10.56	1.81	287.45	0.06	0.18	0.91	0.30	1.77	0.08	3.63
Raisin	17	4.36	3.41	100.19	0.12	0.22	0.23	3.11	1.94	0.11	67.35
Raisin	18	12.23	2.72	160.47	0.09	0.21	0.10	0.86	1.11	0.28	12.06
Raisin	19	4.60	1.78	154.12	0.14	0.26	0.15	0.62	0.88	0.07	12.96
Sultana	11	12.94	0.92	191.84	0.08	0.19	0.28	0.19	0.98	0.24	1.45
Sultana	12	8.32	4.23	212.17	0.21	0.31	0.41	2.44	4.27	0.11	39.32
Sultana	13	7.46	1.33	88.51	0.08	0.15	0.41	0.11	1.08	0.09	1.54
Sultana	14	20.50	5.15	126.73	0.24	0.29	0.27	5.82	4.27	0.19	58.43

Conclusion

- In general all samples are safe for human consumption, however, there are certain samples which are much higher in toxic heavy metals than others. This is likely due to the environmental conditions under which the fruits were grown.
- Consuming more than the recommended daily serving or consuming some of these fruits in combination with other foods, like bread spreads, may yield heavy metal concentrations in excess of recommended daily allowances.
- The relative consistency in results from the cranberry samples may be attributed to the geographical region in which they are all grown.
- It would not appear that raisins have any greater health concern than grapes or wine for arsenic.

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