Heavy Metal Exposure in Common Childhood Food Staples
The Peanut Butter & Jelly Studies

Patricia Atkins, Carlye McConnell – SPEX CertiPrep, 203 Norcross Rd., Metuchen, NJ 08840, United States, www.spexcertiprep.com • Tina Restivo, Macy Barnhill, Robert Lockerman, Leanne Anderson – CEM Corporation, 3100 Smith Farm Rd., Matthews, NC 28104, United States, www.cem.com

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 90's. 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. Many popular breakfast and bread spreads are natural products composed of fruit, nuts, seeds, and yeasts. Children are frequent consumers of many of these popular spreads and dried fruits. Studies of individual spread components such as grapes, nuts and cocoa beans have reported significant amounts of heavy metal contamination. In this study, various samples of dried fruits (including raisins) and bread spreads (including fruit spreads, peanut butter, nut butters, yeast spreads, and cocoa spreads) were tested for heavy metal contamination. Samples were digested using microwave digestion and testing by ICP-MS to determine heavy metal contamination possible in these common foods.

In this study, fruit samples were obtained of popular organic and regular raisins, sultanas and currants from various stores in the US, UK and Germany. Spreads obtained were created from different nuts and seeds and purchased from the US, UK and Germany. Samples were digested using microwave digestion and testing by ICP-MS to determine heavy metal contamination.

Introduction

In countries around the world, nut butter spreads are a staple of the average child's diet. In North America, peanut butter is the most popular bread spread while in Europe, hazelnut spread tops the charts. The largest growth sector for nut butters is Asia as a wide variety of tree nut butters are being introduced into every day diets. In 2018 it is estimated that the nut based and sweet spread products saw €5.75 billion in sales, a 65% increase from 2013.

So, why are nut butters so popular? Nut butters offer a high source of protein and healthy monounsaturated fatty acids as well as a myriad of vitamins and minerals. So how could products which bring so much health benefit be bad for us? Since peanuts and tree nuts are plant based and grown in soil, they are prone to absorb elements contained in the soil. These elements range from uranium, lead, strontium, cadmium, and arsenic from residual fertilizer and pesticide use among other sources of contamination. Many products which are subject to grinding and processing can also become contaminated or adulterated by additives or wear metals from the processing.

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 and bread spreads 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
- Peanut butter
- Almond butter
- Soybean butter
- Cashew butter
- Cookie butter
- Sunflower butter
- Tahini
- Hazelnut spread
- Yeast product spreads

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

Reagents

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

Sample Preparation

Initial Fruit Sample Preparation

Dried fruit samples were ground in a 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 = 2 minutes cooling
- Impact rate = 16 impacts per second

Initial Spread Sample Preparation

Bread spreads were frozen using liquid nitrogen by applying a known amount of sample to a silicone non-stick mold and pouring liquid nitrogen over the sample multiple times in order to flash freeze the sample, see Figure 1. This was done to ensure that all of the sample reached the bottom of the digestion vessel, a task which is difficult when bread spreads are at room temperature.

Figure 1. Sample Preparation of Bread Spreads

Sample Digestion and Analysis

Samples digested in CEM MARS 6 iWave Microwave Unit with MARSXpress Plus Vessels (Fig. 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
- Temp: 210 °C
- Ramp: 20 min
- Hold: 15 min
- 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

Sample Digestion and Analysis

Samples digested in CEM MARS 6 iWave Microwave Unit with MARSXpress Plus Vessels

- 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
- Temp: 210 °C
- Ramp: 20 min
- Hold: 15 min
- 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

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.

Table 1. ICP-MS Elements Monitored

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

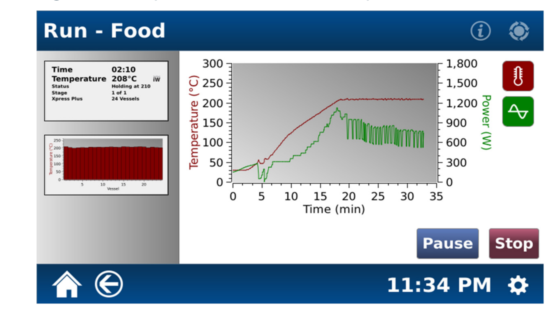
Results

Bread Spreads

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 was set at 200 °C and held at 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.

