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Effect of Temperature on the Diminution of Retained Arsenic in Dried Hijiki, *Sargassum fusiforme* (Harvey) Setchell,[*1] by Water-Soaking[*2]

Masayuki KATAYAMA[*3] and Yohko SUGAWA-KATAYAMA[*4]

Department of Health and Nutrition, Gifu Women's University, Gifu, 501-2577 Japan

Arsenic levels in the sea weed, Hijiki, *Sargassum fusiforme* (Harvey) Setchell, after soaking in water were determined by thermal neutron activation analysis. Commercial dried Hijiki was soaked in purified water for periods of time (20-360 min) at various temperatures (0-90℃). Arsenic concentrations retained in the swollen Hijiki tissues and those dissolved in the aqueous solution were determined. At temperatures higher than 30℃, about 70% of the total arsenic was removed from the swollen Hijiki after discarding the soaking water. The non-extractable arsenic bound to the tissues seems to be about 10% of the total, when estimated at higher temperatures (75 and 90℃). To remove arsenic as much as possible before cooking, it is recommended to soak commercial dried Hijiki in warm water for more than 30 min and discard the water extracts.

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INTRODUCTION

Hijiki, *Sargassum fusiforme* (Harvey) Setchell, which belongs to the Phaeophyta family, contains rather higher amounts of arsenic than the members of other families.[2)-4)] Commercial products of Hijiki have usually been prepared from the sun-dried raw materials by soaking them in boiling water, drying under the air stream and selecting their size for packaging. Substantial amounts of arsenic accumulated in the plant tissues are removed through these steps. However, the levels of retained arsenic in the dried Hijiki are at times high, the large differences depending on their lots[3)5)] or the harvesting locations.[6)-10)] We reported preliminarily the effect of water-soaking on the diminution of arsenic contents.[5)]

In the present paper, we intend to report more detailed conditions to diminish the retained arsenic levels in Hijiki through the pre-cooking treatment by varying the water-temperature and time-lapse of water-soaking.

EXPERIMENTAL

Sample plants

Hijiki was harvested at the seashores of the Tsushima Archipelago, Japan. The commercial products of Hijiki were all dried mixtures of the leaves, stalks and apexes and were stored below 4℃ until use.

Pre-cooking conditions

One gram of the dried Hijiki was sampled while being mixed uniformly from the bulk, cut into pieces of 0.5 to 1 cm in length, and put into a small vial placed in a constant-temperature water-bath. Thirty milliliters of extra pure water was added and the mixture was stirred slowly (one stroke per second) for a lapse of time. Then, the Hijiki samples were rapidly separated through a glass funnel under vacuum. The volumes of the water extracts and the weights of the

[*1] Newly proposed taxonomic name[1)] of *Hizikia fusiforme* Okam.

[*2] The second report of "reliable methods to diminish arsenic levels in Hijiki, *Sargassum fusiforme* (Harvey) Setchell,[*1] through a pre-cooking treatment." The data were presented at the 58th Annual Meetings of the Japanese Society of Home Economics in Akita (2006). The first report is Ref. 5).

[*3] Professor Emeritus of Osaka Prefecture University, Hashimoto, Wakayama 648-0054 Japan.

[*4] To whom the correspondence should be sent. Present address: Department of Health and Nutrition, Osaka-Aoyama University, Minoh, Osaka 562-8580, Japan.

separated residues were measured, and all the solid samples were lyophilized. Two accurately measured aliquots of each sample were used for the thermal neutron activation analysis.

The water-soaking time

The Hijiki samples were soaked in extra-pure water for 20 min, 40 min, 60 min, 180 min or 360 min.

The temperature range

For the water-soaking, the vials containing the samples were placed in a water bath maintained at 30℃, 45℃, 60℃, 75℃ or 90℃, and shaken slowly at one stroke per second. The vials for 0℃ were placed in iced water in a refrigerator and those for 15℃ were placed in a water-bath kept at that temperature by adding some ice continuously.

Arsenic determination[7]

The extracts were micropipetted onto a piece of filter paper, dried, and the whole was subjected to the irradiation analysis. The mean of the two determinations was expressed as the amount of arsenic per unit weight of a dried sample or unit volume of a liquid sample.

The dried samples were separately packaged in small polyethylene bags. To determine the arsenic concentration in the samples, 40 of those bags were put together in a polyethylene Neuma-capsule, with 10 bags of various amounts of a standard arsenic compound; two of the standard specimens were arranged for every 8 specimens of Hijiki. The standard solution of arsenic was prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ of the guaranteed grade reagent into extra pure water.

