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# Chemical composition of *Spirulina* and eukaryotic algae food products marketed in Spain

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## Abstract

Three *Spirulina* and five eukaryotic algal food products available in the Spanish market have been extensively studied. Results are given for their gross chemical composition (water content, crude protein, total carbohydrates, lipids, nucleic acids etc.) and contents of macrominerals, trace elements, fatty acids, amino acids and neutral sugars. The results are compared to those from other studies on natural or laboratory-produced populations. An overall nutritional and toxicological evaluation of these products is included.

## Introduction

The study of the chemical composition of algae has received considerable interest since the beginnings of applied phycology (Soeder, 1986). However, extensive chemical analyses of commercially prepared algal food products are rare. The companies responsible for the products rarely disseminate the results of their studies and quality controls to the scientific community. In spite of there being only a few number of publications by scientists closely related to the companies (e.g. Jassby, 1988a, b; Santillan, 1982), nutritional and toxicological evaluation of these foods is often based on data generated from field and laboratory studies designed from ecological or physiological perspectives (Chapman & Chapman, 1980; Becker, 1988; Ito & Nori, 1989). The commercialization of the algal biomass introduces factors such as environmental pollution and production, processing, package and distribution, that may affect the chemical composition of the product, and hence its nutritional and toxicological properties. For example, local heavy metal concentrations in production sites may lead to high levels in the algal biomass (Payer & Runkel, 1978; Rai *et al.* 1981). Cultivation techniques, developed as a result of increasing demand for these products, enhance the natural productivity (Chapman & Chapman, 1980) and may effect the proportion of chemical constituents; this is particularly important in the case of microalgae. These effects, which are subject to a wide variety of agronomic studies in the case of traditional crops, have been yet not fully covered by scientists in the case of algal cultivation.

Biomass processing in large-scale production systems may be different to the treatment used by ecologists or physiologists to prepare specimens for analysis. Packing and distribution are in many cases carried out a long way from the consumers. The commercialization of algal food products is

carried out in Western countries under confused or null legal regulations, which implies a lack of knowledge for consumers and health administrations. This is particularly true in the case of Spain. Therefore, the considerable general analytical data already available from pure phycological studies need to be complemented by data from commercial materials in order to obtain a realistic nutritional and toxicological evaluation of these foods. In this paper an extensive chemical analysis of selected algal food products available in the Spanish market is reported.

## Materials and methods

### *Algal food products*

The products studied were selected after screening the available algal food products in the Spanish market. In spite of the screening not being exhaustive, a total of 30 different products were detected, commercialized by 13 companies. In general, the information obtained directly from companies was more complete than that obtained in the specialized shops where most of the products were sold. Eight products were selected based on the criteria of presence in high number of shops and available information about the product (Table 1). Generic and specific assignments followed those provided by commercial suppliers. Three different lots (A, B, C) of each product were acquired in randomly chosen dietetic shops from Madrid, Barcelona and Sevilla. These lots corresponded to the same product from the same company. Gross chemical composition and organic components were determined in lot A of each product. A more detailed study of lot-to-lot variability in mineral composition was based on all three lots for each product.

### *Gross chemical composition*

Water content was determined as weight loss of 1 g wet material kept at 105 °C for 4 h. Crude protein was calculated from N content × 6.25. The phenol-sulphuric acid method (Dubois *et al.*,

*Table 1.* Characteristics of the products selected for this study. Cost is indicated in Spanish pesetas (1 USA dollar = 124 ptas approx.).

| Name of product | Organism | Country of origin | Package, presentation | Net weight (g) | Cost (ptas $g^{-1}$ net wt) | Recommended doses (g $day^{-1}$) | Limit for consumption after package (years) |
|---|---|---|---|---|---|---|---|
| Spirulina A | *Spirulina* sp. | Unknown | Glass bottles, pills | 45 | 15 | 1.8–3.6 | 5 |
| Spirulina B | *Spirulina platensis* (Nordst.) Geitl. | USA | Plastic bottles, pills | 90 | 33 | 3.0–4.5 | 3 |
| Spirulina C | *Spirulina maxima* (Setch. & Gardin.) Geitl. | USA | Plastic envelopes, capsules | 24 | 42 | 0.4–3.2 | 3 |
| Chlorella | *Chlorella vulgaris* Beij. var. *vulgaris* | Japan, Taiwan | Glass bottles, pills | 80 | 14 | 3.0–6.0 | 5 |
| Wakame | *Undaria pinnatifida* (Harv.) Suringar | Japan | Plastic bags, dried seaweed | 25 | 7 | Not indicated | 2 |
| Hijiki | *Hijikia fusiforme* Okam. | Japan | Plastic bags, dried seaweed | 80 | 8 | Not indicated | 2 |
| Dulce | *Palmaria palmata* (L.) Kuntze | France | Plastic bags, dried seaweed | 50 | 10 | Not indicated | 2 |
| Fucus | *Fucus* sp. | Unknown | Glass bottles, pills | 50 | 5 | 1.8–5.4 | 3 |

