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Stability of toxic arsenic species and arsenosugars found in the dry alga Hijiki and its water extracts

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ABSTRACT

The achievement of reliable results in speciation analysis requires not only sensitive techniques but also sureness of species stability. Therefore, it is necessary to carry out stability studies because it is important to know with absolute certainty that there is not any species transformation during sample treatment and/or storage. Although several procedures have been recommended for the preservation of species integrity, there is no general agreement, as arsenic species stability depends on the sample matrix, the concentration level and the sample treatment procedure, so it is necessary to assess the arsenic species stability for each case. Thus, the present paper reports the stability tests of arsenic species carried out on the commercially available edible alga Hijiki (*Hizikia fusiformis*), from Japan, in both the dry sample and its water extracts, which were stored in amber glass and polystyrene containers at −18 and +4 °C in the dark. Extractions were carried out with deionized water by microwave-assisted extraction, at a temperature of 90 °C and three extraction steps of 5 min each, whereas arsenic speciation analysis was performed by anion exchange high performance liquid chromatography–photo-oxidation–hydride generation–atomic fluorescence spectrometry. The results obtained for the dry alga showed that the arsenic species present in it (arsenate (As(V)), dimethylarsinic acid (DMA) and the arsenosugars glycerol (Gly-sug), phosphate (PO_4-sug), sulfonate (SO_3-sug) and sulfate (SO_4-sug)) were stable for at least 12 months when the sample was stored in polystyrene containers at +20 °C in the dark. Regarding water extracts, the best storage conditions consisted of the use of polystyrene containers and a temperature of +4 °C, for a maximum storage time of seven days. Therefore, the immediate analysis of Hijiki water extracts would not be necessary, and they could be stored for one week before analysis, ensuring arsenic species stability. This information about species integrity in extracts is especially useful when the sample treatment for arsenic species extraction is time-consuming.

1. Introduction

In speciation analysis of environmental samples, the stability of arsenic species during sampling, storage and processing is a crucial factor, due to losses, interconversion and degradation processes of arsenocompounds that may occur in species characterization. The preservation and stabilization of these chemical species in the time interval between sampling and analysis is a difficult task, since parameters such as pH, temperature, light, microbial activity and the container material are critical for species stability. In this regard, several procedures have been recommended for preservation of species integrity, such as freezing, cooling, acidification, sterilization, deaeration and/or storage in the dark [1]. Furthermore, for samples where bacteria exist naturally, storage at low temperatures, or even lyophilization, is required to prevent biological activity from modifying the sample nature [2]. However, there is no general agreement on these procedures, especially for complex solid matrices such as soils, sediments and biological tissues, mainly because arsenic species stability depends on the sample matrix, the concentration level and the sample treatment procedure [3]. Therefore, carrying out stability studies for arsenic speciation analysis is very interesting in different matrices, and the stability of the arsenic species in the extracts must be guaranteed. Further research into stability is required in order to establish safe periods for extract storage and other suitable conditions, in order to ensure the integrity of arsenic species before their identification and quantification [4].

Several studies have investigated the stability of arsenic species in solution in different media. Many of these studies show that most stability issues are associated with arsenite (As(III)), because it is easily oxidized to As(V) [5]. Published literature on preserving arsenic species in environmental water samples is confusing and

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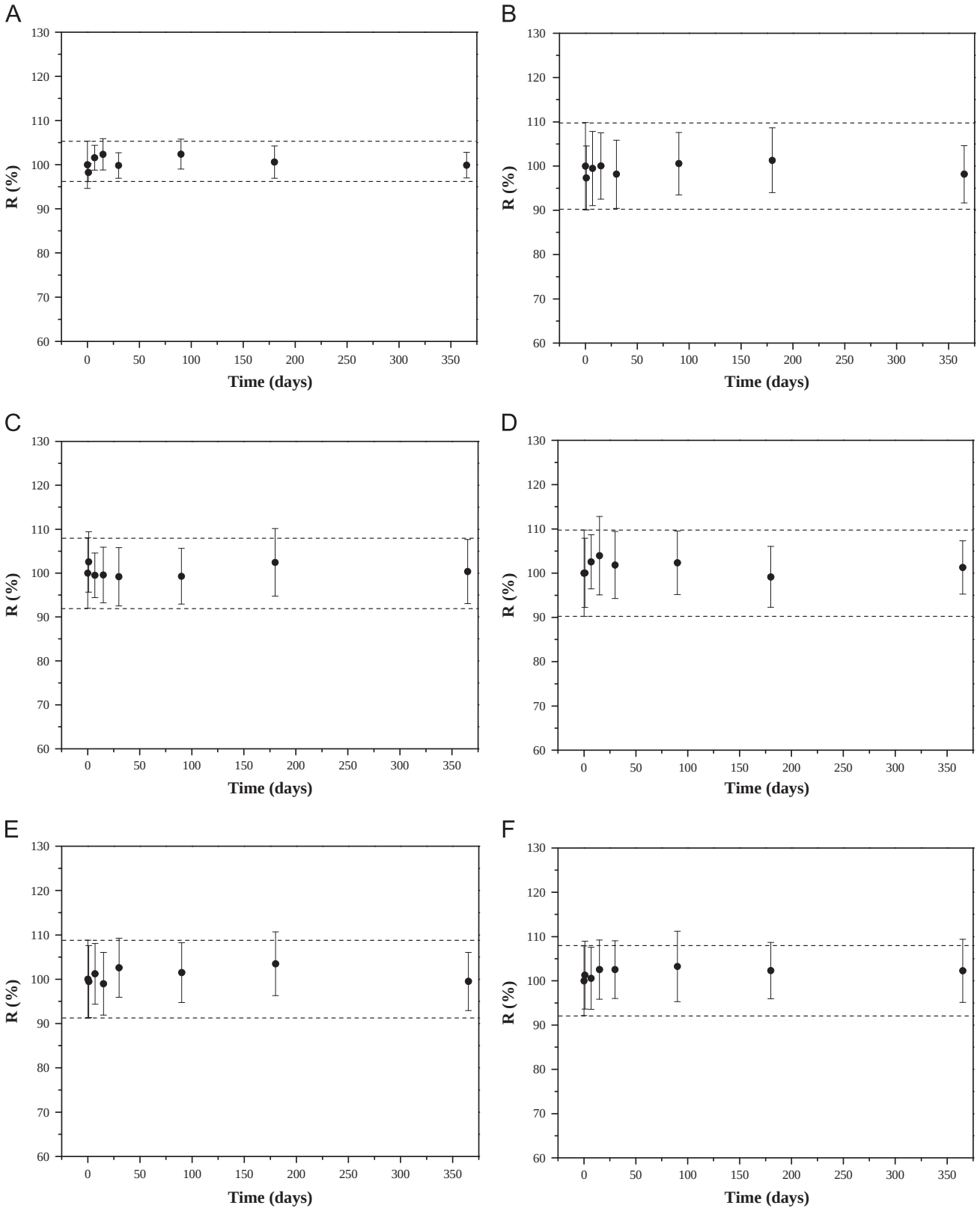