Thermal neutron activation analysis[7]

The samples in the Neuma-capsules were irradiated in a flux of 10^{13} neutrons$\cdot cm^{-2} \cdot s^{-1}$ for 20 min in the center position of the nuclear reactor of the Research Reactor Institute, Kyoto University. After a cooling time of 72 h, the arsenic content in the samples was determined by gamma radiation from ^{76}As using a pure Ge gamma-detector at 559.1 keV. The energy levels of ^{60}Co and ^{137}Cs were used for calibration.

RESULTS

The arsenic level in Hijiki samples

Commercially prepared dried Hijiki samples were obtained in a bulk. To check the homogeneity in their arsenic contents, several small portions were sampled and their arsenic contents were determined. The present lot of the commercial product showed 89.08± 6.40 ppm in average (±standard deviation) of arsenic (Table 1).

The diminution process of retained arsenic in swollen Hijiki (Table 2)

At 0℃; the arsenic retained in the swollen Hijiki diminished only about 13% after 20 min and 38% after 40 min of water-soaking. After 360 min, near by 50% of the total arsenic was still retained.

At 15℃; 37% of the total arsenic was removed in 20 min. The ratio of the eluted arsenic to the retained increased gradually reaching about 60% after 360 min.

At 30℃; 42% was removed in 20 min of water-soaking, and after 40 min 56 to 58% was removed, constantly.

At 45℃; within 20 min the ratio of the retained arsenic became constant (38 to 42%).

At 60℃ and higher temperatures; after 20 min, almost all of the extractable arsenic was removed and only about 30% to 35% was retained in the swollen Hijiki. The amount of retained arsenic was mostly constant, and neither a longer soaking time nor a higher soaking temperature significantly changed the amount of extractable arsenic.

Time course changes of the arsenic release from the Hijiki tissues (Table 3)

The swollen Hijiki contains 11 times as much water as dried tissues of Hijiki. On the assumption that the water compartment in the swollen Hijiki contains the same concentration of arsenic as the eluted arsenic solution outside, the arsenic release from the tissues at temperatures higher than 45℃ seems to be very rapid, and within 20 min, the extractable arsenic approached about 81% to 84%. At 15℃, more than 80% of the total arsenic was removed in 180 min. However, at 0℃, the extractable arsenic was less than 70% even after 360 min.

Table 1. Arsenic concentrations of Hijiki samples

Samples*	As μg/g dry weight
a	90.44
b	99.51
c	84.07
d	84.05
e	87.34
Average	89.08
Standard deviation	±6.40

*Hijiki samples were obtained from several points of a bulk of the dried Hijiki, prepared for commercial products. The arsenic was determined in duplicate by neutron activation analysis.

Table 2. The ratios of the retained arsenic in the swollen Hijiki residue samples to the total arsenic amount

Temperature of the soaking water	Time period of the soaking (min)	Ratio of As amounts retained in the swollen Hijiki to the total	Temperature of the soaking water	Time period of the soaking (min)	Ratio of As amounts retained in the swollen Hijiki to the total
0℃	0	1.000	60℃	0	1.000
	20	0.865		20	0.314
	40	0.623		40	0.379
	60	0.649		60	0.400
	180	0.531		180	0.368
	360	0.499		360	0.378
15℃	0	1.000	75℃	0	1.000
	20	0.630		20	0.302
	40	0.529		40	0.359
	60	0.501		60	0.321
	180	0.425		180	0.354
	360	0.403		360	0.319
30℃	0	1.000	90℃	0	1.000
	20	0.581		20	0.310
	40	0.429		40	0.369
	60	0.420		60	0.319
	180	0.436		180	0.333
	360	0.425		360	0.349
45℃	0	1.000			
	20	0.378			
	40	0.400			
	60	0.398			
	180	0.422			
	360	0.412			

The commercial dried Hijiki samples were soaked in 30 volumes of water at the indicated temperature for the indicated time period, respectively. After being separated rapidly, they were lyophilized to determine their arsenic concentrations. The arsenic concentrations in water-swollen-Hijiki-residue samples were determined, as described in the text.