1956) was used for total carbohydrate determination, except for 'Fucus', in which *R* value was used (Milner, 1953). Lipid content was determined by the sulphophosphovanillin reaction (Zoellner & Kirsch, 1962). Nucleic acids were estimated by absorbance at 260 nm of perchloric acid extracts (Smillie & Krotkov, 1960). Chlorophyll *a* content was estimated spectrophotometrically after extraction with methanol in the dark, using the specific absorption coefficient of 74.5 ml $mg^{-1}$ $cm^{-1}$ (Mackinney, 1941). Ash content was given by weight loss of 1 g wet material kept at 500 °C during 2 h. C, H, N and S were determined with Carlo Erba mod. 1106 and 1500 elemental analysis instruments.

*Inorganic components*

The dry method was used for mineralization of samples. P was determined colorimetrically, and K and Na contents were measured with flame photometry (C.I.I., 1969). Ca, Mg, Cu, Fe, Mn, Zn, Pb, Cd, Cr, Ni and Co levels were determined with a Perkin Elmer mod. 703 flame atomic absorption spectrophotometer equipped with lamps for each element. The detection limit for cadmium was 0.1 ppm.

*Organic components*

Fatty acids were determined, after extraction with dichloromethane/methanol (2:1), as methyl esters ($BF_3$, 12 h) by gas chromatography. Analyses were performed with a Hewlett Packard mod. 5890 gas chromatograph equipped with a HP-5 (25 m × 0.20 mm I.D.) column and connected to a Maxima 820 Chromatography Workstation (Millipore, U.S.A.). The oven temperature was programmed from 60 to 300 °C, at a rate of 6 °C $min^{-1}$. Mass spectra were obtained with a Hewlett-Packard 5890 gas chromatograph coupled to a Hewlett-Packard 5988A quadrupole mass spectrometer, working with electron impact at 70 eV. Identification of compounds was performed by comparison of their mass spectra with those from a library, and with retention times and mass spectra of standard compounds. Amino acid profiles were obtained using the Pico-Tag method (Waters, U.S.A.). Samples were hydrolyzed with HCl, derivatized with phenylisothiocyanate and analyzed with a High Pressure Liquid Chromatograph Waters equipment.

Neutral sugars were analyzed by gas chromatography and gas chromatography-mass spectrometry as alditol acetates, after hydrolysis with sulphuric acid. Analyses were performed with the same equipment as fatty acids, but using a CP-Sil 88 (25 m × 0.32 mm I.D.) column. After injection at 70 °C, oven temperature was inmediately increased to 150 °C, and subsequently programmed to 230 °C at a rate of 3 °C/min. Final time was 40 min. Identification of compounds was also achieved by using library mass spectra and retention times and mass spectra of standard compounds.

## Results

*1. Gross chemical composition*

The results for general composition of the products are shown in Table 2. Seaweed products were characterized by higher levels of carbohydrates (up to 65.1 g 100 $g^{-1}$ in the case of 'Dulce') and ash. Microalgal products were typically richer in protein, lipids, nucleic acids and chlorophyll *a*.

*2. Inorganic components*

The inorganic components were studied in detail in three lots of the products, including macrominerals (Table 3) and trace elements (Table 4). *Spirulina* products showed some differences in macromineral composition, specially in Ca and Na contents, although different lots of the same product had few differences. The lower Na content of 'Spirulina C' product was striking. Seaweed products contained much more K and less P than microalgal products. There was low variability between lots of the same product observed with

*Table 2.* Chemical composition of lot A of the studied algal products.