Fig. 1. Stability of the As species As(V) (A), DMA (B), Gly-sug (C), PO_4-sug (D), SO_3-sug (E) and SO_4-sug (F) in dry Hijiki alga sample, determined by HPLC-(UV)–HG–AFS, and stored at +20 °C in polystyrene containers (*dots* stability R_x; *I* uncertainty for each point U_x; *dashes* uncertainty associated with $t=0$ days).

contradictory, mainly because of the reactions of the Fe(III)/Fe(II) redox system and the microbe-mediated arsenic-species transformations [6]. Some prerequisites for stabilization of As(V)/As(III) are filtration (removes suspended matter and most microbes), refrigeration (suppresses most biotic and abiotic reactions) and storage in the dark (avoids photochemical reactions of Fe(III) and As(III)). Several reagents have been used to the oxidation and precipitation processes, but the efficiency of preservation depends greatly on the sample matrix [6]. Several acids (hydrochloric, nitric or ascorbic acid) have been proposed for arsenic stabilization

in water samples, in order to reduce sample pH below 2, since acidification is necessary to keep the iron in solution, which avoided co-precipitation of arsenic or adsorption onto the iron oxy-hydroxide [7]. Daus et al. [8] studied pre-treatment procedures based on complexation of metal ions and moderate acidification of iron-rich water samples, and proposed the use of 0.01 mol L^{-1} phosphoric acid as stabilization agent and a storage temperature of +6 °C. Segura et al. [9] found that As(V), monomethylarsonic acid (MMA) and DMA were stable in raw and treated urban wastewater samples, over a four month period at +4,+20 and +40 °C, whereas the concentration of As(III) in raw samples decreased after 2 weeks of storage.

In soil extracts, it is important to check the stability of As(III), which depends on the pH of the extraction media and on the other soil components extracted [10]. At this regard, García-Manyes et al. [11] reported the instability of As(III) in extracts from contaminated soils, using phosphoric acid 1 mol L^{-1} and ascorbic acid 0.1 mol L^{-1}. Later, Ruiz-Chancho et al. [12] assessed the stability of As(III), As(V), MMA and DMA in 1 mol L^{-1} phosphoric acid extracts of polluted soils from France over time (just after extraction, 24, 48, 72, 96, 120, 144, 168 and 190 h) and under different storing conditions (addition of 0.1, 0.5 and 1 mol L^{-1} ascorbic acid to the extracting agent and purging of the final extracts in argon). The authors recommended using a mixture of ascorbic acid 0.5 mol L^{-1} and phosphoric acid 1 mol L^{-1} as extractant solution and purge the extracts in an inert gas. Under these conditions, the analysis of arsenic species in the extracts can be performed within 24 h after extraction, thus ensuring the stability of As(III).

The stability of arsenic species has also been studied in some food extracts. Pizarro et al. [13] demonstrated that As(III), As(V), MMA, DMA and arsenobetaine (AsB) in rice extracts remained stable during a three month period, whereas in fish and chicken tissue extracts, AsB was transformed into DMA over time. Lewis et al. [14] assessed the stability of inorganic arsenic in fish muscle samples, under different storage and sample preparation conditions, over a nine month period, finding that the relative levels of inorganic arsenic did not vary over this time interval. Regarding sample preparation, the authors observed that the relative levels of inorganic arsenic were lower in lyophilized samples than in ground samples and stored at −18 °C. The stability of the arsenosugars Gly-, PO_4-, SO_3- and SO_4-sug in oysters and shellfish has been studied over a 48 h period in simulated gastric juice and acidic environments (0.078 mol L^{-1} hydrochloric and nitric acid) [15], as well as over an eight hour period in basic environments (2.5% tetramethylammonium hydroxide, +60 °C) [16]. In the first case, the arsenosugars were found to degrade at the rate of 1.4% per hour at +38 °C and 12.2% per hour at +60 °C, whereas in the second case, Gly- and SO_3-sug were found to be relatively stable, and PO_4- and SO_4-sug formed detectable quantities of DMA and Gly-sug within 0.5 and 2 h,