Arrhenius plots for the extraction process of arsenic (Fig. 1)

The time course changes of the retained arsenic reflect the elution pattern of the arsenic from the Hijiki plant during water-soaking. These curves suggest that the processes of the arsenic elution do not take a simple pattern. At the early stage of the extraction of the arsenic, *i.e.* at 20 min after the start of soaking in water, the Arrhenius plots indicated more than one inflection point, suggesting that the elution process consists of more than one mechanism. The less steep slope at temperatures higher than the inflection point of about 50℃ suggests that the elution process occurs easily. The lower temperature slope of the inflection point suggests more complicated mechanisms.

DISCUSSION

Japanese people traditionally soak dried, stiffened Hijiki in water in a pre-cooking process at home, although the soaking conditions remain undetermined.

The values of Table 2 are useful, because Hijiki is cooked in the swollen state. From the commercial products of dried Hijiki, more than 60% of the total arsenic has been removed after 40 min at temperatures higher than 45℃. The Hijiki swollen at temperatures higher than 30℃ contains more than 10 times the amount of water in the dried tissues. Thus the arsenic contents in the tissue residues (Table 3) are less than those in Table 2. These values indicated that the arsenic retained in the tissue residues are less than 20% of

Table 3. The ratios of the retained non-extractable arsenic in the Hijiki residues to the total arsenic amount

Temperature of the soaking water	Time period of the soaking (min)	Ratio of As amounts retained in the Hijiki residues to the total	Temperature of the soaking water	Time period of the soaking (min)	Ratio of As amounts retained in the Hijiki residues to the total
0℃	0	1.000	60℃	0	1.000
	20	0.858		20	0.078
	40	0.584		40	0.146
	60	0.599		60	0.157
	180	0.391		180	0.142
	360	0.326		360	0.142
15℃	0	1.000	75℃	0	1.000
	20	0.571		20	0.062
	40	0.403		40	0.141
	60	0.341		60	0.084
	180	0.207		180	0.115
	360	0.155		360	0.074
30℃	0	1.000	90℃	0	1.000
	20	0.440		20	0.073
	40	0.233		40	0.145
	60	0.203		60	0.075
	180	0.206		180	0.099
	360	0.204		360	0.117
45℃	0	1.000			
	20	0.189			
	40	0.184			
	60	0.177			
	180	0.163			
	360	0.182			

The dried commercial Hijiki samples were soaked in 30 volumes of water at the indicated temperature for the indicated time period, respectively. After being separated rapidly, they were lyophilized to determine their arsenic concentrations in the swollen Hijiki fractions. Arsenic amounts in Hijiki residues were obtained by subtracting the arsenic amounts in the water compartment from the arsenic in the swollen Hijiki fractions.

the total, and the higher the temperature of soaking water, the less arsenic was retained. It is also suggested that at temperatures higher than 60℃, a certain amount of arsenic was re-adsorbed to the tissues during extended soaking.

The elution process of arsenic from Hijiki seems to occur easily after the preliminary process of tissue swelling as indicated by the less gradient curve of the Arrhenius plots at temperatures higher than 50℃ (Fig. 1). Within the first 20 min soaking, arsenic elution seemed to occur at least in two processes below 50℃. The processes occurring within 20 min may include modification of the tissue structures through swelling, although other kinds of mechanism may continue for more than several hours.

As previously reported,[3)5)6)] several lots of commercial Hijiki obtained on general Japanese markets showed a very wide range of arsenic contents, from several to more than 100 ppm. This may mostly be owing to the greatly varying levels of the arsenic contents in fresh Hijiki at different harvesting sites.[6)-10)] Moreover, it was reported[11)] that the processes producing commercial dried Hijiki may have contributed much less to their arsenic levels than other factors.

The arsenic contents expressed in Table 2 are composed of arsenic in bound form and water-soluble form. The former is 10 to 20% of the total arsenic (Table 3) and resistant to various treatments