ICP-MS analysis results in Table 2 show higher than expected levels of the heavy metals uranium (U), lead (Pb), arsenic (As), strontium (Sr), and cadmium (Cd) in many samples. Interestingly, uranium (U) is present in high levels in tree nut butters including almond, cashew, and hazelnut while very low in peanut butter. This could be due to the length of time the nut spends on the plant prior to harvesting. Also notable was the lead (Pb) levels in some approach maximum daily limits for a child for some regulatory bodies around the world.

Figure 3. Temperature and Power Graph from MARS 6



ICP-MS analysis results in Table 2 show higher than expected levels of the heavy metals uranium (U), lead (Pb), arsenic (As), strontium (Sr), and cadmium (Cd) in many samples. Interestingly, uranium (U) is present in high levels in tree nut butters including Almond, Cashew, and Hazelnut while very low in peanut butter. This could be due to the length of time the nut spends on the plant prior to harvesting. Also notable was the lead (Pb) levels in some approach maximum daily limits for a child for some regulatory bodies around the world.

Table 2. Heavy Metals Content of Bread Spreads (µg in 30 g (2 tablespoon average serving))

Type	Sample #	Cr	As	Se	Sr	Cd	Sb	Hg	Tl	Pb	Th	U
Almond	57	16.50	2.98	3.84	448.56	1.06	0.91	1.16	0.57	3.59	0.02	9.23
Cashew	60	7.42	3.56	13.29	140.61	0.76	0.99	0.95	0.40	2.97	0.01	8.87
Cashew	64	7.42	2.38	9.28	91.51	0.67	1.01	0.73	0.29	3.15	0.02	8.01
Cookie	63	9.28	3.06	3.83	12.79	0.81	0.81	1.26	0.28	2.60	0.02	7.59
Hazelnut	65	23.46	1.11	2.65	118.46	2.25	0.72	1.56	0.18	1.70	0.05	4.01
Hazelnut	66	16.59	6.44	4.09	127.04	1.03	0.96	1.39	0.36	5.48	0.06	8.79
Hazelnut	67	3.78	2.85	4.15	83.44	0.62	0.92	1.87	0.29	2.89	0.06	7.71
Hazelnut	68	20.55	2.79	2.95	92.15	1.49	0.89	1.54	0.31	4.39	0.05	8.06
Hazelnut	69	21.83	1.45	2.73	58.21	1.08	0.37	0.80	0.13	2.70	0.12	2.87
Multi	48	6.99	0.64	5.34	49.47	2.68	0.20	0.26	0.14	0.62	0.02	1.79
Peanut	28	5.32	0.79	6.08	63.69	1.86	0.16	0.23	0.11	0.74	0.06	1.15
Peanut	29	6.26	0.78	6.42	64.03	1.59	0.18	0.08	0.10	0.90	0.05	1.14
Peanut	30	5.46	0.84	5.47	67.93	1.95	0.23	ND	0.10	0.80	0.07	1.18
Peanut	31	8.98	0.71	8.21	60.41	1.38	0.24	ND	0.08	1.19	0.03	1.04
Peanut	32	5.19	0.56	5.83	71.08	2.63	0.15	ND	0.08	1.00	0.03	1.02
Peanut	33	5.08	0.76	4.60	68.05	2.04	0.19	0.07	0.03	0.92	0.04	0.59
Peanut	34	10.50	0.92	7.80	73.15	1.52	0.11	0.16	0.03	0.95	0.04	0.62
Peanut	34	6.79	1.55	12.07	58.14	0.57	0.69	1.45	0.14	1.74	0.04	3.67
Peanut	35	19.56	0.62	6.66	65.09	1.70	0.21	0.03	0.03	1.52	0.07	0.59
Peanut	36	4.96	0.86	6.10	62.94	1.97	0.20	ND	0.03	0.70	0.03	0.61
Peanut	37	4.98	0.37	6.80	66.32	1.48	0.13	0.03	0.03	0.68	0.01	0.59
Peanut	38	7.30	3.63	7.43	66.17	1.65	0.18	0.15	0.07	1.63	0.07	0.75
Peanut	39	5.41	0.70	7.77	71.17	1.89	0.35	0.07	0.08	0.82	0.04	0.68
Peanut	40	7.02	0.95	8.21	63.68	1.77	0.22	0.22	0.10	1.25	0.05	1.35
Peanut	41	5.58	0.74	6.04	58.13	1.42	0.14	0.13	0.07	1.87	0.06	0.82
Peanut	42	6.02	0.50	10.29	57.93	2.17	0.22	0.20	0.10	1.97	0.04	1.25