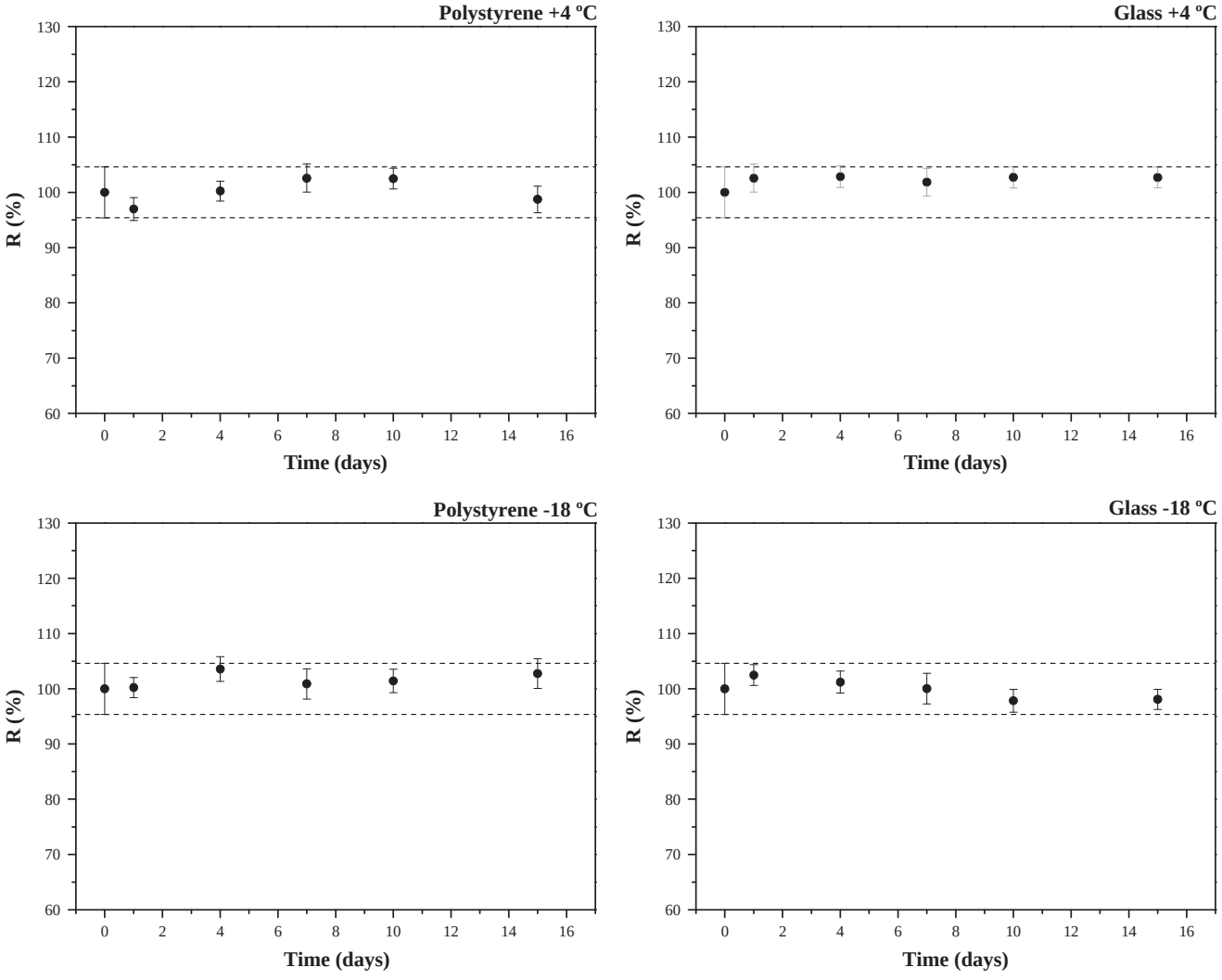

Fig. 2. Stability of As(V) species in the Hijiki water extracts, determined by HPLC-(UV)–HG–AFS, and stored at +4 and −18 °C in polystyrene and amber glass containers (*dots* stability R_x; *I* uncertainty for each point U_x; *dashes* uncertainty associated with $t=0$ days).

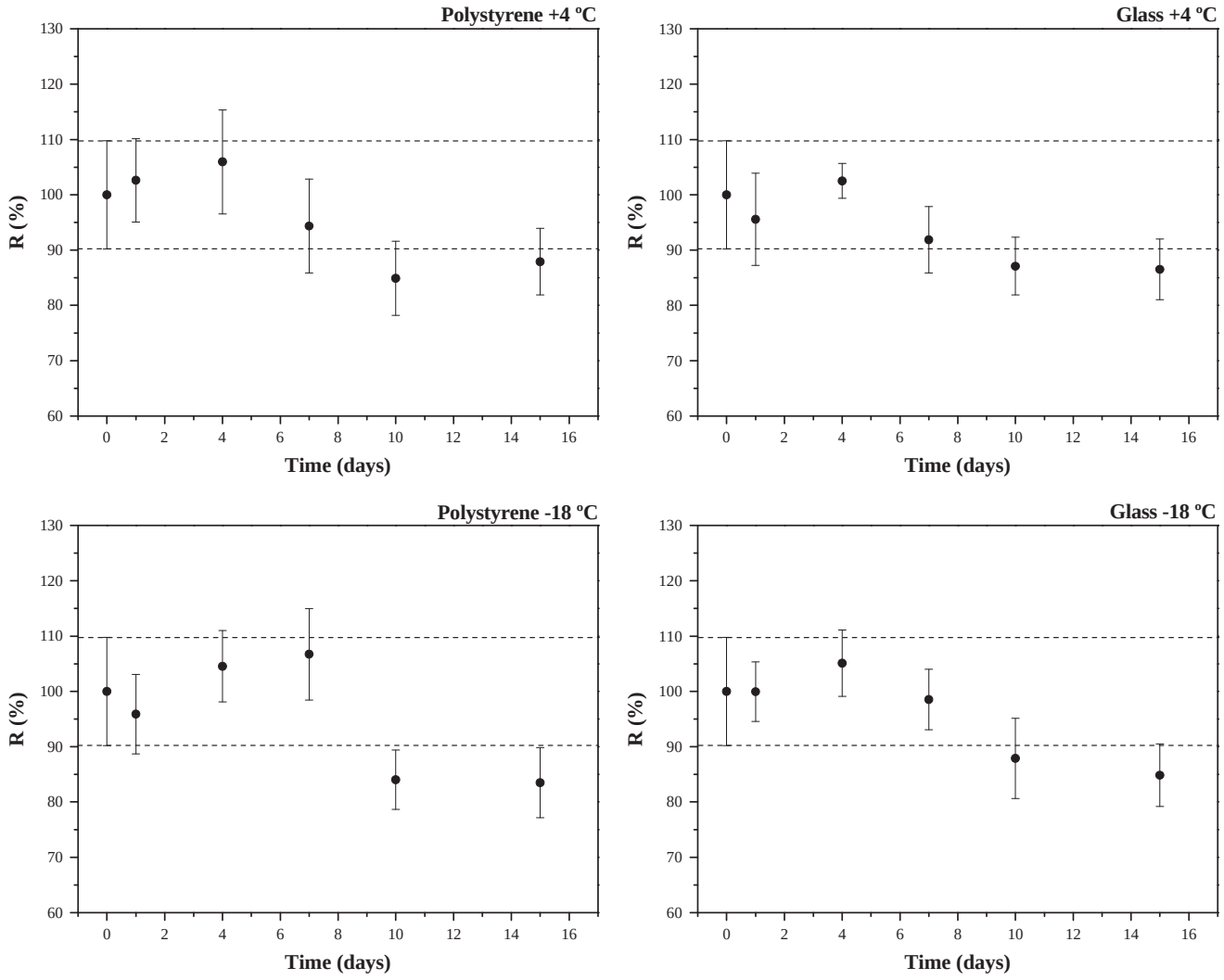

Fig. 3. Stability of DMA species in the Hijiki water extracts, determined by HPLC-(UV)–HG–AFS, and stored at +4 and −18 °C in polystyrene and amber glass containers (*dots* stability R_x; *I* uncertainty for each point U_x; *dashes* uncertainty associated with $t=0$ days).

respectively. Recently, Pell et al. [17] have studied the effects of storage and processing on arsenic compounds on the marine macroalgae *Cystoseira mediterranea* Sauvageau, which was stored under different conditions (nonfrozen; frozen at −18 °C for 24 h and 45 days; frozen at −80 °C for 24 h and 45 days) and subjected to chopping, grinding, drying at +25 or +40 °C, or lyophilization. According to these authors, freezing is an unsuitable storage method for macroalgae because losses of arsenic may occur, whereas drying is the most convenient processing method, so they recommended lyophilization.

