ISSN : 0974-7419 Volume 10 Issue 5

Analytical CHEMISTRY
An Indian Journal

Trade Science Inc.

Full Paper

ACAIJ, 10(5) 2011 [294-299]

Atomic absorption spectroscopic determination and comparison of trace elements in the seaweeds collected at Mandapam, Tamil Nadu, India

A.Bhanu Prasad[1]*, D.Raman[2], Pasham Venkateshwalu[2], M.Vijay Kumar[2], B.Gouthami[2], B.Sarala[2], R.Nageswra Rao[2], U.S.N.Murthy[2], Y.V.Swamy[2]

[1]Department of Chemistry, Osmania University, Hyderabad-500607, (INDIA)

[2]Analytical Chemistry Division, Indian Institute of Chemical Technology, Tarnaka, Hyderabad-500607, (INDIA)

E-mail : bhanuprasad99@gmail.com

Received: 9th September, 2010 ; Accepted: 19th September, 2010

ABSTRACT

Many marine algae are being used by human beings, in many edible, medicinal and commercial products. *Sargassum Wightii, Dictyota dichotoma, Hypnea musciformis, Jania Rubens, Halimeda, Kappaphycus Alvarezii, Turbinaria conoides, Cylindracea* and *Padina Gymnospora* were collected from Palk bay, mandapam, Tamilnadu, India. Toxic (Pb, Cd, Pt, Pd and Cr) and essential (Zn, Mn, Ni, Co, Cu and Fe) metals in eight algae were determined by Flame atomic absorption spectrometry (FAAS). Our results showed that Fe, Zn, Pb, Mn and Cd were found insignificantly more than the other assessed elements in the studied algae. Of all the studied seaweed species the concentration of Cd, Ni, Cu and Cr were above the ADI limits except in Kappaphycus alvarezii (Cu and Cr<ADI). Palladium concentration in Dictyota dichotoma was below the detection limit, whereas in all other algal species it was observed above the ADI limit. Lead content in *Dictyota dichotoma* (28.5ppm), *Hypnea musciformis* (22.5 ppm), *Jania Rubens* (54.8 ppm) and *Halimeda Cylindracea* (78.8 ppm) was observed to be above the ADI limits. The trace elements Zn, Fe, Co and Mn were also found in some edible and non edible algae beyond the ADI limits.

KEYWORDS

Heavy metals;
Seaweeds;
India;
ADI;
FAAS.

INTRODUCTION

Seaweeds are one of the commercially important marine living and renewable resources in India. Algae are enriched with many trace elements, protein, vitamins, several bioactive substances and secondary metabolites[1-3] which are having economic importance as well as feed for different types of animals[4]. Seaweeds have been used since ancient times as food[5], fuel[6,7] fertilizer[8], and as source of medicine[9-11]. Now a days seaweeds are the raw material for many industrial products like agar[12-14], algin[15] and carrageenan[16]. Many countries in the world consume algae as food[17]. Certain edible seaweeds are with low caloric value[18] but rich in proteins, lipids, minerals, vitamins and daily fibres[19]. They are nutritionally valuable as fresh or dried vegetables, or as ingredients in a wide variety of prepared foods. Depending on the type of species, seaweeds are generally suitable for making cool, gelatinous concoctions. The composition of the trace elements in the seaweeds is effected by species, geographic area, and season of the year and temperature of water.

In recent years, with enhanced awareness of the importance of trace elements in health and disease, an increasing number of reports on the role of trace elements in seaweeds have been reported. K. Manivannan[20]. reported that different group of seaweeds such as Chlorophyceae (*Ulva lactuca, Enteromorpha intestinalis*) Phaeophyceae (*Turbinaria ornata, Padina gymnospora*) and Rhodophyceae (*Hypnae valentiae, Gracilaria folifera*) were collected from Mandapam coastal regions, Southeast coast of India for analyzing mineral composition. In their study, *P. gymnospora* showed the maximum content of mineral composition such as Cu, Cr, Fe, Pb, S and Ca content and K than other seaweeds. *H. valentiae* showed the minimum level of mineral content such as Cd, Fe, Mg and Ca. The range of Cr content was reported between 0.308-1.378 ppm. The highest level of Cr was observed in brown seaweed *P. gymnospora* and the minimum content was observed in green seaweed *E. intestinalis*. The highest Cu concentration was observed in the brown seaweed *P. gymnospora* and the lowest level was observed in red alga *G.folifera*. Karthikai Devi[21] reported the elemental concentration in various seaweeds such as *Codium tomentosum, Enteromorpha clathrata, Enteromorpha compressa, Turbinaria conoides, Colpomenia sinuosa, Sargassum tenerimum, Sargassum wightii and Acanthophora spicifera*, collected from Gulf of Mannar marine biosphere reserve; Southeast coast of India. They reported that *S. wightii* showed the highest level of elemental composition such as Cr, Cu, Mn, Ni, Pb and Zn content than other seaweeds and *A. spicifera* recorded the lowest level of element content such as Cr, Cu, Pb and Zn. R. Riosmena-Rodríguez[22] determined the concentration range, and the spatial and temporal variation of heavy metal concentrations in the seaweeds and seagrasses of Magdalena Bay. They found that significant temporal and spatial variation of heavy metal concentration in seaweeds and sea grasses species and also found Fe, Cu and Mg were the most abundant metals.