| | Spr. A | Spir. B | Spir. C | Chlor. | Wakame | Hijiki | Dulce | Fucus |
|---|---|---|---|---|---|---|---|---|
| Gross composition (g 100 g$^{-1}$ d wt) | | | | | | | | |
| Water | 7.4 | 6.9 | 7.2 | 6.5 | 10.9 | 10.2 | 6.9 | 9.3 |
| Ash | 9.7 | 14.0 | 7.3 | 7.3 | 30.2 | 25.7 | 16.2 | 30.9 |
| Carbohydrates | 18.8 | 16.0 | 12.6 | 17.9 | 39.2 | 52.7 | 65.1 | 56.0 |
| Lipids | 6.5 | 7.5 | 6.4 | 8.6 | 1.9 | 0.7 | 0.9 | 1.4 |
| Protein | 60.9 | 56.6 | 68.9 | 56.0 | 12.5 | 10.0 | 10.1 | 7.3 |
| Nucleic acids | 4.8 | 4.8 | 5.7 | 5.4 | 1.2 | 1.2 | 1.3 | 1.6 |
| Chlorophyll *a* | 0.93 | 0.86 | 0.90 | 1.11 | 0.09 | 0.07 | ND | 0.04 |
| Element composition (g 100 g$^{-1}$ ash-free d wt) | | | | | | | | |
| C | 51.71 | 53.29 | 53.45 | 54.95 | 49.79 | 46.99 | 45.19 | 44.67 |
| H | 7.48 | 7.92 | 7.62 | 8.07 | 7.66 | 6.47 | 7.12 | 6.23 |
| O | 29.19 | 27.45 | 25.51 | 25.83 | 37.60 | 41.86 | 45.58 | 45.05 |
| N | 10.99 | 10.66 | 12.45 | 10.65 | 3.06 | 2.67 | 1.81 | 1.57 |
| S | 0.63 | 0.68 | 0.97 | 0.50 | 1.89 | 2.01 | 0.30 | 2.48 |

*Table 3.* Macromineral content of three lots of the studied algal products (g 100 g$^{-1}$ d wt).

| Product | Lot | P | Na | K | Mg | Ca |
|---|---|---|---|---|---|---|
| Spir. A | A | 1.141 | 1.363 | 1.897 | 0.342 | 0.960 |
| | B | 1.122 | 1.742 | 1.936 | 0.356 | 0.953 |
| | C | 1.235 | 1.242 | 1.868 | 0.363 | 1.501 |
| Spir. B | A | 1.023 | 1.768 | 1.649 | 0.503 | 1.541 |
| | B | 0.965 | 1.400 | 1.786 | 0.410 | 2.246 |
| | C | 0.967 | 1.445 | 1.901 | 0.411 | 2.108 |
| Spir. C | A | 1.328 | 0.123 | 1.134 | 0.461 | 0.687 |
| | B | 1.397 | 0.121 | 1.267 | 0.453 | 0.838 |
| | C | 1.354 | 0.202 | 1.220 | 0.454 | 0.672 |
| Chlorella | A | 1.883 | 0.034 | 0.919 | 0.451 | 0.484 |
| | B | 1.798 | 0.029 | 1.070 | 0.455 | 0.485 |
| | C | 1.455 | 0.080 | 0.856 | 0.352 | 0.303 |
| Wakame | A | 0.465 | 7.935 | 5.104 | 0.854 | 1.232 |
| | B | 0.422 | 7.526 | 5.409 | 0.577 | 1.214 |
| | C | 0.422 | 5.634 | 5.880 | 0.597 | 1.063 |
| Hijiki | A | 0.142 | 3.324 | 12.426 | 0.533 | 1.410 |
| | B | 0.127 | 3.436 | 13.365 | 0.490 | 1.360 |
| | C | 0.141 | 2.860 | 9.879 | 0.559 | 1.328 |
| Dulce | A | 0.223 | 0.810 | 10.206 | 0.158 | 0.340 |
| | B | 0.174 | 0.927 | 8.229 | 0.159 | 0.239 |
| | C | 0.160 | 0.802 | 9.630 | 0.150 | 0.267 |
| Fucus | A | 0.150 | 4.286 | 3.689 | 0.549 | 2.600 |
| | B | 0.136 | 3.435 | 3.827 | 0.474 | 5.078 |
| | C | 0.129 | 4.415 | 4.239 | 0.612 | 1.584 |

*Table 4.* Trace elements in three lots of the studied algal products (mg kg$^{-1}$ d wt). ND: not detected.