It is well known that inorganic arsenic species are more toxic than organic arsenic compounds, so the Food and Agriculture Organization/World Health Organization (FAO/WHO) recommends that a provisional tolerable weekly intake (PTWI) of inorganic arsenic be not more than 15 μg kg^{-1} body weight [18]. Hence, the determination of arsenic species is important in foodstuffs, in order to make an implementation of the risk assessment and the safety evaluation. Marine algae are very important components of the Japanese diet, and their consumption is widespread in Occidental countries, due to their high mineral content and their recognized therapeutic properties. In particular, Hijiki has been pointed to be one of the most popular food substances among marine algae in Japan, and its daily consumption has been estimated to be in the range 1.1–14 g day^{-1} [19]. However, Hijiki has been reported to contain high amounts of inorganic arsenic (As(V)) among marine algae [20,21], which has led to the publication of different works related to arsenic speciation and the possible toxicity implications derived from its consumption [22–24]. On the other hand, lower concentration levels of DMA and arsenosugars are also present together with As(V), being of interest the arsenic species stability studies in this alga [25].

The aim of this work was the assessment of arsenic species stability in the commercially available edible alga Hijiki (*Hizikia fusiformis*), from Japan, in both the dry sample and its water extracts. For this purpose, storage time and temperature were studied, as well as the container material. Stability tests on alga water extracts allowed us to know the time interval during which arsenic species integrity can be maintained, in order to avoid the immediate analysis.

2. Material and methods

2.1. Instrumentation

A MARS 5 microwave oven (CEM, Matthews, NC, USA), with Pyrex extraction vessels, was used for the microwave-assisted extraction (MAE). A centrifuge model 5804 R Eppendorf (Hamburg, Germany) was used for phase separation after MAE.

For arsenic speciation analysis, the HPLC-(UV)–HG–AFS system used consists of a Jasco PU-2089 plus quaternary gradient pump (Jasco, Tokyo, Japan) and a Rheodyne 7725 six-port sample injection valve, fitted with a 100 μL sample loop (Rheodyne, CA, USA). Chromatographic separations were carried out in a Hamilton PRP-X100 anion exchange column (250 × 4.1 mm, 10 μm) (Phenomenex, Torrance, CA, USA), using the corresponding guard column (25 × 2.3 mm, 12–20 μm) (Phenomenex). The column outlet was coupled to a (UV)–HG–AFS system, from PS Analytical (Sevenoaks, Kent, UK).

2.2. Reagents, standard solutions and alga sample

All solutions were prepared from analytical reagent grade chemicals using deionized water obtained from a Millipore water purification system (Elix®, Molsheim, France).

As(V) (1000 mg L^{-1}) stock standard solution was purchased from Merck (Darmstadt, Germany). 1000 mg L^{-1} standard solution of DMA was prepared by dissolving the appropriate amount of $C_2H_6AsNaO_2 \cdot 3H_2O$ (DMA) from Fluka (Sigma-Aldrich, Steinheim, Germany). An aliquot freeze-dried extract of *Fucus serratus*, kindly donated by Prof. Kevin A. Francesconi (Department of Analytical Chemistry, Institute of Chemistry, Karl-Franzens University Graz, Graz, Austria), containing the four common arsenosugars (glycerol (Gly-sug), phosphate (PO_4-sug), sulfonate (SO_3-sug) and sulfate (SO_4-sug) sugars) [26], was used for the determination of arsenosugars. Further reagent solutions used for the analysis by HPLC-(UV)–HG–AFS are described elsewhere [25].

The sample selected for this study was the edible alga Hijiki (*Hizikia fusiformis*), from Japan, purchased at local markets as dried product, which was ground to a fine powder in a tungsten carbide disc mill (Retsch MM 301 mixer mill, Haan, Germany) and kept into pre-cleaned polystyrene containers at room temperature. The alga sample was previously analyzed for total arsenic by ICP-AES after microwave digestion with nitric acid and hydrogen peroxide [25].

2.3. Procedures

2.3.1. Arsenic species extraction

Arsenic species extraction from Hijiki was carried out by a microwave-assisted extraction method previously developed [27]. Portions of Hijiki (200 mg) were weighed into Pyrex vessels and 8 mL of deionized water were added. The vessels were introduced in the microwave oven and they were heated for 5 min at 90 °C. Then, the extract was centrifuged for 10 min at 14,000*g*, the supernatant was collected and the residue was put through the same extraction procedure two times more. The three supernatants were combined, diluted up to 25 mL with deionized water and centrifuged for 10 min at 14,000*g*. Prior to the chromatographic

