Applied Organometallic Chemistry (1990) 4 287–291
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0268-2605/90/030287-05$05.00

Determination of arsenic and other elemental abundances in marine macro-algae by photon activation analysis

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Received November 1989 *Accepted 24 February 1990*

A non-destructive photon activation analysis technique with 30-MeV bremsstrahlung followed by high-resolution γ-spectrometry is applied to multielement analysis of two brown algae, *Laminaria religiosa* and *Sargassum horneri*, and one red alga, *Heterosiphoia japonica*. This method is quite simple and gives good, reproducible results. Elemental abundances of nine elements including arsenic were determined. Arsenic content in the above algae are 50.8, 92.1, and 8.3 mg kg^{-1} (dry weight base), respectively. Arsenic contents in algae indifferent seasons and different locations do not show a large scatter. The concentration ranges of arsenic together with other essential main components (e.g. sodium, magnesium, phosphorus and chlorine) in a number of samples are summarized. The mean concentrations for these five elements are compared with the elemental abundance of these elements in seawater, and the high enrichment of arsenic and phosphorus is clearly observed.

Keywords: Arsenic, marine macro-algae, photon activation analysis, multielement analysis, elemental abundances

INTRODUCTION

Of the elements commonly found in animal and plant materials, a number of minor and trace elements are essential for life processes. Some of the other elements such as arsenic are known generally to be toxic, and special attention has been given to their levels from the environmental viewpoint. Arsenic is an environmentally ubiquitous Group Va element. During the past 20 years organic arsenical herbicides have come into extensive use. In the natural environment, most arsenicals degrade to form arsenate. Biotransformations may occur which result in various organo- and other arsenicals. In studies of the roles of these elements, multielement analysis has become increasingly attractive, for it can give an overall view of elemental patterns which may be important in living matter.

The impressive potential of activation analysis for this purpose has prompted a large volume of work on its application to the determination of many elements in a variety of biological materials. Thermal neutron activation followed by high-resolution γ-spectrometry has been successfully applied to the nondestructive determination of many elements in actual samples. With instrumental neutron activation analysis, however, the high activities produced from abundant, readily activated elements, such as manganese and sodium, often distort or mask lower activities from the elements of interest. For example, neutron activation analysis is also a highly sensitive method for arsenic via ^{75}As(n, γ) ^{76}As, but when this method is applied to marine biological materials such as macro-algae, it is impossible to expect reliable results for low levels or arsenic, due to severe induced radioactivity from alkaline and halogen elements present. An alternative nuclear method which can meet various requirements for multielement work is photon activation analysis, and several reviews of the method are available.[1–3] In a series of research work, multielement photon activation analysis has been applied to biological[4,5] and environmental materials.[6–12]

The present paper describes the application of bremmstrahlung activation analysis to the nondestructive determination of several elements including arsenic in biological materials. Marine macro-algae are chosen as samples. Systematic and cumulative data on the elemental abundances of marine macro-algae are not available. In the present paper the emphasis is placed on elemental abundances including arsenic in different algae,

Table 1 Elemental composition of a synthetic multielement reference material used as comparative standard in photon activation analysis

Element	Content (%)[a]	Element	Content (ppm)[b]
C	41.8	V	2.87
H	4.1	Cr	0.711
N	2.1	Mn	3.31
O	32.4	Fe	41.1
		Co	0.251
Na	3.49	Ni	1.09
Mg	1.14	Cu	1.34
P	0.036	Zn	26.2
S	0.13	As	155
Cl	6.17	Br	2060
K	6.79	Rb	372
Ca	1.51	Sr	538
		I	156

[a] g (100 g)$^{-1}$. [b] mg kg^{-1}.

and the bias of the arsenic abundance in different seasons and sampling stations is discussed. The general range of arsenic abundance is also given.

EXPERIMENTAL

Samples and standard

Marine macro-algae samples, *Laminaria religiosa* (Hosomekonbu is the Japanese name), *Sargassum horneri* (Akamoku) and *Heterosiphoia japonica* (Isohagi) were taken at Onagawa Bay, Miyagi Prefecture, Japan. To compare the bias of the elemental abundance within a species, *Laminaria religiosa* samples were taken at different sampling stations on the Pacific coast side of the north east of Japan, Hachinohe-Kanahama in Aomori Prefecture, Sanriku-Kokabehama in Iwate Prefecture, and Oshika-Niiyamahama in Miyagi Prefecture. Immediately after sampling, these algae samples were washed with filtered seawater and frozen with dry ice. After complete freeze–drying *in vacuo* for 48 h the samples were powdered in a high-purity alumina ball mill. All samples were dried for 2 h at 85°C before irradiation. A portion (1 g) of the dried sample was compressed to a cylindrical pellet with a diameter of 10 mm.