| Product | Lot | Fe | Mn | Zn | Cu | Ni | Co | Cr | Pb | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| Spir. A | A | 751.0 | 117.7 | 49.8 | 48.0 | 5.4 | 1.7 | 3.3 | 7.2 | 0.2 |
| | B | 633.6 | 104.9 | 45.8 | 21.6 | 4.5 | 0.9 | 1.2 | 2.1 | ND |
| | C | 646.2 | 122.4 | 50.0 | 17.5 | 7.7 | 2.3 | 2.8 | 8.1 | ND |
| Spir. B | A | 2016.4 | 64.4 | 28.8 | 17.6 | 5.8 | 0.5 | 7.1 | 4.3 | 0.2 |
| | B | 1614.6 | 67.0 | 18.4 | 14.8 | 4.0 | 1.5 | 4.8 | 3.0 | ND |
| | C | 1631.8 | 63.5 | 20.7 | 17.3 | 6.0 | 2.0 | 5.5 | 7.0 | 0.1 |
| Spir. C | A | 945.0 | 36.0 | 23.8 | 6.5 | 6.1 | 0.9 | 5.0 | 9.2 | 0.2 |
| | B | 752.0 | 36.7 | 21.2 | 5.0 | 3.9 | 0.9 | 2.7 | 2.9 | ND |
| | C | 822.6 | 32.8 | 21.6 | 4.6 | 5.7 | 0.8 | 4.0 | 5.6 | 0.2 |
| Chlorella | A | 3486.0 | 83.7 | 21.4 | 21.4 | 5.6 | 1.6 | 3.9 | 7.2 | 0.2 |
| | B | 3404.7 | 88.4 | 21.0 | 6.4 | 4.9 | 1.4 | 3.4 | 5.1 | ND |
| | C | 1970.9 | 62.8 | 10.3 | 4.2 | 4.2 | 0.7 | 2.9 | 3.3 | 0.2 |
| Wakame | A | 95.3 | 9.9 | 16.5 | 7.7 | 3.6 | 1.2 | 3.6 | 4.5 | 0.6 |
| | B | 149.5 | 11.8 | 15.2 | 5.9 | 8.1 | 1.8 | 7.3 | 5.9 | 1.8 |
| | C | 48.5 | 6.3 | 69.1 | 4.9 | 5.3 | 2.2 | 3.2 | 4.8 | 1.0 |
| Hijiki | A | 60.3 | 8.0 | 9.1 | 6.5 | 5.4 | 2.3 | 3.5 | 13.8 | 2.3 |
| | B | 68.9 | 7.7 | 8.4 | 7.3 | 5.5 | 2.3 | 2.5 | 5.9 | 2.4 |
| | C | 472.9 | 30.2 | 13.7 | 5.2 | 7.6 | 2.9 | 6.0 | 5.1 | 0.8 |
| Dulce | A | 55.1 | 9.4 | 32.8 | 7.6 | 6.1 | 1.7 | 2.0 | 4.9 | 0.3 |
| | B | 182.0 | 44.7 | 14.2 | 6.2 | 4.7 | 1.2 | 1.5 | 2.2 | ND |
| | C | 192.6 | 47.4 | 12.8 | 5.3 | 4.3 | 1.4 | 1.6 | 4.4 | 0.4 |
| Fucus | A | 2340.8 | 85.4 | 45.8 | 16.9 | 11.8 | 4.5 | 6.5 | 14.0 | 1.1 |
| | B | 4099.2 | 103.8 | 44.6 | 17.8 | 9.1 | 5.2 | 8.8 | 11.8 | 1.0 |
| | C | 1528.4 | 101.6 | 43.6 | 9.7 | 9.7 | 3.1 | 4.3 | 11.3 | 1.1 |

macrominerals, but greater variability for some trace elements, such as Fe and Zn (Table 4). For example, Fe content ranged from 60.3 to 472.9 and from 55.1 to 192.6 mg kg$^{-1}$ d wt in 'Hijiki' and 'Dulce' lots, respectively.

In order to characterize the mineral composition in seaweed products, the exponential relation between concentration factor ($y$) and oceanic

residence time ($x$) of each element (Log $y$ = log $a$ + $b$ log $x$, being log $a$ and $b$ constants) proposed by Yamamoto *et al.* (1979) for seaweed was applied to these results. The parameters of the regression line (log $a$, $b$ and $r$ – correlation coefficient) were calculated for each lot (Table 5), using theoretical values of oceanic residence time and concentration in seawater (Yamamoto *et al.*, 1979). A statistically significant correlation ($p < 0.005$) was obtained in all cases (e.g. Fig. 1). In spite of the differences introduced by lot-to-lot variability (Tables 3, 4), different trends were observed between products.

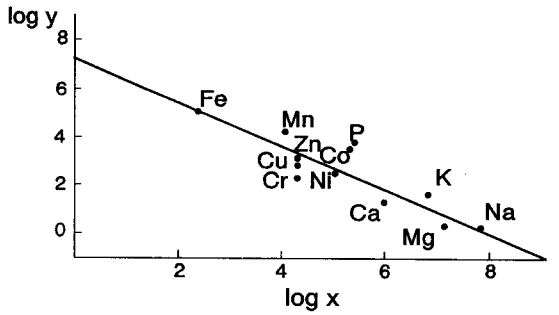


*Fig. 1.* Characterization of mineral composition in lot C of 'Fucus' product, showing the exponential relation between concentration factor ($y$) and oceanic residence time ($x$) for each element.

## 3. *Organic components*

### 3.1. *Fatty acids*

The fatty acid compositions are shown in Table 6. Macroalgal products presented a more complex pattern of fatty acids than microalgal products, composed by acids of 16 and 18 carbon atoms. *Spirulina* products showed strong differences in their fatty acid profiles, as reflected in their different polyunsaturated/saturated fatty acid ratio (0.48–0.75).