Atomic spectroscopic techniques viz., AAS, ICP-AES and ICP-MS are widely used for analysis of trace metals. AAS is the most extensively used technique for determination of metals in deferent sample matrices. Generally flame-AAS (FAAS) and graphite furnace AAS (GFAAS) are used depending upon the concentration of the analytes to be determined. The present paper describes the estimation of trace levels of Zn, Cu, Fe, Mn, Pb, Ni, Cr, Co, Cd, Pt and Pd in eight marine algae, which could potentially be either dangerous or useful for humans who are consuming for dietary and medicinal purpose and also to herbivores when fed on marine algae.

EXPERIMENTAL

Apparatus

Atomic absorption spectrophotometer (Perkin Elmer Analyst 300, USA), Hollow cathode lamp was used for detection of Pb, Cd, Cu, Ni, Fe, Co, Cr, Mn, Zn Pt and Pd. The instrument was calibrated with standard solutions using the concentration mode and instrument conditions were given in the TABLE 1. The standard reference materials of all the metals (E. Merck, Germany) were used to provide calibration and quality assurance for each analytical batch. Replicate ($n = 3$) analyses were conducted to assess precision of the analytical techniques.

Reagents

All reagents were of analytical grade. Sub-boiled water and conc. HNO_3 (69%) (Merk, India) were used for the preparation of samples. Standard stock solutions of Pb, Cd, Cu, Ni, Fe, Co, Cr, Mn, Zn Pt and Pd containing 1000 ppm of each metal, were prepared. Calibration standards of each element were obtained by appropriate dilution of the stock solutions.

Sample collection and preparation

The algae samples were collected from Palk Bay Mandapam, Tamilnadu, and South India region. To estimate the metals in the different sea weed samples, 1.0 g of powdered weed was taken in 100 ml beaker, 5 ml conc. HNO_3 was added and kept overnight (16 h). The solution was digested on a hotplate at 80°C for 10

TABLE 1 : Operating condition of flame atomic absorption spectrometry

Conditions	pd	Fe	Pt	Zn	Cu	Mn	Ni	Co	Cr	Pb	Cd
Slit width (mm)	0.2	0.2	0.7	0.7	0.7	0.2	0.2	0.2	0.7	0.7	0.7
Cathode lamp current (mA)	30	30	30	15	15	20	25	30	25	10	4
Relative Noise	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Resonance line (nm)	244.8	248.8	269.9	213.9	324.7	279 .5	232	240.7	357.9	217.0	228.9
Air flow liter. Min^{-1}	10	10	10	12	10	10	10	10	10	10	10
Acetylene flow Liter. min^{-1}	3	1	3	2	1	3	3	1	3	3	1
Read time	2	2	2	2	2	5	3	3	2	2	2
Read delay	1	1	1	1	1	1	1	1	1	1	1

