1. Introduction

The environment in space is very different from the environment on Earth, and gamma rays, high-energy protons, and heavy ions from cosmic rays pose a great threat to nutrient stability. Nutrition is of critical concern for crewmembers served on long-term space flight missions, such as the Space Station, Lunar Station, and Mars Station, as body weight loss is a primary consequence of altered nutrition and insufficient nutrient supply, which is frequently observed during space flight (Convertino, 2002; Winitz, Graff, Gallagher, Narkin, & Seedman, 1965; Stein, 2001). The environmental factors in space are likely to cause changes in the flavor and vitamin content of food, and these changes may affect the nutritional value and sensory acceptability of space food, thus further affecting the health of astronauts (Lane, Smith, Rice, & Bourland, 1994).

Currently, space food is mostly pre-packaged and ready-to-eat (Sun, Tou, Yu, Girten, & Cohen, 2014). As human footsteps reach further into outer space, measures must be taken to maintain proper nutrition for crew members during long-term space flights, including how to maintain the nutrients and acceptability of foods, which is a major issue faced by space food scientists (Smith, Rice, Dlouhy, & Zwart, 2013). The United States performed space food nutrient assessment experiments during ISS missions for a period of 880 days, and even for three years (Cooper, Perchonok, & Douglas, 2017; Zwart, Kloeris, Perchonok, Braby, & Smith, 2009). The variations in the vitamin and amino acid contents of five foods and compound vitamin tablets were investigated during storage in earth orbit. Farming in space or on land away from the Earth will be considered due to launch capacity limitation (Bamsey et al., 2009; Jr & Brown, 2006; Monje, Stutte, Goins, Porterfield, & Bingham, 2003), which will provide crewmembers with fresh food such as cereals, fruits, and vegetables.

Chinese cuisine is vacuum packaged and heat-stabilized to serve as space food, which is very popular among Chinese astronauts. It is possible that radiation from the space environment may degrade nutrients or even create off-flavors as a result of oxidation. We hypothesized that susceptible vitamins and flavor substances may be the first to degrade in...
space, since they are the first to degrade on Earth (Gamboa-
Santos et al., 2014; Kong et al., 2017). An effective method
for assessing flavor and nutrient stability in space is to per-
form experiments under real radiation exposure during the
long-term storage conditions associated with long-term
space flight. We therefore carried out this research with the
objective of determining the stability of the vitamins and
flavors in foods and food materials after long-term space
flights on the TG-1 spacecraft.

2. Materials and methods

2.1. Chemicals and materials

Standards of riboflavin, nicotinic acid, nicotinamide, pan-
tothenic acid, pyridoxine, pyridoxal, biotin, folic acid, cobal-
amin, ascorbic acid, and tocopherol (including the α, β, γ,
and δ active forms) were purchased from Sigma. Ammonium
acetate was HPLC grade, acetonitrile was HPLC grade, and
ultra-pure water was obtained from a commercial ultrapure
water instrument (Milli-Q Advantage A10).

The foods and food materials were selected based on the
following criteria: a. currently used in the Shen Zhou space
food system, b. a potential source of space food material, and
c. representative of a typical type of space food (such as
canned food, or a natural food rich in vitamins). The quanti-
ties of the foods and materials used in the study were limited by
the volume and mass of the TG-1 spacecraft. Three foods were
vacuum packaged in four-layer aluminum foil bags (PET/Al/
PA/CPP) for the study, including braised beef with potatoes,
stewed duck with sauce, and freeze-dried black tomato pow-
der, with the former two were sterilized to make the product
thermal stable. The tea seed oil and fish oil were packaged in
three-layer aluminum foil bags (PET/Al/CPP) without vacuum
packaging. All food items and materials were obtained from
the same batch production from the same manufacturer to
ensure that the samples were homogeneous. It should be
pointed out that since the place in the spaceships is limited,
only one batch has been taken into space and then was
analyzed, so the differences between batches were not prop-
erly taking into account.