*Table 5.* Regression line parameters for the relation between concentration factor (y) and oceanic residence time (x) of each element in the lots of the seaweed products studied (being r the correlation coefficient when applied the ecuation log y = log a + b log x). Due to the different production techniques used with microalgae, involving the use of artificial ponds and culture media, these products were not considered for such calculations.

| Product | Lot | Log a | b | r |
|---|---|---|---|---|
| Wakame | A | 5.77 | −0.68 | −0.82 |
| | B | 6.08 | −0.73 | −0.84 |
| | C | 5.76 | −0.68 | −0.79 |
| Hijiki | A | 5.66 | −0.67 | −0.81 |
| | B | 5.65 | −0.67 | −0.81 |
| | C | 6.59 | −0.83 | −0.88 |
| Dulce | A | 6.25 | −0.81 | −0.80 |
| | B | 6.63 | −0.88 | −0.83 |
| | C | 6.65 | −0.89 | −0.83 |
| Fucus | A | 7.45 | −0.95 | −0.92 |
| | B | 7.78 | −1.01 | −0.93 |
| | C | 7.26 | −0.93 | −0.91 |

### 3.2. *Amino acids*

The amino acid patterns of the proteins are shown in Table 7, together with a comparison of an 'ideal' protein proposed by the World Health Organization (WHO). As previously reported (Paoletti *et al.*, 1980), the protein of *Spirulina* showed great nutritional value when compared to the WHO pattern and other plant foods.

### 3.3. *Neutral sugars*

Glucose, galactose and fucose were the major neutral sugars in most of the products (Table 8), although high levels of xylose were also observed in 'Dulce'. The proportions of rhamnose, ribose and galactose varied markedly between *Spirulina* products.

## Discussion

The gross chemical composition of the products (Table 2) showed in general good agreement with previous analyses of the corresponding genera and species (Black, 1949; Morgan *et al.*, 1980; Becker, 1988; Perez *et al.*, 1988; Ito & Nori, 1989). Water content was below the 12% level, suggested as a limit to prevent microbial growth (Jassby, 1988b). The chlorophyll *a* content of 'Chlorella' (1.11%) was low in comparison to the usual levels in 'Chlorella' products (2–3%). This is remarkable, if we consider that the presence of

*Table 6.* Fatty acid composition of lot A of the studied algal products. Results are expressed as percentage of total fatty acids.

| Fatty acid | Spir. A | Spir. B | Spir. C | Chlorella | Wakame | Hijiki | Dulce | Fucus |
|---|---|---|---|---|---|---|---|---|
| 12:0 | – | – | – | – | 2.5 | 0.7 | 5.1 | – |
| 14:0 | – | – | – | – | 3.4 | 3.7 | 19.3 | 13.5 |
| 15:0 | – | – | – | – | 0.4 | 0.4 | 0.8 | 0.2 |
| 16:1 | 7.0 | 7.0 | 9.3 | 18.7 | 1.0 | 4.3 | – | 1.0 |
| 16:0 | 56.2 | 52.4 | 49.1 | 25.1 | 25.5 | 31.0 | 65.8 | 23.1 |
| 18:3 | 10.3 | 5.9 | 15.8 | – | – | – | – | – |
| 18:2 | 17.7 | 12.6 | 21.7 | 16.1 | 18.4 | – | 0.7 | – |
| 18:1 | tr. | tr. | tr | 25.3 | 22.7 | 26.8 | – | 48.5 |
| 18:0 | 2.6 | 21.3 | 1.0 | 5.6 | 2.7 | 0.8 | 3.7 | 2.0 |
| 19:0 | – | – | – | – | – | – | 0.4 | 1.0 |
| 20:4 | – | – | – | – | 18.4[a] | 14.1[a] | – | 4.9[a] |
| 20:2 | – | – | – | – | 0.5 | 5.6 | – | 3.9 |
| 20:1 | – | – | – | – | – | 2.8 | – | 1.0 |
| 20:0 | – | – | – | – | 0.8 | 3.1 | 0.2 | 0.4 |
| 22:0 | – | – | – | – | – | 4.2 | – | – |
| 22:0 | – | – | – | – | – | 0.7 | 0.6 | – |
| 24;0 | – | – | – | – | – | – | 1.1 | – |
| PIN/SAT[b] | 0.48 | 0.25 | 0.75 | 0.71 | 1.10 | 0.50 | 0.00 | 0.20 |

[a] Sum of 20:3 and 20:4 fatty acids.
[b] Polyunsaturated/saturated fatty acid ratio.

a chlorophyll-degradation product, pheophorbide, has been reported to cause skin problems (Jassby, 1988b). Nucleic acids content of one 'Spirulina' product (*S. maxima*) was above pre-