The comparative standard is a synthetic one and this has a similar biological matrix composition with algae samples and contains known amounts of the elements of interest.[13] The elemental composition of the comparative standard, which is shown in Table 1, can be adjusted arbitrarily; for example, the main components—hydrogen, carbon, nitrogen, and oxygen—can be regulated by changing the mixing ratio of the raw materials of the two monomers, acrylic acid and acrylamide. In the preparation of the present standard, the main components were regulated to be of the same order of magnitude as those of an alga, *Laminaria religiosa* (C, 34%; H, 4.6%; N, 1.9%). The elemental compositions of other minor and trace elements were adjusted by adding a known amounts of these elements in the polymerization reaction starting from the monomers.[13]

Irradiation and radioactivity measurement

Bremsstrahlung irradiation was carried out in the linear electron accelerator of Tohoku University. The accelerator was operated at 30 MeV, and the electron beam produced bremsstrahlung in a platinum convertor with a thickness of 3 mm located 3 cm from the beam exit window. The sample and the comparative-standard pellets were wrapped with high-purity aluminium foil and were stacked in a silica tube, the standards being placed in front of and behind the sample for simultaneous irradiation. The tube was placed in a water-cooled sample holder and aligned along the beam axis with the front face of the tube 10–15 cm from the photon-producing convertor. A typical irradiation was performed for 2 h at a dose rate of 10^6 R min^{-1}. The heat generated by the remaining electrons in the bremsstrahlung tended to cause chemical decomposition of biological samples, which therefore could not be positioned close to the convertor. Under typical irradiation conditions with a 70-μA beam (on average) of 30 MeV electrons, however, no significant damage was observed over 2 h at a position 10 cm downstream from the convertor.

A 33-cm^3 lithium-drifted germanium detector (Ortec Model 8101-0525) was coupled to a 4096-channel pulse-height analyser (Toshiba Electric Co. Ltd, Japan). The counting system has a resolution of 2.4 keV for the 1332-keV γ-line of ^{60}Co. Counting was done consecutively for increasing intervals from 2 h to nearly one month. For nuclides with intermediate half-lives, the counting times were 30–60 min and, for long-lived nuclides, the counting times were 5–20 h. In obtaining full-energy peak areas, the total peak counts were computed and the background contribution was subtracted. Decay curve analyses were made to check for interferences.

RESULTS AND DISCUSSION

The principal products and their nuclear data from nine elements are given in Table 2. ^{74}As has two γ-rays of 596 keV and 635 keV, but the 596-keV peak was used for determination due to its higher sensitivity down to 1 μg (the detection limit)[4] without any interference. The 1369-keV peak of ^{24}Na was used for the magnesium determimination, but this is interfered with by the ^{23}Na(n, γ) ^{24}Na reaction by a secondary neutron; hence this interference is corrected by irradiating a known amount of sodium carbonate. The 881-keV and 389-keV peaks of ^{127}I interfere with the determination of rubidium (883 keV) and strontium (388 keV), respectively, but the contribution of ^{127}I to these two γ-ray regions was corrected by previous knowledge of the three peak ratios at 389 keV, 666 keV and 881 keV for pure ^{127}I. A possibility of loss of arsenic and iodine by vaporization and/or decomposition in the bremmsstrahlung irradiation was examined by radioactivity measurements on the wrapped aluminium foil of the pellets after irradiation. Only the radioactivity of ^{127}I was observed but it was as little as under 0.4% of total iodine in the sample or the standard. No loss of arsenic was observed.

Three different algae were analysed. Analyses were made at least in triplicate for each alga sample. Results are summarized in Table 3. Arsenic in *Laminalia religiosa* and *Sargassum horneri* is determined with a good reproducibility (relative standard deviation of under 3%), but the relative standard deviation of *Heterosiphoia japonica* seems to be higher; this may be due to a lower arsenic content in this sample. It is very interesting that brown algae of *Laminaria religiosa* and *Sargassum horneri* contain higher amounts of arsenic of 50.8 ppm (mg kg^{-1}) and 92.1 ppm respectively, and this must be compared with the lower content of the red alga *Heterosiphoia japonica* of 8.3 ppm. Arsenic content of these marine macro-algae, however, seems to be higher compared with that found in terrestrial plants; for example, orchard leaves contain 11 ppm and tobacco leaves 1.4 ppm of arsenic.[4]

Table 2 Radioisotopes and nuclear data used for determination

Element	Nuclear reaction	Half-life	Energy (keV)
Na	^{23}Na(γ, n)^{22}Na	2.60 y	1275
Mg	^{25}Mg(γ, p)^{24}Na	15.0 h	1369
Cl	^{35}Cl(γ, n)^{34m}Cl	32.0 m	146
Ca	^{44}Ca(γ, p)^{43}K	22.2 h	618
As	^{75}As(γ, n)^{74}As	17.8 d	596
Br	^{79}Br(γ, 2n)^{77}Br	57.0 h	239
Rb	^{85}Rb(γ, n)^{84}Rb	32.8 d	883
Sr	^{88}Sr(γ, n)^{87m}Sr	2.81 h	388
I	^{127}I(γ, n)^{126}I	13.0 d	389