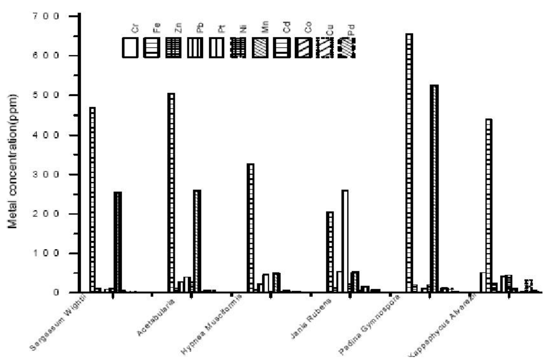

Figure 1 : Heavy metal concentrations in the edible algae

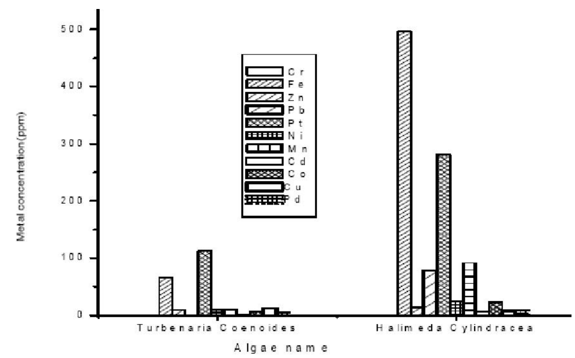

Figure 2 : Heavy metal concentrations in the nonedible algae

min and allowed to cool at room temperature. 20 ml of sub-boiled distilled water was added to the solution and filtered through Whattman filter paper No.42 into a standard flask. The final volume was made up to 100 ml with sub-boiled distilled water. Necessary precautions were adopted to avoid possible contamination of the samples.

RESULTS AND DISCUSSION

Heavy metals such as Pb, Cd, Cu, Ni, Fe, Co, Cr, Mn, Zn Pt and Pd were estimated by FAAS. The method was developed by varying slit width, cathode lamp current and resonance line width by analyzing standard reference materials supplied by E.Merck, Germany. The optimized instrumental parameters are given in TABLE 2. The method was validated in terms of accuracy, precision, linearity and range, the linearity of detector response was estimated by each metal standard solution of 1.0, 2.0, 5.0, 10.0 μg/ml. By plotting absorbance Vs metal concentration, a linear relationship was obtained. The results were found to be in agreement with RSD<4% (average of three determinations). The RSD values in all measurements of drug samples were <5%.

Toxic metals

Acceptable daily intake limit (ADI) of Pd was 0.015 ppm. The observed levels of concentration were very high in the marine algal samples. The maximum level of Pd concentration was observed in *Halimeda cylindreca* and lowest concentration was observed in *Sargassum wightii* (Table.3). Among the edible algae, *Jania rubens* was having the highest level of Pd and in *Dictyota dichotoma* the concentration was below the detection limit (Figure 1). Among the nonedible algae, *Turbinaria conoides* was having the highest concentration and the *Halimeda cylindreca* was having the lower level (Figure 2). Except *Dictyota dichotoma* all other algae were showing the Pd concentration beyond the ADI level.

The maximum concentration of Pt was observed in *Halimeda cylindreca* and the lowest concentration was observed in *Sargassum wightii*. Among the edible algae, the highest level of Pt was observed in *Jania rubens* whereas the lowest level was observed in *Sargassum*

TABLE 2 : Heavy metals under investigation: Name, acceptability daily intake and disorders

Metal name	Acceptable daily Intake (ADI) for adult (PPM)	Disorders
Cd	0.3	Osteomalacia and pylenephrities
Co	8	Irritation of gastrointestinal tract, nausea, diarrhea, lung and heart diseases
Cr	1.54	Respiratory cancers
Cu	21.5	Vineyard sprayer's lung and Wilson disease
Fe	231	Vomiting, cardiac depression, metabolic acidosis and Hepatic cirrhosis
Ni	1.85	Dermatitis, pulmonary fibrosis, reduces sperm count and nasopharyngeal tumors
Zn	169	Anemia and neurological degeneration
Mn	69.2	Parkinson like syndrome, respiratory and Euro psychiatric disorders
Pb	10	Adverse effects on the renal and nervous systems
Pd	0.015	Induces lung malfunction and produces abnormal fetuses. Cause appetite loss, hemolysis, renal deposition and bone marrow damage

wightii (Figure 1).and, in non edible algae the higher level was observed in *Halimeda cylindreca* (Figure 2).

The highest Pb concentration was found in *Halimeda Cylindreca* followed by *Jania Rubens*, *Dictyota dichotoma*, and *Hypnea musciformis*. The least concentration was found in *Kappaphycus alvarezii* and, *Sargassum wightii*. *Turbinaria conoides*, sea grass and *Padina gymnospora* were having below the detection limit of Pb (TABLE 3). According to the WHO[23], a permissible limit of Pb in human beings and the acceptable Daily intake (ADI) is 10 ppm[24,25] (TABLE 1). *Halimeda cylindracea*, *Jania rubens*, *Dictyota dichotoma*, and *Hypnea musciformis* contained in the range 22.5 ppb to 78.8 ppm, higher than the permissible limit 10 ppm.