*Table 7.* Aminoacid profiles of lot A of the studied algal products. The values are expressed as g/16 g N. Essential aminoacids are indicated.

| Aminoacid | WHO | Spir. A | Spir. B | Spir. C | Chlorella | Wakame | Hijiki | Dulce | Fucus |
|---|---|---|---|---|---|---|---|---|---|
| Asp | – | 8.3 | 7.6 | 11.2 | 11.7 | 4.4 | 4.4 | 9.9 | 5.9 |
| Glu | – | 11.4 | 10.4 | 10.7 | 10.4 | 9.6 | 7.9 | 13.9 | 8.9 |
| Ser | C | 5.4 | 5.4 | 5.5 | 5.3 | 6.7 | 6.4 | 7.5 | 7.5 |
| Gly | – | 6.8 | 6.4 | 6.0 | 7.9 | 9.5 | 10.5 | 9.8 | 10.2 |
| Arg | – | 10.2 | 9.9 | 10.0 | 9.7 | 2.5 | 10.3 | 9.2 | 10.3 |
| Ala | – | 9.5 | 8.8 | 8.9 | 10.9 | 8.7 | 10.3 | 9.1 | 9.1 |
| Pro | – | 4.6 | 4.5 | 4.4 | 6.0 | 7.1 | 7.9 | 6.1 | 7.7 |
| Hys | – | 1.7 | 1.6 | 1.7 | 2.6 | 2.5 | 1.9 | 1.3 | 2.1 |
| *Tre* | 4.0 | 6.5 | 6.6 | 6.1 | 6.6 | 7.1 | 8.3 | 6.7 | 8.8 |
| *Tyr* | 6.0[a] | 6.8 | 8.6 | 7.3 | 6.4 | 6.3 | 6.7 | 5.5 | 6.6 |
| *Phe* | – | 1.7 | 1.7 | 1.3 | 2.0 | 1.5 | 1.5 | 0.8 | 1.4 |
| *Val* | 5.0 | 8.1 | 8.7 | 8.4 | 0.8 | 5.7 | 7.2 | 5.9 | 5.8 |
| *Met* | 3.5[b] | 1.2 | 2.0 | 2.0 | 2.1 | 2.5 | 3.0 | 1.8 | 2.2 |
| *Cys* | – | 0.5 | 0.3 | 0.6 | 0.4 | 0.4 | 0 | 0.8 | 0.2 |
| *Ile* | 4.0 | 4.5 | 4.8 | 4.2 | 3.7 | 2.1 | 3.2 | 1.9 | 2.4 |
| *Leu* | 7.0 | 6.4 | 6.4 | 5.5 | 6.9 | 3.5 | 4.7 | 3.4 | 3.4 |
| *Lys* | 5.5 | 6.1 | 6.2 | 6.1 | 6.9 | 7.0 | 5.9 | 6.7 | 7.5 |

[a] Tyr + Phe.
[b] Met + Cys.

*Table 8.* Content of major neutral sugars in lot A of the studied algal products (g 100 $g^{-1}$ d wt). X: not identified sugar.

| Sugar | Spir. A | Spir. B | Spir. C | Chlorella | Wakame | Hijiki | Dulce | Fucus |
|---|---|---|---|---|---|---|---|---|
| Erythrose | 0.28 | 0.05 | 0.31 | – | – | – | – | – |
| Rhamnose | 0.33 | 0.57 | 0.85 | 0.63 | – | – | – | 0.08 |
| Fucose | – | 0.10 | tr. | 0.04 | 1.30 | 1.83 | – | 2.86 |
| Ribose | 0.43 | 0.57 | 0.77 | 0.25 | 0.17 | – | 0.20 | 0.05 |
| Arabinose | – | 0.05 | tr. | 0.22 | 0.08 | 0.13 | 0.51 | 0.03 |
| Xylose | 0.24 | 0.20 | 0.13 | 0.07 | 0.13 | 0.21 | 28.82 | 0.50 |
| Mannose | 0.29 | 0.26 | 0.30 | 0.15 | 0.62 | 1.12 | 0.24 | 0.31 |
| Galactose | 1.10 | 1.11 | 2.29 | 1.78 | 1.00 | 1.48 | 1.54 | 0.58 |
| Glucose | 7.78 | 6.94 | 6.84 | 2.65 | 6.11 | 14.69 | 6.11 | 5.97 |
| X | – | – | – | – | – | – | 2.91 | – |

vious data (Becker, 1988). Nevertheless, it did not represent a risk considering a maximum permissible intake of 2 g $d^{-1}$ (PAG, 1975). The amount of product needed to overcome this recommendation was ten times higher than the corresponding to a normal use (0.4–3.2 g $d^{-1}$). Ash analyses (Tables 3 and 4) revealed that these products contained high amounts of the macrominerals and trace elements needed in human nutrition. Ca and P contents were higher than in apples, oranges, carrots, potatoes and dried grapes (Morgan *et al.*, 1980). Microalgal products had more P than vegetables rich in this element such as pea and peanut. In spite of the higher chlorophyll content of microalgal products, their Mg levels were not much higher. All showed higher Mg levels than other plant foods (legumes, carrots, apples, oranges), whose Mg content does not exceed 0.19% (as edible portion), and animal foods (meat, fish and dairy products), with a Mg content below 0.04% (Czarnecki & Kritchevsky, 1980).