Two identical retardant cloth bags (Beijing Leather
Factory, Beijing, China) were prepared at the Astronaut
Center of China, with two replicates of the previously men-
tioned food items and materials from a single batch based
on the limited experimental item load of the spacecraft, and
the differences between batches is eliminated (Wu, Sun,
Zhang, Shen, & Weng, 2016). The two bags were launched
on the TG-1 spacecraft in September 2011, and were
brought back to Earth 274 days and 636 days later on the
TG-1 spacecraft flights by SZ-9 and SZ-10 manned space
flight missions, respectively, as shown in Table 1. Due to
the limited flight load on the manned spaceships, only a
limited amount of the research samples without repeti-
tions was brought back by the crewmembers during the
space flight missions from the TG-1 spacecraft.

2.2. Volatile compound analysis

The volatile compounds in the four kinds of canned food
were extracted using the SPME method. The needle for
SPME was CAR/PDMS (75 μm). A homogenous sample (6 g)
was placed into the solid phase microextraction vial, and
1 μL of 2-methyl-3-heptanone (1.632 μg/μL) was added as an
internal standard. The sample was equilibrated at 50°C for
30 min, and then the SPME needle was inserted, and the
sample was adsorbed for 40 min, and then analyzed by a
Sniffer 9000 sniffing instrument coupled with a Agilent
7890A –7000B GC-MS. After the compound was detected
by mass spectrometry and identified by a search of the
NIST2.0 library with MS interpreter after retention index
calibration, a quantitative analysis was conducted by calcu-
ling the peak area (Baker et al., 2003; Dionisio, Gomes, &
Oetetterer, 2009; Keast & Lau, 2006).

2.3. Vitamin analysis

Based on the nutritional properties of certain food samples
launched and that of concern for spaceflight and especially
for long-term duration spaceflight such as space station and
residence in Lunar base missions, the contents of 10 water-
soluble vitamins, including thiamine, riboflavin, niacin, niacin-
amide, pantothenic acid, pyridoxine, topiramate pyridoxal, bio-
tin, folic acid, and cobalamin in freeze-dried black tomato
powder were determined by LC-MS-MS method, as described
previously (Chen & Wolf, 2007; Gratacos-Cubarsi, Sarraga,
Clariana, Regueiro, & Castellari, 2011; Holler, Wachter, Wehrli,
& Fizet, 2006; Schimpf, Spiegel, Thompson, & Dowell, 2012)
using a Acquity UPLC and Xevo TQ ultra-performance liquid
chromatography-tandem mass spectrometry. The vitamin
C content of the freeze-dried black tomato powder and the
tocopherol content in fish oil and tea seed oil was assessed
according to a previously reported method (Gimeno,
Castellote, Lamuelaraventã3s, Torre, & Lã3lopezsabater,
2016). The tea seed oil and fish oil were packaged in
three-layer aluminum foil bags (PET/Al/CPP) without vacuum
packaging.

Two identical retardant cloth bags (Beijing Leather
Factory, Beijing, China) were prepared at the Astronaut
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flight missions, respectively, as shown in Table 1. Due to
the limited flight load on the manned spaceships, only a
limited amount of the research samples without repeti-
tions was brought back by the crewmembers during the
space flight missions from the TG-1 spacecraft.

Table 1. Food样品 information.

| No. | Food Item                  | Net weight/ g | Duration in orbit/ days |
|-----|----------------------------|---------------|-------------------------|
| 1   | Braised beef with potatoes | 90            | 274                     |
| 2   | Stewed duck with sauce     | 90            | 636                     |
| 3   | Freeze-dried black tomato  | 5.5           | 274                     |
| 4   | Fish oil                   | 5.5           | 274                     |
| 5   | Tea seed oil               | 5.5           | 274                     |

3. Results and discussion

3.1. Volatile compound variation

Samples of braised beef with potatoes and stewed duck
with sauce were launched on the TG-1 spacecraft and
brought back by the SZ-10 mission after storage in orbit
for 636 days. The volatile compound analysis was con-
ducted six days after return to earth. The total ion current
charts of the volatile compounds are shown in Figures 1
and 2, and the identified flavor compounds are shown in
Tables 2 and 3.