Table 3 Multielement photon activation analysis of marine macro-algae[a]

Element[b]	*Laminaria religiosa*	*Sargassum horneri*	*Heterosiphoia japonica*
Na (%)	4.49 ± 0.05	3.42 ± 0.10	6.36 ± 0.13
Mg (%)	1.03 ± 0.03	2.46 ± 0.06	1.19 ± 0.01
Cl (%)	13.4 ± 0.1	10.4 ± 0.2	13.2 ± 0.2
Ca (%)	0.955 ± 0.040	1.17 ± 0.02	1.38 ± 0.05
As (ppm)	50.8 ± 0.7	92.1 ± 2.4	8.3 ± 3.3
Br (ppm)	437 ± 10	354 ± 10	10700 ± 200
Rb (ppm)	46.8 ± 1.4	20.1 ± 2.8	< 2
Sr (ppm)	655 ± 15	1460 ± 90	14.4 ± 3.4
I (ppm)	1180 ± 10	573 ± 22	512 ± 24

[a] Sampling date and station: 4 May 1984; Onagawa bay, Japan. [b] Dry weight base; % = g (100 g)$^{-1}$, ppm = mg kg^{-1}.

Elemental composition is of course different between biological species; furthermore, even for single biological species, the elemental composition may fluctuate in different sampling seasons and indifferent sampling areas. Arsenic contents of *Laminaria religiosa* taken in different seasons over six years at the same sampling station in Onagawa Bay are summarized in Fig. 1, where each small circle corresponds to an individual sample. Arsenic contents of multiple samples taken at the same day are scattered but not by so large an amount except in one season (November) which is the last part of the one year life cycle of *Laminaria religiosa*. Figure 2 shows the arsenic content of *Laminaria religiosa* taken at different sampling stations on the Pacific coast. As a reference the range and the standard deviation of the arsenic content of 23 samples of *Laminaria religiosa* taken at the same sampling station (Onagawa Bay) are also shown. The scattering range of the arsenic content of the same alga taken at different sampling stations is close to the range of the arsenic content of the same alga taken at Onagawa Bay, and this shows that the arsenic content of *Laminaria religiosa* seems to be in a limited range (Fig. 2).

Many data were accumluated year by year, and the arsenic content of *Laminaria religiosa* taken in the growing season of this marine algae (May

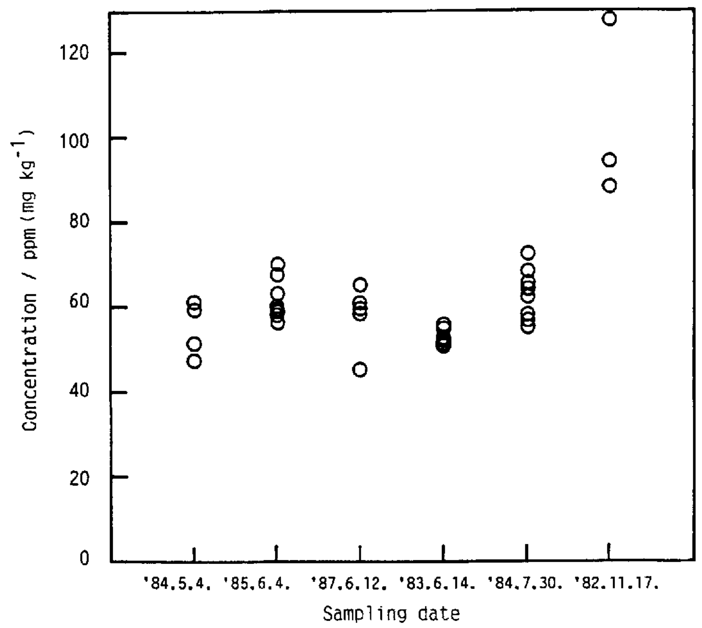

Figure 1 Arsenic concentration in *Laminaria religiosa* taken at different seasons.

to July) is summarized in Table 4, together with some other elemental contents of essential main components such as sodium, magnesium, phosphorus and chlorine; phosphorus was determined independently by α-particle activation analysis via ^{31}P(α, n) ^{34m}Cl.[14] In Fig. 3 the average elemental concentrations for these five elements in *Laminaria religiosa* are plotted against the elemental abundance of the corresponding elements in seawater.[15] In this case the elemental concentration in *Laminaria religiosa* is shown on a fresh weight basis. The elemental concentrations of sodium, magnesium and chlorine of *Laminaria religiosa* are of the same magnitude as those in