Most of the algal food products showed a relatively high Na content, which is relevant from the point of view of nutrition, because the intake of sodium chloride and diets with a high Na/K ratio have been related to the incidence of hypertension. However, Na/K ratios were below 1.5 in all the products studied. These are low values in comparison with other foods having a high Na content, such as olives (Na/K = 43.63) and sausages (Na/K = 4.89), with a Na content of 1–2.4%. 'Spirulina C' (*S. maxima*) had the lowest Na/K ratio among the 'Spirulina' products, due to its lower Na content. Na is the only element not accumulated by *Spirulina*, its cellular content being maintained at a constant level regardless of the external concentration. K can be accumulated up to 10 times the Na concentration (Laquerbe *et al.*, 1970; Vonshak *et al.*, 1988). This suggests that the differences between the Na/K ratios of 'Spirulina' products are due to components of the culture medium (sodium salts usually added during medium preparation) which were not washed out during the processing of *Spirulina* sp. and *S. platensis* biomass. It is concluded that sometimes the product available to the consumer may differ from the 'ideal' one known from scientific studies.

The content in trace elements, specially Fe, Cu, Mn, Co and Cr, was also high in comparison to other plant foods. The levels detected in the present paper fit within the wide ranges observed in other studies (Table 9). There were, however, higher values for some elements than those previously reported, such as Pb in several lots of 'Spirulina' products, and Cu, Cd and Pb in 'Wakame' lots. Surprisingly, published data on mineral composition of mass-cultivated *Chlorella* are very scarce (Yannai *et al.*, 1980).

In spite of the difficulties associated with the generalization of theoretical values of oceanic residence time and concentration in seawater, the values log *a*, *b* and *r* obtained for the exponential relation between concentration factor and oceanic residence time of each element (Table 5)

*Table 9.* Trace element levels observed in other studies of the genera and species of algae corresponding to the products studied (mg $kg^{-1}$ d wt).

| Organism | Fe | Mn | Zn | Cu | Ni | Co | Cr | Pb | Cd | Refs.[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| *Spirulina* | 500–1000 | 13–205 | 24.1–185 | 2.6–16 | 2.5–12.9 | 1.9 | 2.2–6.5 | 1.3–6.7 | 0.2–0.7 | 1, 2, 3, 4 |
| *Chlorella* | – | – | – | 24.2 | – | – | – | 8.1 | 1.4 | 5 |
| *Undaria pinnatifida* | 103–430 | – | 24.0 | 3.5 | – | – | – | 0.41 | 0.42 | 6, 7, 8 |
| *Hijika fusiforme* | 160 | – | 80 | – | – | – | – | – | – | 8 |
| *Palmaria palmata* | 153–4400 | 11–110 | 41–200 | 22–48 | – | 0.5–2.6 | 34 | 28 | – | 9 |
| *Fucus* | – | 33–190 | 42–37000 | 1.7–107.0 | – | – | 1–4 | 0.5–163 | 0.4–20.8 | 10 |

[a] References: 1-Johnson & Shubert, 1986b; 2-Mannino & Benelli, 1980; 3-Jassby, 1988a; 4-Becker & Benkataraman, 1982; 5-Yannai *et al.*, 1980; 6-Chapman & Chapman, 1980; 7-Perez *et al.*, 1988; 8-Yamamoto *et al.*, 1979; 9-Morgan *et al.*, 1980; 10-Rai *et al.*, 1981.

agree with the model proposed by Yamamoto *et al.* (1979), although these authors found *r* (correlation coefficient) to be −0.9 for most of the species tested. Probably, the low value of *r* in 'Fucus' product observed in this study is due to the processing of the biomass during production of pills, when elements could have been washed out. The results in Table 5 suggest that the establishment of these parameters for each species may be useful for the detection of adulterations in cases where identification is difficult, for example in products sold as pills.