As shown in Table 2, the major volatile compounds in
the braised beef with potatoes sample were spathulenol,
2-butyl 4-ethylbenzoate, ethyl acetate, 6-methyl-5-hep-
ten-2-one, and anethole. The compounds that contribute
to the flavor of braised beef with potatoes are mainly
aliphatic alcohols, esters, ketones, and alkenes, and have fewer irritating aldehyde flavor substances. The flavor ingredients found in braised beef with potatoes may have come from the food material, spices or compounds generated during processing. After storage, there was little variation in the volatile compounds, including higher relative levels of spathulenol, 6-methyl-5-hepten-2-one, anethole, α-pinene, 4-terpineol, linalool, isopulegol, and d-limonene in the ground control samples and higher levels of 2-butyl 4-ethylbenzoate, ethyl acetate, α-hydrophyllene, camphene, α-curcumín, α-cypresene, benzaldehyde, acetic acid, nonanal, 2-furanemethanol, and 3-methyl-4-hydroxybenzaldehyde in the space flight samples. The volatile compounds increased in the ground control samples mainly consisted of enols.

As shown in Table 3, the main volatile compounds in the stewed duck with sauce samples were 2-pentylfuran, ethyl acetate, 2-ethylfuran, 2-butyl 4-ethylbenzoate, and 1-octen-3-ol. The compounds that contribute to the flavor of stewed duck with sauce are mainly furans, esters, and aliphatic alcohols; and it has few irritating aldehyde flavor substances. After storage for nine months, there were slight, but not significant variations in several volatile compounds, including 2-pentylfuran and ethyl acetate, as well as higher levels of 2-ethylfuran, spathulenol, 2-(1-pentenyl)-furan, gingerene, anethole, and thujaopsene in space flight samples, and higher levels of 2-butyl 4-ethylbenzoate, 1-octen-3-ol, camphene, benzaldehyde, α-curcumín, furfural, α-cypresene, hexanol, d-limonene, hexanal, 6-methyl-5-hepten-2-one, and 2-furanemethanol in the ground control samples. The different canned foods had different volatile compounds compositions, which were derived from the food ingredients and condiments added during processing and contributed to their unique flavor.

3.2. Variations in vitamins

3.2.1. Natural vitamins in freeze-dried black tomato powder

The standard curves of each vitamin are shown in Table 4. The correlation coefficients (R values) of the standard curves were greater than 0.996, and thus could be used to determine the concentrations in the test samples. Vitamin contents in the ground control and space flight freeze-dried black tomato powder samples are shown in Table 5.

As shown in Table 5, vitamin B₁₂ and folic acid were not detected in either the ground control and space flight samples, and no notable variations were observed in the concentrations of biotin, niacin, pantothenic, pyridoxal, vitamin C, riboflavin, and thiamine between the space flight and ground control samples. Freeze-dried black tomato powder is rich in natural water soluble vitamins, which can be developed as a nutrient supplement or rehydration drink without
Table 2. Flavor substance content variation of braised beef with potatoes.

| No. | Compounds          | Samples brought back by SZ-10 mission/% | Ground control samples/% |
|-----|--------------------|----------------------------------------|--------------------------|
| 1   | Spathulenol        | 20.3                                   | 27.6                     |
| 2   | 2-ethyl-4-ethylbenzoxa | 13.5                                   | 12.3                     |
| 3   | Ethyl acetate      | 9.2                                    | 2.1                      |
| 4   | 4-methyl-5-hepten-2-one | 7.2                                    | 7.4                      |
| 5   | Anethole           | 6.7                                    | 7.5                      |
| 6   | α-Hydrophyllene    | 5.3                                    | 4.6                      |
| 7   | α-Pinene           | 5.0                                    | 6.0                      |
| 8   | Camphene           | 4.9                                    | 4.8                      |
| 9   | 4-terpinol         | 4.3                                    | 5.2                      |
| 10  | Curcumín           | 3.6                                    | 2.4                      |
| 11  | Cypresene          | 3.3                                    | 1.3                      |
| 12  | Benzyaldehyde      | 3.3                                    | 2.3                      |
| 13  | Linalool           | 3.1                                    | 3.3                      |
| 14  | α-Terpinol         | 3.1                                    | 3.1                      |
| 15  | Acetic acid        | 2.1                                    | 1.8                      |
| 16  | Isopulegol         | 1.5                                    | 4.0                      |
| 17  | Nonanal            | 1.3                                    | 1.0                      |
| 18  | δ-limone           | 1.1                                    | 2.8                      |
| 19  | 2-furanemethanol   | 1.0                                    | 0.6                      |
| 20  | 3-methyl-4-hydroxybenzaldehyde | 0.2                  | 0.1                     |