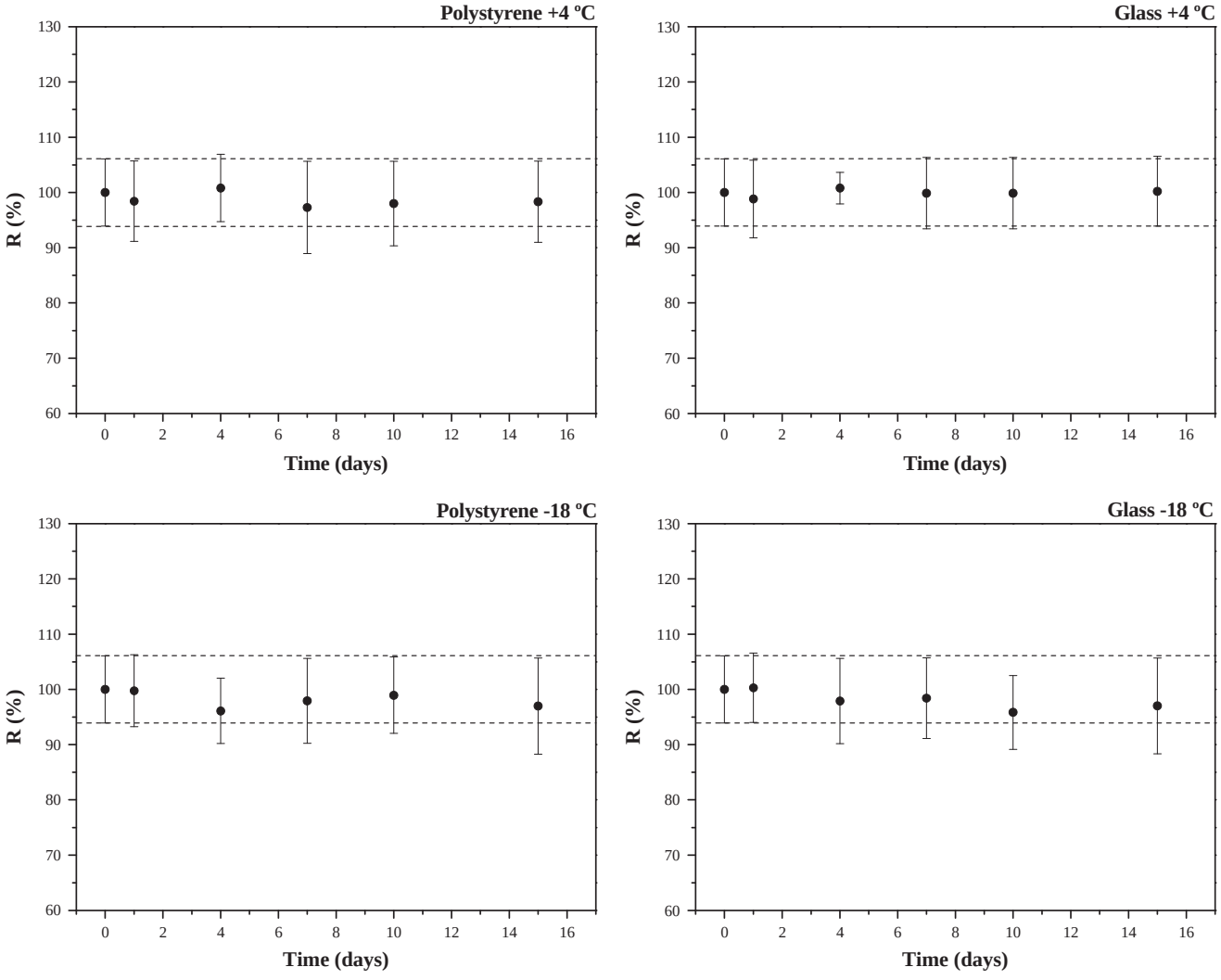

Fig. 4. Stability of Gly-sug species in the Hijiki water extracts, determined by HPLC-(UV)–HG–AFS, and stored at +4 and −18 °C in polystyrene and amber glass containers (*dots* stability R_x; *I* uncertainty for each point U_x; *dashes* uncertainty associated with $t=0$ days).

analysis, final alga extracts were filtered through 0.22 μm nylon syringe filters (Osmonics Inc., Minnetonka, MN, USA).

2.3.2. Arsenic species determination by HPLC-(UV)–HG–AFS

The arsenic species present in Hijiki water extracts (As(V), DMA and the arsenosugars Gly-, PO_4-, SO_3- and SO_4-sug) were identified and quantified by anion exchange HPLC-(UV)–HG–AFS, following the chromatographic method previously developed [25]. This method allowed us to separate eight arsenic species (Gly-sug, As(III), DMA, PO_4-sug, MMA, SO_3-sug, As(V) and SO_4-sug) in less than 17 min. Limits of detection for Gly-sug, DMA, PO_4-sug, SO_3-sug, As(V) and SO_4-sug were 0.030, 0.007, 0.048, 0.062, 0.028 and 0.076 $\mu g\, g^{-1}$ of As, respectively, whereas relative standard deviations were between 2.6 and 4.6% for these species.

The stability of As(V) and DMA (as well as of As(III) and MMA, which were not found in Hijiki) during the extraction method was confirmed by spiking studies on Hijiki alga in a previous work [27]. However, it was not possible to carry out spiking studies of arsenosugar species, due to the absence of standard solutions that led us to the addition of appreciable concentration levels of these species on alga samples. Taking into account that it was possible to detect the four arsenosugars in Hijiki, with reproducible results, and that the rest of the arsenic species studied remained stable during the sample treatment, it can be considered that these arsenic species are likely to remain stable as well, which is in agreement with other authors [28,29].

2.3.3. Design of the stability study

Containers of polystyrene (60 mL) and vials of amber glass and polystyrene (12 mL) were used as storage containers for stability tests on dry Hijiki and its water extracts, respectively. They were previously washed with deionized water, immersed in a 5% (v/v) HNO_3 bath for 24 h, and finally rinsed with deionized water before use.

2.3.3.1. Stability test on dry Hijiki. Different portions of dry Hijiki (24×200 mg) were homogenized by manual shaking for 10 min and placed in 60 mL polystyrene containers, which were kept in the dark at +20 °C. The reference concentration values (C_{ref}) of arsenic species identified in the sample (As(V), DMA and Gly-, PO_4-, SO_3- and SO_4-sug) were determined by the immediate analysis of ten independent Hijiki portions. The arsenic species stability on dry Hijiki was assessed after 1, 7, 15, 30, 90, 180 and 365 days of storage.