In the case of *Spirulina*, Johnson and Shubert (1986a) showed in experiments with rats that the non-heme iron present in its biomass is absorbed very well, which is unusual with the iron of plant foods. They considered that *Spirulina* products are a concentrated source of Fe, even when they found lower amounts than in the present paper. Most of the lots analyzed of 'Fucus' and 'Chlorella' products showed even an higher Fe content than 'Spirulina' products (Table 4), although the presence of variable amounts of Ca and P, which diminish Fe absorption (Johnson & Shubert, 1986a), its chemical form (Jassby, 1988a) and the composition of other foods taken together with the algae may influence the availability of this iron.

Most of the trace elements present in the algal biomass are heavy metals. Algae have been reported to be highly active in heavy metal concentration (Rai *et al.*, 1981; Whitton, 1984). The toxic effects of heavy metals present in foods have induced the establishment of maximum permissible intakes by international organizations (Czarnecki & Kritchevsky, 1980; Cuthbertson, 1989). When applying these limits to the analyzed algal products, the amounts necessary to exceed them are well above those corresponding to 'normal' use. For example, the amount of 'Fucus' that supplies the maximum permissible daily intake of Pb (500 μg) is 40 g, while the commercial suppliers of this product recommend doses of 1.8–5.4 g $d^{-1}$. The levels of Pb in 'Spirulina' products were also lower than the 20 ppm recommended by a Japanese manufacturers' association (Jassby, 1988b). However, the product 'Chlorella' did exceed the proposed permissible maximum Pb content (2 ppm) for this type of product. Recommendations for Pb content in single cell protein (5 ppm) were also exceeded by some lots of microalgal products.

The results for fatty acid composition agree with other published studies of the same species, although it has been shown that there is great heterogeneity (Hayashi *et al.*, 1974; Sato, 1975; Pohl & Zurheide, 1979; Morgan *et al.*, 1980; Takagi *et al.*, 1985; Cohen *et al.*, 1987). A high content of polyunsaturated fatty acids increases the nutritive value of foods, the recommendation for the human diet being a polyunsaturated/saturated fatty acid ratio (PIN/SAT) higher than 0.45

(Cuthbertson, 1989). Five of the eight products studied followed this recommendation (Table 6).

The low content of the 18:3 acid in 'Chlorella' products may be explained if one considers the effect of heterotrophic culture conditions on fatty acid composition. When *C. vulgaris* is cultured in a medium with an organic carbon source, the 18:3 acid content is extremely low when compared to autotrophic culture conditions (Nichols, 1965). Indeed, this fatty acid is absent in *C. vulgaris* (Podojil *et al.*, 1978) and *C. kessleri* (Diab *et al.*, 1976) cultured heterotrophically in a fermentor. This is remarkable considering that the addition of a organic carbon source, such as glucose or acetate, is a common practice in *Chlorella* factories (Richmond, 1986). The exposure of the algal biomass to the sun during several days (Soong, 1980) may also have an effect on polyunsaturated fatty acids content, due to photooxidation processes, in analogy to oils (Lundberg, 1954) and several fried foods (Usuki, 1989) containing chlorophylls and exposed to air and light. These possible changes during marketing should be considered, specially when polyunsaturated fatty acid production has been suggested as one important future market application for microalgae (Kyle, 1989). The products 'Dulce' and 'Spirulina' (A, B, C) showed a neutral sugar pattern compatible with the predominance of easily digestible polysaccharides. Xylose and glucose were the major sugars in 'Dulce' product. This agrees with the fact that in *Palmaria palmata* the main polysaccharides are xylan and floridean starch, which can be absorbed in the human digestive tract (Chapman & Chapman, 1980; Morgan *et al.*, 1980). The predominance of glucose in the total sugar content of 'Spirulina' products agrees with the results of Casu *et al.* (1980), who, studying the reserve carbohydrates of *S. platensis*, isolated and characterized a glucan with all the characteristics of glycogen. This polysaccharide was the main carbohydrate, constituting the 15% of the biomass. Shekharam *et al.* (1987) also reported glucose as the major sugar in *S. platensis*. However, there have also been reports on the carbohydrate composition of *Spirulina* stating that the main sugar is rhamnose (Quillet, 1975; Santillan, 1982).

## Conclusions

It has been shown that the chemical analysis of algal food products provides data on which a more realistic nutritional and toxicological evaluation can be based. The products studied showed a gross chemical composition (ash, lipids, carbohydrates, protein etc.) similar to what has been published previously for natural or laboratory-produced populations of the corresponding genera and species. However, detailed study of each fraction revealed in some cases differences from previous data. Lot-to-lot variability was more pronounced in trace elements than in macrominerals. In some cases, chemical characteristics of the products could be explained considering events related to production procedures. From the results obtained in this paper, it can be concluded that these products were suitable for human use, in relation to their content in water, chlorophyll *a*, nucleic acids and heavy metals, although some microalgal products did exceed the Pb limits suggested by a Japanese manufacturers' association and by recommendations for single cell protein.

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