The observed Cd concentration was in the range of 1.5 ppm to 5.7 ppm. The highest concentration was found in the *Halimeda cylindracea* followed by *Jania rubens*, *Sargassum wightii* and *Dictyota dichotoma* and, least was found in *Turbinaria conoides* and *Kappaphycus alvarezii* (TABLE 3). All the studied algae were having the higher concentration than the ADI of Cd is 0.3 ppm (TABLE 2). This might be due to the abundance of Cd in the sea water and high biosorption ability of algae.

Among all the studied algae, *Kappaphycus alvarezii* was having highest concentration of Cr i.e., 52 ppm, higher than the permissible limit 1.54 ppm. All nonedible algae and edible algae except *Kappaphycus alvarezii* were having the below the detection of Cr concentration (TABLE 3).

Essential metals

Acceptable daily intake for Mn is 69.2 ppm. The maximum concentration was found in the *Padina gymnospora* (525.3ppm) while minimum was found in the *Turbinaria conoides* (9.8ppm) (TABLE 3). The highest total Mn concentration was found in the edible algae rather than non edible plants. Among the edible algae, *Padina gymnospora* (525.3ppm) was having the highest concentration and *Kappaphycus alvarezii* (10.6ppm) was having the lowest concentration (Figure 1). Among the non edible algae *Halimeda cylindreca* was having the highest concentration (92.1ppm) and *Turbinaria conoides* was having the lowest concentration (9.8ppm) (Figure 2). In edible algae *Sargassum wightii*, *Dictyota dichotoma*, and *Padina gymnospora* were having beyond the ADI concentration limits (Figure 1). Amongst the non edible algae *Halimeda cylindreca* was having more concentration levels of Mn than the ADI limits (Figure 2).

The maximum Ni concentration was found in the *Kappaphycus alvarezii* followed by *Dictyota dichotoma*, *Halimeda cylindracea* and *Jania rubens*(TABLE 3). The total highest Ni concentration was found in the edible algae. Among all the edible algae *Kappaphycus alvarezii* was having high content of Ni (44.9ppm) whereas low content of Ni was observed in the *Hypnea musciformis* (3.1ppm). While in non edible algae, highest amount of Ni was reported in the *Halimeda Cylindracea* (24ppm) (Figure 2). ADI limit for the Ni is 1.85 ppm (TABLE 2). All the algae were having more concentration levels of Ni than the ADI limits.

ADI for Cu is 21.5 ppm (TABLE 2). The maximum concentration of Cu was found in the *Kappaphycus alvarezii* (31.9 ppm) while minimum concentration was found in the *Sargassum wightii* (2.6ppm) (TABLE 3). The Cu concentration reported in *Hypnea musciformis* and *Jania rubens* was below the detection limit. In edible algae, *Kappaphycus alvarezii* was having the highest Cu concentration where as in non edible algae, *Turbinaria conoides* was having the high amount of Cu concentration (11.8ppm).

TABLE 3 : Heavy metal concentrations (ppm) in the algae

Algae name	Edible/non edible	Essential elements						Toxic elements				
		Mn	Fe	Zn	Co	Ni	pt	Pb	Cd	Cr	Cu	Pd
Sargassum Wightii	Edible	255.2±8.2	468.4±15.2	9.9±0.4	0.8±0.1	11.1±0.2	9.4±0.3	0.5±0.1	4.6±0.2	B.D	2.6±0.4	0.6±0.1
Dictyota dichotoma		259.1±4.9	504±12.4	11.7±0.3	5.5±0.2	27±0.4	40.1±0.4	28.5±3.5	3.9±0.3	B.D	6.4±0.3	B.D
Hypnea Musciformis		49.8±2.8	326.2±10.2	8.6±0.4	5.7±0.3	3.1±0.2	45.2±0.3	22.5±2.5	3.5±0.2	B.D	B.D	2.5±0.1
Jania Rubens		52.8±2.4	205.2±2.9	13.5±0.6	15.9±0.2	22.7±0.3	259.6±3.6	54.8±2.5	5.1±0.6	B.D	B.D	6.8±0.3
Padina Gymnospora		525.3±16.2	654.6±12.1	21±0.6	11.6±0.3	21.1±0.4	10.3±0.5	B.D	2.5±0.2	B.D	10.1±0.9	2.3±0.2
Kappaphycus Alvarezii		10.6±0.5	438.7±6.5	25.5±0.5	3.9±0.3	44.9±0.5	42.1±1.5	4.8±0.2	1.5±0.2	52±2.8	31.9±2.5	3.6±0.3
Turbinaria conoides	Non edible	9.8±0.2	65.2±3.1	9±0.2	6.6±0.3	9.9±0.4	112.2±3.6	B.D	1.9±0.2	B.D	11.8±0.6	4.9±0.3
Halimeda Cylindracea		92.1±3.4	496.6±6.4	13.9±0.4	22.5±0.6	24±0.7	280.9±5.9	78.8±3.9	5.7±0.5	B.D	6.9±0.8	8.1±0.5