2.3.3.2. Stability test on Hijiki water extracts. The storage conditions evaluated were two temperatures (−18 and +4 °C) and two different containers (amber glass and polystyrene), maintaining

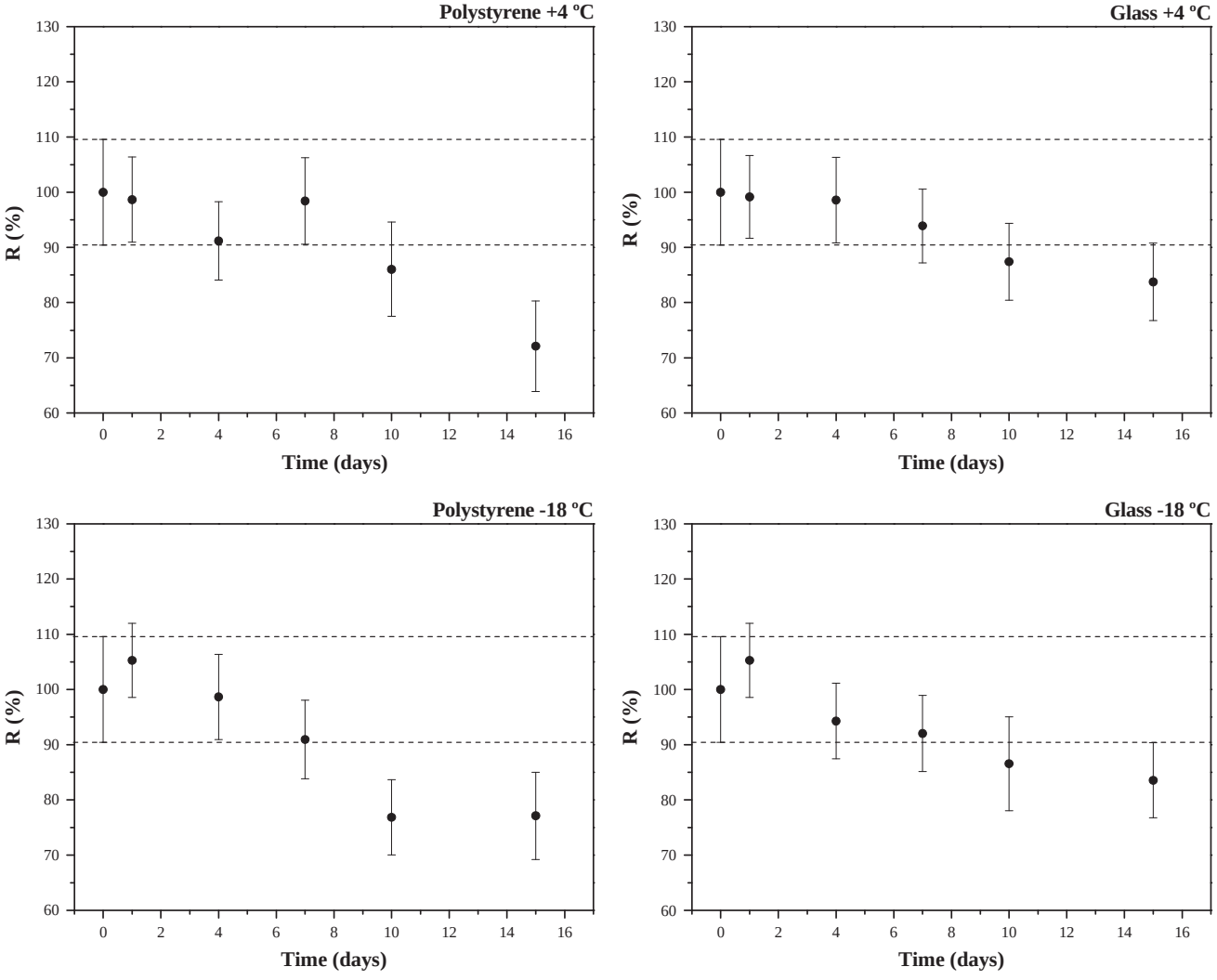

Fig. 5. Stability of PO_4-sug species in Hijiki water extracts, determined by HPLC-(UV)–HG–AFS, and stored at +4 and −18 °C in polystyrene and amber glass containers (*dots* stability R_x; *I* uncertainty for each point U_x; *dashes* uncertainty associated with $t=0$ days).

the samples in the dark. The temperature of +20 °C was excluded in order to avoid the microbiological activity, which may cause sample decomposition. The stability study was limited to 15 days because the decomposition of the water extracts was observed after that time interval.

Portions of Hijiki (24 × 200 mg) were put through the extraction method described in Section 2.3.1. The water extracts obtained were mixed and distributed in 30 polystyrene and 30 amber glass vials. Half of the vials of each material were kept in the dark at +4 °C, and the other half at −18 °C. The reference concentration values (C_{ref}) of arsenic species identified in the sample (As(V), DMA and Gly-, PO_4-, SO_3- and SO_4-sug) were determined by the immediate analysis of the Hijiki water extracts, carrying out ten independent measurements. The arsenic species stability on the Hijiki water extracts was assessed after 1, 4, 7, 10 and 15 days of storage, analyzing three vials of each type and using every vial only once.

3. Results and discussion

Studies of total arsenic stability in dry Hijiki and its water extracts were performed by ICP-AES in a previous work [30]. The results obtained showed that total arsenic in dry Hijiki was stable when the sample was stored in polystyrene containers at +20 °C, for at least one year. Regarding the Hijiki water extracts, total arsenic was stable for at least 15 days, in extracts stored at both −18 and +4 °C, in both kind of containers. However, this fact does not ensure the absence of transformations between the arsenic compounds, so it is necessary to assess the stability of the species present.

Arsenic species stability studies were carried out in both dry Hijiki and its water extracts, in order to know how long the extracts could be stored to avoid the immediate analysis. As previously described [30], the stability R_x, expressed as a percentage, was evaluated as the ratio of the average of three concentration measurements made under each storage condition (C_x) to the mean value (C_{ref}) of ten different measurements made at reference time (t=0 days), as follows [9,31]:

$$R_x = \frac{C_x}{C_{ref}} \times 100$$

The uncertainty U_x of the ratio R_x was obtained from the coefficient of variation of each set of measurements, according to the following expression:

$$U_x = \sqrt{(CV_x^2 + CV_{ref}^2)} \times R_x$$

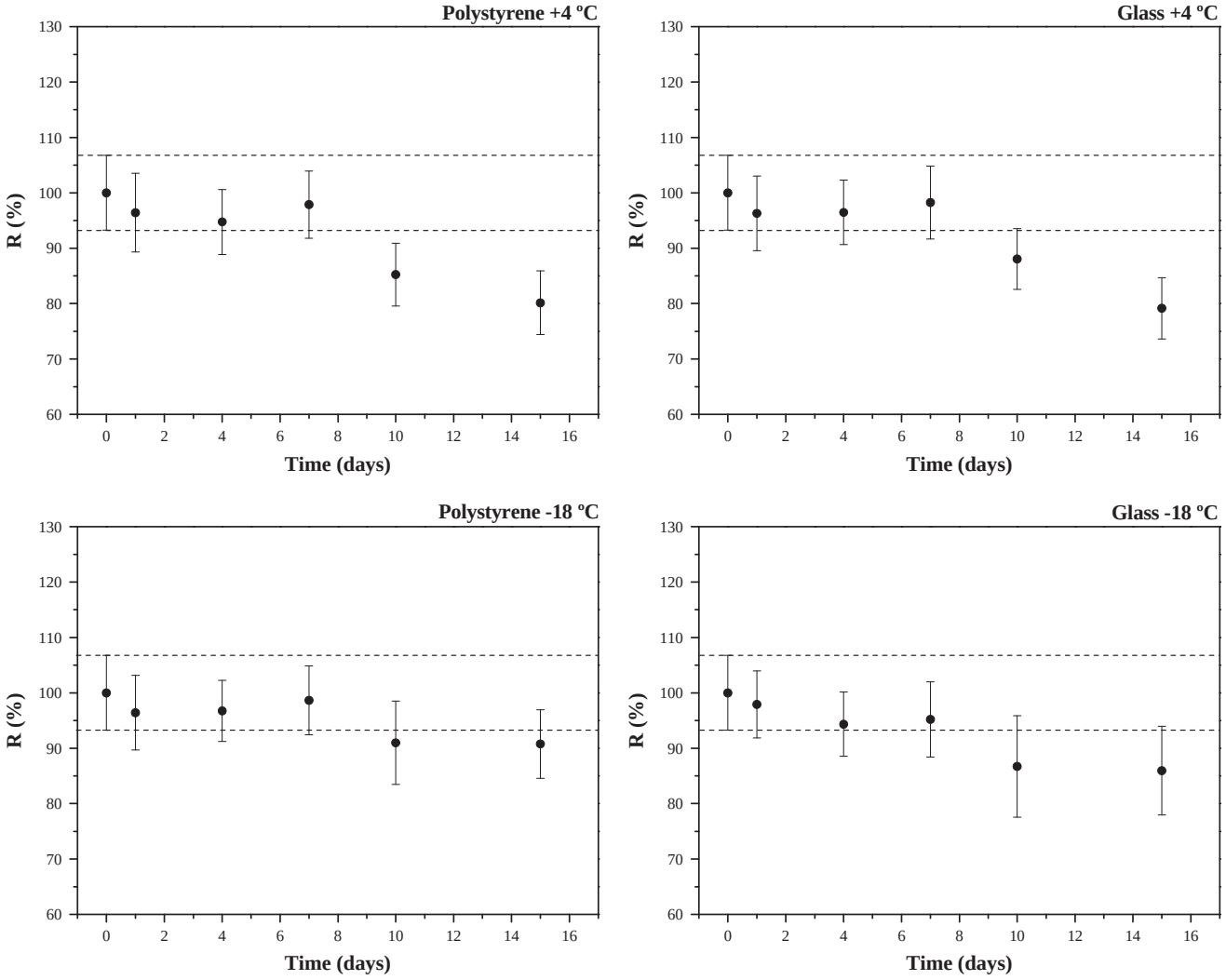

Fig. 6. Stability of SO_3-sug species in Hijiki water extracts, determined by HPLC-(UV)–HG–AFS, and stored at +4 and −18 °C in polystyrene and amber glass containers (*dots* stability R_x; *I* uncertainty for each point U_x; *dashes* uncertainty associated with t=0 days).

where CV_x is the coefficient of variation of three independent measurements under each storage condition, and CV_{ref} is the coefficient of variation obtained for the reference conditions.

In the case of ideal stability, R_x should be 100%, but in practice there are random variations due to the uncertainty in the measurements because of the standard deviation observed. Therefore, the value R_x should be between the limits $(100-U_x)$ and $(100+U_x)$ to conclude the species stability [9,30].

3.1. Arsenic species stability in dry Hijiki

Arsenic species stability studies on dry Hijiki were carried out for the species found in the sample, which were As(V), DMA and the arsenosugars Gly-, PO_4-, SO_3- and SO_4-sug, by anion exchange HPLC-(UV)–HG–AFS. The reference concentration values, C_{ref} ($t=0$ days, $n=10$) used in the stability test of the arsenic species present in dry Hijiki were $(50.9\pm0.8)\,\mu g\,g^{-1}$ As(V), $(0.50\pm0.05)\,\mu g\,g^{-1}$ DMA, $(1.17\pm0.04)\,\mu g\,g^{-1}$ Gly-sug, $(0.5\pm0.1)\,\mu g\,g^{-1}$ PO_4-sug, $(0.6\pm0.1)\,\mu g\,g^{-1}$ SO_3-sug and $(2.4\pm0.2)\,\mu g\,g^{-1}$ SO_4-sug. The results obtained for dry Hijiki after 1, 7, 15, 30, 90, 180 and 365 days of storage are shown in Fig. 1. The results obtained confirmed the stability for at least one year of the six arsenic species present in Hijiki alga, when the dry sample was stored in polystyrene containers at +20 °C. Therefore, these conditions were selected for the storage of dry Hijiki.

3.2. Arsenic species stability in Hijiki water extracts

Stability studies of arsenic species in Hijiki water extracts were performed following the experimental procedure described in Section 2.3.3.2

The reference concentration values, C_{ref} ($t=0$ days, $n=10$), of the arsenic species As(V), DMA, Gly-sug, PO_4-sug, SO_3-sug and SO_4-sug found in the Hijiki water extracts were (50.9 ± 0.8), (0.50 ± 0.05), (1.17 ± 0.04), (0.5 ± 0.1), (0.6 ± 0.1) and (2.4 ± 0.2) $\mu g\,g^{-1}$ of As, respectively. The results obtained for the stability of these arsenic species, after 1, 4, 7, 10 and 15 days, stored in amber glass and polystyrene containers at −18 and +4 °C, are shown in Figures from 2 to 7, for As(V), DMA, Gly-sug, PO_4-sug, SO_3-sug and SO_4-sug, respectively.