Peanut	43	2.03	0.48	6.73	73.70	3.31	0.16	0.22	0.11	0.94	0.03	1.47
Peanut	44	3.15	0.66	7.96	158.10	1.02	0.19	0.14	0.11	1.21	0.03	1.36
Peanut	44	4.38	0.92	34.72	87.16	22.52	0.77	0.58	0.12	1.22	0.01	2.29
Peanut	45	4.78	0.72	11.40	154.10	7.92	0.21	0.28	0.12	0.76	0.02	1.73
Peanut	45	3.59	1.44	10.13	202.81	10.63	0.46	0.81	0.13	1.43	0.02	2.74
Peanut	47	16.04	2.55	29.75	306.70	2.24	0.38	2.44	0.15	1.51	0.03	2.01
Peanut	55	3.61	1.06	14.09	531.38	0.87	0.23	0.29	0.19	0.74	0.01	2.43
Peanut	56	4.20	1.23	7.20	375.25	0.76	0.15	0.26	0.15	0.62	0.07	2.07
Peanut	70	6.67	1.55	48.70	956.35	5.88	0.11	0.52	0.11	0.68	0.03	1.44
Peanut	71	4.99	1.12	7.01	85.35	1.32	0.16	0.25	0.15	1.21	0.04	1.67
Peanut	72	5.24	1.93	1.05	150.37	0.12	0.25	0.15	0.15	1.10	0.04	1.67
Peanut	73	2.75	2.96	1.62	206.55	0.14	0.13	0.01	0.15	0.73	0.06	1.57
Peanut	76	6.32	1.22	13.85	117.91	2.45	0.28	0.32	0.16	4.54	0.10	2.60
Peanut/Date	46	6.80	1.40	8.20	331.39	1.58	0.13	0.19	0.10	0.81	0.19	1.28
Soybean	61	5.08	2.20	13.81	1132.38	0.91	0.55	1.37	0.12	3.41	0.04	4.06
Soybean	62	3.75	1.66	2.91	14.95	0.60	0.49	0.98	0.20	1.50	0.01	3.12
Sunflower	49	6.50	1.77	26.04	79.54	17.66	0.57	1.42	0.15	5.93	0.01	4.09
Sunflower	52	3.73	1.35	4.16	125.66	3.36	0.74	0.69	0.13	1.43	0.03	2.37
Sunflower	53	1.94	0.91	2.97	75.26	7.67	0.61	0.59	0.13	1.31	0.01	2.53
Sunflower	54	4.39	5.25	38.37	205.44	0.52	3.18	0.78	0.60	3.82	0.03	2.12
Tahini	58	5.90	1.15	9.08	417.83	0.87	0.45	0.97	0.15	1.14	0.01	3.11
Tahini	59	18.10	1.16	4.76	408.07	0.35	0.39	0.88	0.10	1.37	0.04	2.78
Yeast	74	5.14	5.41	53.79	123.66	0.60	0.79	0.95	0.14	1.61	0.03	2.59
Yeast	75	4.51	0.66	12.88	156.96	1.13	0.40	0.48	0.11	1.77	0.02	2.19

Dried Fruit

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.

Table 3 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 3. Heavy Metal Content of Dried Fruits (µg in 30 g (average serving))

Type	Sample #	Cr	As	Se	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
Peanut/Jelly Candy	50	12.10	0.92	105.11	1.42	0.27	0.27	0.18	0.68	0.11	1.58
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

Conclusions

While peanut and tree nut butters are excellent sources of protein, vitamins, and minerals, one should be aware of the amount of these products that they consume on a daily basis to ensure exposure levels for toxic heavy metals such as lead, arsenic, strontium, and cadmium are minimized. It is also interesting to note that peanut butter seems to contain some of the lowest amounts of toxic metals compared with the tree nut butters.

Manufacturers should be aware of the values of heavy metals contained in their product and should inform consumers of high levels of such metals are present in their products. Heavy metals should be reported as part of the nutritional label to ensure consumer knowledge.

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.

spex certiprep
203 Norcross Avenue • Metuchen, NJ 08840 • USMet-CRMSales@antylia.com • spex.com

3100 Smith Farm Road • Matthews, NC 28104 • info@cem.com • www.cem.com