B.D=below detection limit

Among all stated algae, *Kappaphycus alvarezii* was having beyond the ADI limits of Cu concentration (TABLE 3).

The maximum concentration was found in the *Halimeda cylindracea* followed by *Jania rubens* and *Padina gymnospora*(TABLE 3). Among edible algae, *Jania rubens* (15.9 ppm) was having the highest concentration of Co where lowest concentration was found in the *Sargassum wightii* (0.8ppm) (Figure 1). In non edible algae, *Halimeda cylindracea* was having the highest concentration of Co (Figure 2). *Halimeda cylindracea*, *Jania rubens* and *Padina gymnospora* were having the higher concentration than the ADI i.e. 8 ppm The average concentration found in the algae is 3.5 ppm. The high concentration of Co in algae might be due to the physiological participation of Co in the certain enzymes.

Acceptable Daily intake of Zn is 169 ppm (TABLE 2). The observed Zn concentration in the studied algae was in the range of 8.6 ppm to 25.5 ppm. The highest concentration was found in the *Kappaphycus alvarezii* followed by *Halimeda cylindracea* and *Jania rubens*. Hundred percent of the studied algae were below the acceptable Daily intake limit of Zn (TABLE 3). On the basis of ADI it could be suggested that the algae are safe in terms of Zn toxicity.

As a micro nutrient, the observed Fe concentration was in the range of 65.2 ppm to 645.6 ppm. The highest concentration was found in the *Padina gymnospora* (654.6ppm) followed by *Dictyota dichotoma* (504ppm), *Halimeda cylindracea* (496.6ppm) and Sargassum *wightii* (468.4ppm) (TABLE 3). The permissible limit of Fe is 231 ppm. *Padina gymnospora*, *Dictyota dichotoma*, *Halimeda cylindracea*, *Sargassum wightii*, *Kappaphycus alvarezii* and *Hypnea musciformis* were beyond the permissible limit. The highest concentration of Fe presents in the edible and non edible algae were *Padina gymnospora* and *Halimeda cylindracea*, respectively (Figure 2 & 3) and it might be due to the most abundance of Fe in the earth crust and sea water.

CONCLUSIONS

The present study gives a new picture about the presence of heavy metals in the marine algae. The maximum Pd concentration was observed in *Halimeda cylindreca* and minimum concentration was found in *Sargassum wightii* and, *Dictyota dichotoma* was having the higher concentration than ADI Pd concentration level. The highest total Mn concentration was found in the edible algae rather than non edible plants. The maximum Cu concentration was found in the *Kappaphycus alvarezii* while minimum concentration was found in the *Sargassum wightii*. Among all algae, *Kappaphycus alvarezii* was having beyond the ADI limits of Cu concentration. The observed Cd concentration was in the range of 1.5 ppm to 5.7 ppm. The highest Cd concentration was found in the *Halimeda cylindracea* whereas least was found in *Turbinaria conoides* and *Kappaphycus alvarezii*. *Halimeda cylindracea*, *Jania rubens*, *Dictyota dichotoma*, and *Hypnea musciformis* contained Pb concentration in the range of 22.5 ppb to 78.8 ppm, higher than the permissible limit 10 ppm. All the studied algae were having the higher concentration than the ADI limits of

Cd and Cu. This investigation provides a status of heavy metal concentration in various marine algae. There should be periodical assessment of heavy metal concentration in marine algae, in order to have quality assurance and safer use of marine algae.