The results obtained for the Hijiki water extracts showed that the species As(V) (Fig. 2), Gly-sug (Fig. 4) and SO_4-sug (Fig. 7) remained stable for at least 15 days, regardless of the temperature or type of container. However, the stability of the rest of the arsenic species, DMA (Fig. 3), PO_4-sug (Fig. 5) and SO_3-sug (Fig. 6), with concentrations between 0.5 and 0.6 $\mu g\,g^{-1}$, can only be assured during the first week of storage, since significant losses of these species were observed from the tenth day, under all the storage conditions tested.

The instability observed for DMA, PO_4-sug and SO_3-sug species cannot be associated to precipitation or adsorption processes of

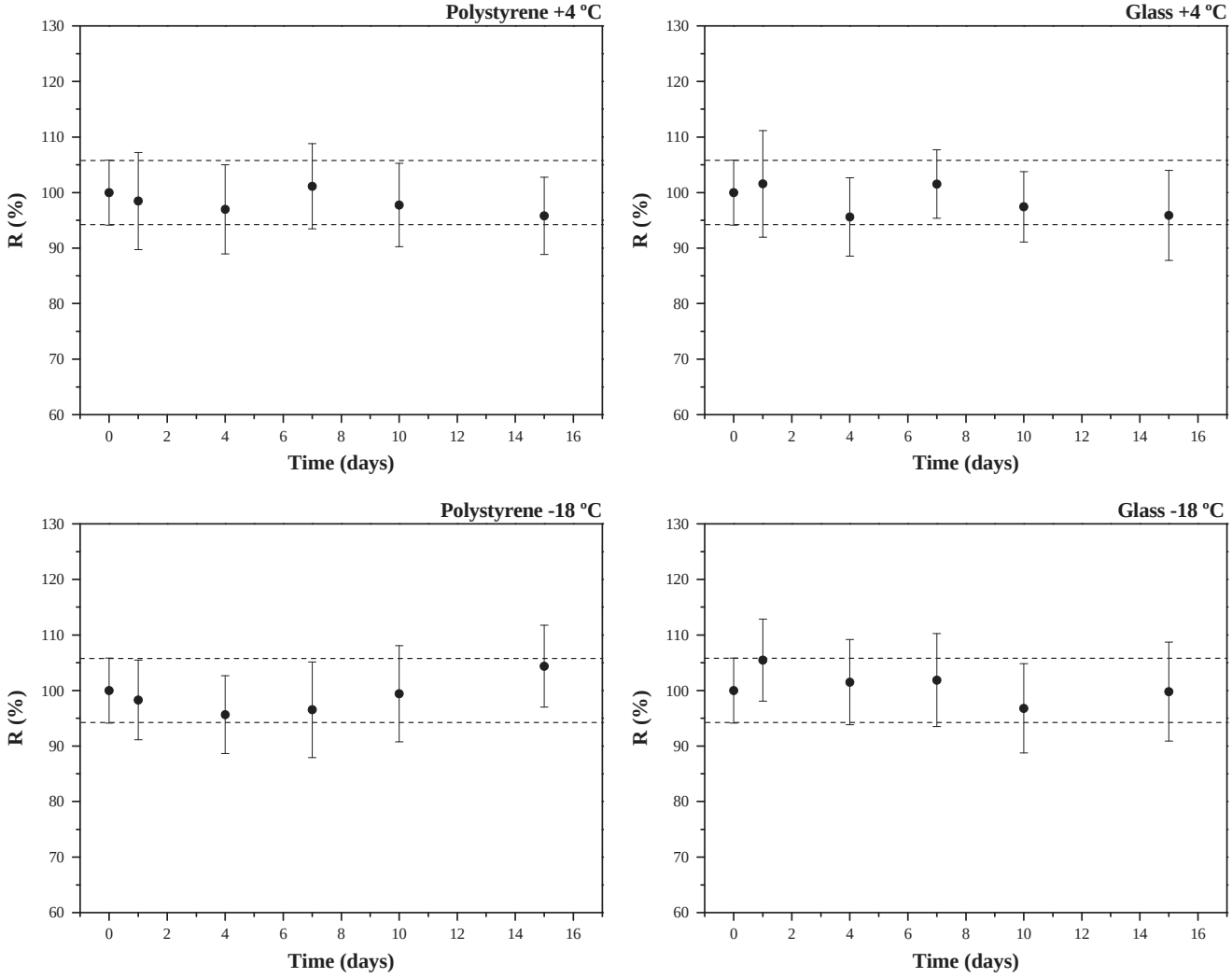

Fig. 7. Stability of SO_4-sug species in the Hijiki water extracts, determined by HPLC-(UV)–HG–AFS, and stored at +4 and −18 °C in polystyrene and amber glass containers (*dots* stability R_x; *I* uncertainty for each point U_x; *dashes* uncertainty associated with $t=0$ days).

these species, because the total arsenic concentration observed in Hijiki water extracts under the storage conditions remained constant. However, the decrease in the concentration of these species, observed from the tenth day, represents only a maximum of 0.44% of the total arsenic in the extract ($72 \pm 4\ \mu g\ g^{-1}$) [30], so it is within the uncertainty of the total determination. On the other hand, species transformations cannot be confirmed since the chromatographic analysis by HPLC-(UV)–HG–AFS did not show the presence of new arsenic species. Furthermore, it should be noted that it was not possible to detect approximately 20% of the arsenic present in the Hijiki water extracts. The reason for this may be that a fraction of these species is transformed or captured as a complex form, which can be retained in any step of the chromatographic method. Furthermore, the instability of DMA, PO_4-sug and SO_3-sug is coincident with the lowest arsenic concentration levels (lower than $1\ \mu g\ g^{-1}$), so this factor may be an important one to consider for further studies, regardless of the physicochemical properties of the compounds [8].

4. Conclusions

The results obtained for the arsenic species stability tests on dry Hijiki showed that transport and storage of this kind of samples can be carried out at room temperature, using polystyrene containers. Therefore, the lyophilization of the sample is not necessary in order to enhance its stability.

Regarding Hijiki water extracts, the arsenic species studied remained stable for seven days under all the storage conditions tested, i.e. amber glass and polystyrene containers and storage temperatures of $+4$ and $-18\ ^{\circ}C$. Therefore, in order to avoid the immediate analysis of the extracts, a maximum storage time of one week is recommended to ensure arsenic species stability in them. Finally, the low arsenic species concentration levels may be responsible for species instability in Hijiki water extracts.

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