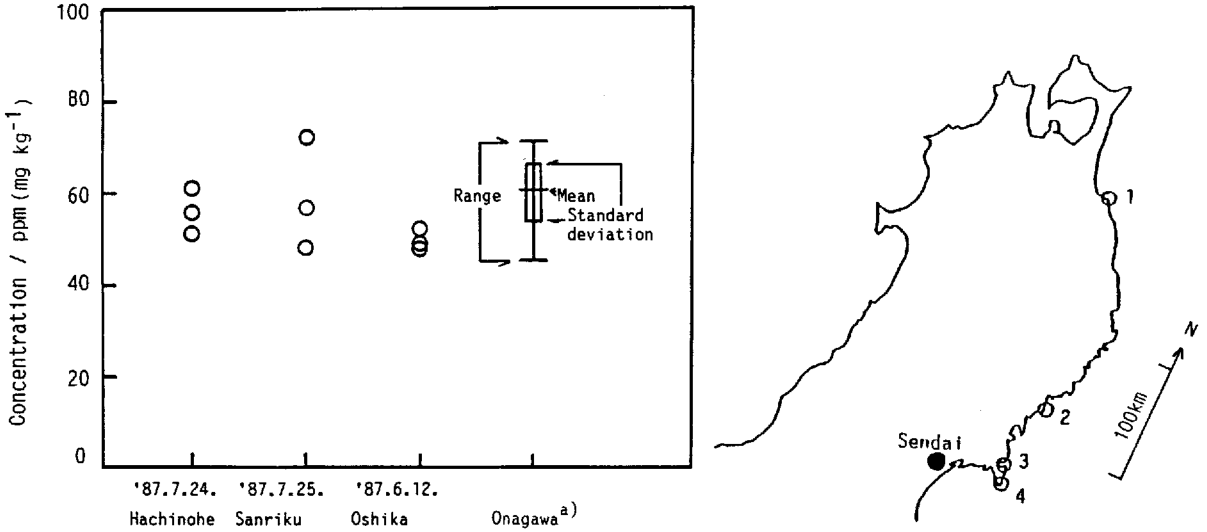

Figure 2 (a) Arsenic concentration in *Laminaria religiosa* taken at different locations (see the text). (b) Sketch map showing the sampling stations in the north-eastern provinces of Japan. 1, Hachinohe; 2, Sanriku; 3, Onagawa; 4, Oshika.

Table 4 Elemental abundances in *Laminaria religiosa*[a]

Element[b]	Average	Range	(*n*)[c]
Na (%)	4.13	2.86–5.41	(43)
Mg (%)	1.07	0.879–1.28	(43)
P (%)[d]	0.129	0.0702–0.185	(16)
Cl (%)	12.6	6.79–20.4	(43)
As (ppm)	60.9	45.2–72.7	(43)

[a] Dry weight base. [b] % = g (100 g)$^{-1}$; ppm = mg kg^{-1}. [c] Number of individual samples. [d] α-Activation analysis.[14]

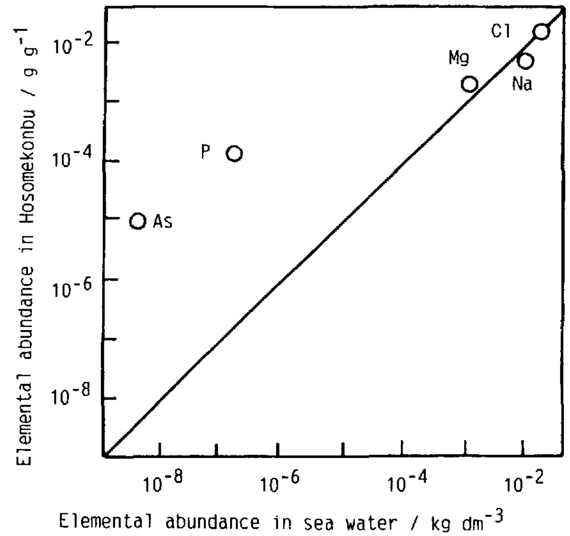

Figure 3 Comparison of elemental abundances in *Laminaria religiosa* and seawater.

seawater, but arsenic and phosphorus are highly enriched in *Laminaria religiosa*, even though the elemental abundances of these trace elements in seawater at the sampling locations are uncertain. The accumulation mechanism and the role of arsenic in marine macro-algae are of considerable research interests, particularly with regard to the nature of the arsenic present, which may be in the organic form in part.

Acknowledgements The authors express their appreciation to the Linac group at the Institute of Nuclear Science, Tohoku University, and also to the faculty members at the sampling stations for their cooperation with the irradiation and the sampling of algae.

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