Table 3. Variation of flavor substances of stewed duck with sauce.

| No. | Compounds          | Samples brought back by SZ-10 mission/% | Ground control samples/% |
|-----|--------------------|----------------------------------------|--------------------------|
| 1   | 2-Pentylfuran      | 32.9                                   | 29.2                     |
| 2   | Ethyl acetate      | 10.7                                   | 10.0                     |
| 3   | 2-ethylfuran       | 7.1                                    | 2.6                      |
| 4   | 4-butyl-4-ethylbenzoxa | 6.9                                    | 7.1                      |
| 5   | 1-octen-3-ol       | 5.7                                    | 5.8                      |
| 6   | Spathulenol        | 5.5                                    | 2.7                      |
| 7   | Camphene           | 5.0                                    | 5.4                      |
| 8   | Benzyaldehyde      | 4.5                                    | 5.0                      |
| 9   | 2-(1-pentyl)-furan | 3.6                                    | 2.1                      |
| 10  | α-Curcumín         | 2.9                                    | 3.1                      |
| 11  | Furfural           | 2.2                                    | 3.2                      |
| 12  | α-Cypresene        | 2.2                                    | 3.3                      |
| 13  | Hexanol            | 2.0                                    | 5.2                      |
| 14  | Gingerene          | 1.5                                    | 0.1                      |
| 15  | Anethole           | 1.5                                    | 1.2                      |
| 16  | D-limonene         | 1.4                                    | 1.8                      |
| 17  | Hexanal            | 1.4                                    | 7.6                      |
| 18  | Thujopenes         | 1.3                                    | 0.7                      |
| 19  | 6-methyl-5-hepten-2-one | 1.1                  | 2.7                     |
| 20  | 2-furanemethanol   | 0.6                                    | 1.3                      |

3.2.2. Tocopherol variation in tea seed oil and fish oil

The standard curve for tocopherol is shown in Table 4. In this table, the tocopherol standard curve correlation coefficient ($R^2$) was 0.996 or greater, and therefore could be used for the analysis of tocopherol contents.

The tocopherol contents of tea seed oil and fish oil are shown in Table 6. As shown in Table 6, the tocopherols in tea seed oil were mainly the α-tocopherol type, with small amounts of the other three types of tocopherol. The tocopherol in fish oil is mainly the (β + γ)-tocopherol type, followed by the α-tocopherol and δ-tocopherol types. Compared with the ground control samples, the tocopherol levels in the space flight samples were slightly lower. Compound application of tea seed oil and fish oil can be a better natural vitamin E source to provide different types of tocopherol for astronaut during spaceflight missions.

Flavor and nutrition as vitamins are two important attributes of space foods. Vitamins are closely related to the health of astronauts during long term space flight. Changes in the volatile compound contents directly affect the sensory acceptance of space foods, which in turn affects the astronauts’ food intake. Compared to other nutrients in foods, such as proteins, fats, carbohydrates, and minerals, vitamins are more environmentally susceptible, more easily degraded, and undergo structural changes under certain conditions encountered during processing or storage, such as heat, oxidation, and radiation (Dionisio et al., 2009; Jeong et al., 2017; Leskova et al., 2006). In this study, water-soluble vitamins and vitamin E (a fat-soluble vitamin) were selected as representative indicators. The samples were packed in aluminum foil bags, which have excellent oxygen and moist-

Table 4. Standard curves used for each vitamin analysis.

| No. | Vitamins | Standard curve | Correlation coefficient |
|-----|----------|----------------|-------------------------|
| 1   | Biotin   | $y = 1027.4x + 152.52$ | 0.9999 |
| 2   | Vitamin B$_{12}$ | $y = 483.85x + 187.48$ | 0.9990 |
| 3   | Folic acid | $y = 42.51x + 5.01$ | 0.9998 |
| 4   | Niacin   | $y = 36.23x + 23.37$ | 0.9989 |
| 5   | Pantothenic | $y = 324.41x + 17.16$ | 0.9999 |
| 6   | Pyridoxal | $y = 4891.9x + 1620.6$ | 0.9997 |
| 7   | Riboflavin | $y = 524.01x + 7.10$ | 0.9999 |
| 8   | Thiamine | $y = 13915x + 9471.4$ | 0.9995 |
| 9   | Vitamin C | $y = 2.04x + 1.5$ | 0.9966 |
| 10  | δ-tocopherol | $y = 21000x + 19336$ | 0.9991 |
| 11  | (β + γ) - tocopherol | $y = 44668x + 14643$ | 0.9996 |
| 12  | δ-tocopherol | $y = 34191x + 56606$ | 0.9969 |

a: $y$ indicates peak area, $x$ indicates concentrations of vitamins (ng/mL). y indica el área pico, x indica la concentración de vitaminas (ng/mL).