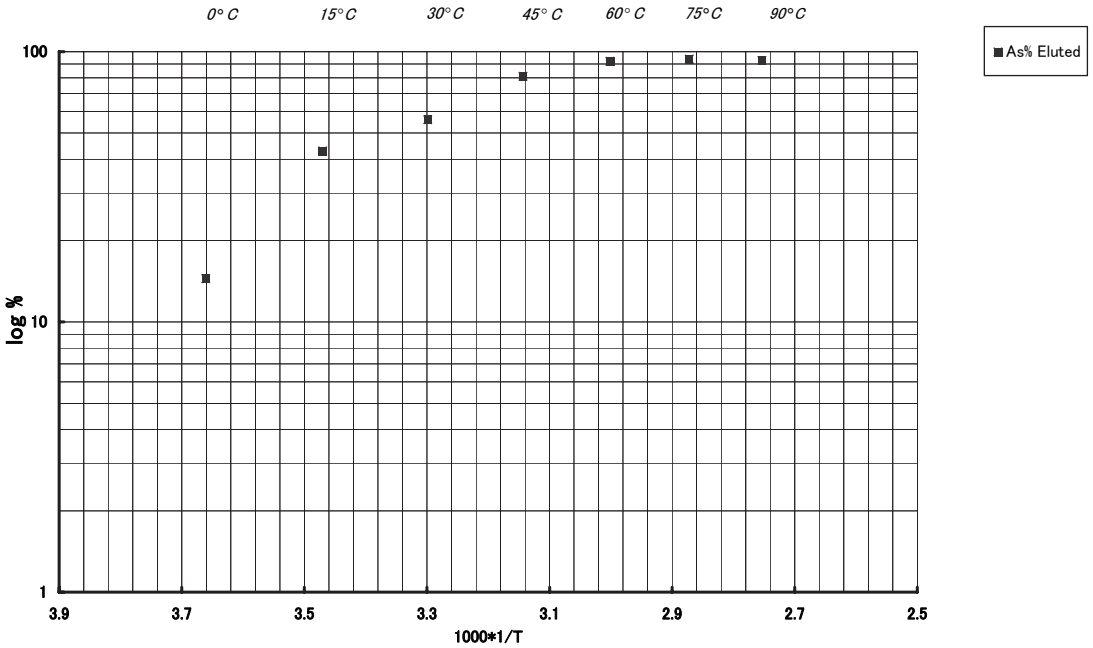

Fig. 1. Arrhenius plots of the extraction process of arsenic by water soaking for 20 min

The ordinate axis represents the log of the ratio of the arsenic amounts eluted from the Hijiki residues to the total, calculated as described in Table 3. The abscissas axis represents the reciprocal of the absolute temperature (T).

(unpublished data). The latter exists in the water compartments of the swollen Hijiki, amounting to 10 to 20% of the total arsenic, as shown by the difference between the values of Table 2 and Table 3. Out of the soluble arsenic compounds, about half was in the inorganic form, arsenate (publication in preparation).

Under the assumption that the average per capita consumption of Hijiki in Japan is about 1 g/day, the intake of inorganic compounds (mostly arsenate) would be at most 10 μg As/day after the water-soaking and discarding process, even if the commercial dry Hijiki containing the highest level of arsenate concentration, 100 ppm, were taken into account. In this connection, the lethal dose of arsenate to rat was reported to be 14–18 mg As/kg body weight.[12]

The above results led us to a recommendation that, for a pre-cooking treatment, the commercial dried Hijiki should be soaked in warm water for more than 30 min and the soaking water should be discarded.

Moreover, repeating the water-soaking and discarding processes will result in further removal of the remaining extractable arsenic in the water compartment. However, as the water-soaking brings about some loss of beneficial elements such as calcium and iron, we are investigating a better and simpler combination of pre-cooking treatments.

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ヒジキ（*Sargassum fusiforme*（Harvey）Setchell）含有のヒ素量を調理前処理によって軽減させる条件について

片山眞之，片山（須川）洋子

（岐阜女子大学健康栄養学科）

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市販乾燥ヒジキ（*Sargassum fusiforme*（Harvey）Setchell）に含まれるヒ素は，調理前処理として乾燥ヒジキを水に浸し一定時間水戻しすると溶出されてくる．浸漬水の液温を 0℃，15℃，30℃，45℃，60℃，75℃，90℃とし，各々浸漬時間を 20 分，40 分，60 分，180 分，360 分に設定して溶出ヒ素量を定量した．同時に，膨潤ヒジキ画分のヒ素含量も定量した．ヒ素の定量は熱中性子放射化分析によった．乾燥ヒジキを 75～90℃の浸漬水で水戻しすると，20 分以内に総ヒ素量の約 70%が溶出されて膨潤ヒジキ中には約 30%が保持されている．この内ヒジキ固形物に結合されているのは約 10%である．45℃で水戻しを行うと 20 分以内に総ヒ素量の約 60%が溶出され，約 40%が膨潤ヒジキ画分に残存するが，この時ヒジキ固形物中に結合するヒ素は総ヒ素量の 20%以下である．なお，ヒ素溶出の機構が単一ではないことが推察された．

キーワード：ヒ素含有量軽減，ヒジキ，*Sargassum fusiforme*（Harvey）Setchell，水戻し，熱中性子放射化分析，調理前処理．