REFERENCES

[1] Y.C.Shen, M.C.Hung, C.V.S.Prakash, J.J.Wang; J.Chin.Chem.Soc., **47**, 567 **(2000)**.

[2] D.Abatis, C.Vagias, D.Galanakis, J.N.Norris, D.Moreau, C.Roussakis, V.Roussis; Tetrahedron Lett., **46(49)**, 8525 **(2005)**.

[3] M.Kladi, C.Vagias, G.Furnari, D.Moreau, C.Roussakis, V.Roussis; Tetrahedron Lett., **46(34)**, 5723 **(2005)**.

[4] Anon, Seaweeds: Wonder Plants of the Sea. In: V.Krishnamurthy Ed., Aquaculture Foundation of India, Neelangarai, Chennai, 30 **(2005)**.

[5] K.Ito, K.Hori; Seaweed: Chemical composition and potential food uses. Food Rev.Int., **5(1)**, 101 **(1999)**.

[6] J.Raynal, J.P.Delgenes, R.Moletta; Bioresource Technology, **65**, 97 **(1998)**.

[7] B.Goel, D.C.Pant, V.Kishore; Bioresource Technology, **80(2)**, 153 **(2001)**.

[8] B.K.Ahring; 'Perspectives for Anaerobic Digestion', In: T.Scheper, Ed., Biomethanation 1, Advances in Biochemical Engineering / Biotechnology, 81. Springer Berlin/Heidelberg, 1-30 **(2003)**.

[9] Y.Okai, K.Higashi-Okai, S.Nakamura, T.S.Yano; Otani.Canc.Lett., **87(1)**, 25 **(1994)**.

[10] Y.Athukorala, W.K.Jung, P.J.Park, Y.J.Lee, S.K.Kim, T.Vasanthan, H.K.No, Y.J.Jeon; J.Microbiol.Biotechnol., **18(3)**, 503 **(2008)**.

[11] W.K.Jung, Y.Athukorala, Y.J.Lee, S.H.Cha, C.H.Lee, T.Vasanthan, K.S.Choi, S.H.Yoo, S.K.Kim, Y.J.Jeon; J.Appl.Phycol., **19**, 425 **(2007)**.

[12] J.N.C.Whyte, Jr.; Englar.Phytochemistry., **20(2)**, 237 **(1981)**.

[13] R.Armisen; J.Appl.Phycol., **7(3)**, 231 **(1995)**.

[14] Kamalesh Prasad, A.K.Siddhanta, M.Ganesan, B.K.Ramavat, B.Jha, K.Pushpito Ghosh; Bioresource Technology, **98(10)**, 1907 **(2007)**.

[15] K.I.Draget, O.Smidsrod, G.Skjak-Braek; 'Alginates from Algae', In: E.J.Vandamme, A.Steinbuchel, S.De Baets, Ed., Biopolymers: Polysaccharides 2, Polysaccharides from Eukaryotes, 6, John Wiley & Sons, Inc., Hoboken, New Jersey, 215-244 **(2002)**.

[16] G.Zhou, W.Sheng, W.Yao, C.Wang; Pharmacol.Res., **53(2)**, 129 **(2006)**.

[17] V.K.Mishra, F.Temelli, P.F.Ooraikul Shacklock, J.S.Craigie; Bot.Mar., **36(2)**, 169 **(1993)**.

[18] S.Kaehler, R.Kennish; Bot.Mar., **39**, 11 **(1996)**.

[19] M.H.Norziah, Ch.Y.Ching; Food Chem., **68**, 69 **(2000)**.

[20] K.Manivannan, G.Karthikai Devi, G.Thirumaran, P.Anantharaman; Am-Euras.J.Bot., **1(2)**, 58 **(2008)**.

[21] G.Karthikai Devi, G.Thirumaran, K.Manivannan, P.Anantharaman; Element World J.of Dairy & Food Sci., **4(1)**, 46 **(2009)**.

[22] R.Riosmena-Rodríguez, A.Talavera-Sáenz, B.Acosta-Vargas, S.C.Gardner; J.Appl.Phycol., DOI 10.1007/s10811-009-9457-2**(2009)**.

[23] WHO, 'Guidelines for Drinking-Water Quality', Recommendations, Second Ed., World Health Organization, Geneva, Switzerland, **1**, **(1993)**.

[24] G.Ysart; Food Addit.Contam., **16**, 319 **(1999)**.

[25] G.Ysart; Food Addit.Contam., **17**, 775 **(2000)**.