Table 5. Content of vitamins for freeze-dried black tomato powder.

| No. | Vitamins | Samples brought back by SZ-9 mission (%) |
|-----|----------|------------------------------------------|
| 1   | Biotin   | 3.96                                     | 3.82                          |
| 2   | Vitamin B$_{12}$ | <0.1                                   | <0.1                          |
| 3   | Folic acid | <0.2                                    | <0.2                          |
| 4   | Niacin   | 3.75                                     | 3.58                          |
| 5   | Pantothenic | 418                                     | 409                           |
| 6   | Pyridoxal | 347                                      | 333                           |
| 7   | Riboflavin | 14.2                                    | 16.5                          |
| 8   | Thiamine | 162                                      | 163                           |
| 9   | Vitamin C | 292.8                                    | 287.0                         |

Table 6. Tocopherol content of tea seed oil and fish oil samples.

| No. | Food item   | Tocopherol (mg/100g) | Ground control samples (mg/100g) | Samples brought back by SZ-9 mg/100g |
|-----|-------------|----------------------|----------------------------------|-------------------------------------|
| 1   | Tea seed oil | α-tocopherol         | 13.4                             | 12.9                                |
|     |             | (β + γ) -tocopherol   | 1.1                              | 0.7                                 |
|     |             | δ-tocopherol         | 0.6                              | 0.4                                 |
| 2   | Total       |                      | 15.1                             | 14.0                                |
| 3   | Fish oil    | α-tocopherol         | 19.8                             | 17.9                                |
|     |             | (β + γ) -tocopherol   | 34.8                             | 30.6                                |
|     |             | δ-tocopherol         | 19.2                             | 17.7                                |
| 4   | Total       |                      | 73.8                             | 66.2                                |

Deep processing, to serve as a routine supply of water-soluble vitamins in the space diet.
ure barrier properties. Because of the absence of protection by the atmosphere, the radiation levels in space are higher than those on the surface of Earth. However, because of the physical radiation shielding of the manned spacecraft, the radiation level inside the cabin is greatly reduced compared with that outside (Shinn, Nealy, Townsend, Wilson, & Wood, 1994). As enols, a type of volatile compound, are mainly small molecules that are more sensitive to radiation or oxidation than vitamins, protective measures should be taken to offset their reduction or variation. Various aspects of the space environment, including vibrations, noise, microgravity, and electromagnetic radiation, may significantly affect the human body but have little effect on the properties of well-packed food items. The results of this study are consistent with other results reported in the literature (Zwart et al., 2009). In contrast to the unique weightlessness conditions in space, other environmental conditions that could affect the physical and chemical properties of foods, such as temperature and humidity, were the same as those on the ground. However, the radiation levels in spacecraft are higher, which may harm the more sensitive flavor substances (Townsend, 2005). The mechanism underlying these related changes is unclear, and should be examined in a subsequent study.

4. Conclusion

Variations of the volatile compounds in traditional Chinese canned food items and vitamins in natural food ingredients were investigated after storage on the TG-1 spacecraft. Since independent packaged samples assignment was not enough, which did not take batches and repetitions into account because of the space limitation of the manned spaceship, making further statistical analysis of the results impossible. However, based on available data, it is reasonable to assume that compared with the ground control samples, some of the trace alkene-type volatile compounds were decreased in both braised beef with potatoes and stewed duck with sauce after 274 and 636 days of space flight, respectively. Our findings on volatile changes between the ground control and flight samples give reference to offset their reduction or variation. Various aspects of the space environment, including vibrations, noise, microgravity, and electromagnetic radiation, may significantly affect the nutritional quality of the space food system over three years of ambient storage. Npj Microgravity, 3(1), 17.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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