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NEUTRON ACTIVATION ANALYSIS OF SOME MARINE MACROPHYTES ALONG THE ROMANIAN BLACK SEA SHORE

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ABSTRACT:

The concentration of 23 chemical elements contained in 11 species of marine algae and phanerogams collected along the Romanian Black Sea coast have been determined. A comparison with earlier chemical determinations of Na, K, Ca and Mg concentrations is briefly presented.

INTRODUCTION

The knowledge of the elemental chemical composition of marine organisms and particularly of that of seaweeds is important due to the concentration capacity of these elements from the environment. It is also known that the analysis of the chemical composition of marine flora is an useful and inexpensive method for evaluating metal contamination (7). Thus, some species can be used as environmental indicators for different chemical elements (1,10,13).

The present paper deals with the chemical analysis of the main macrophytes existing nowadays along the Romanian Black Sea shore.

These data constitute a completion, as to the number of investigated species, of previous results obtained by means of the neutron activation analysis in Romanian algological researches (5, 6).

MATERIAL AND METHOD

Samples of marine banthic macrophytes, namely 5 chlorophyceans, 2 phaeophyceans, 2 rhodophyceans and 2 phanerogams, collected during 1978 and 198o (Table 1), were washed, dried (1o5°C) and ashed (480°C).

The mean hydrature (% of fresh weight) and the dry weight/ash ratio were determined for each species.

Ashed samples in thin aluminium foils were irradiated for 5o hours at 2.3×10^{11} n/cm^2.s neutron flux of VVRS-2 reactor (IFIN-Bucharest). After a cooling time of about 1o and 3o days the samples were measured at 65 cm^3 Ge(Li)-ORTEC detector (2.5 KeV resolution at ^{60}Co) in connection with a multichannels analyser (ICA-7o). The measurement time was 3o minutes or 1 hour.

The concentration of the following long lived elements Ba, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Rb, Sc, Sm, Sr, Th, Yb and Zn has been determined. GSP-1, Soil-5 and SL-1 standard rocks were irradiated together with samples; for Ca and Sr determinations CaO and $SrCO_3$ standards were used. The gamma spectrum of Ceramium elegans, obtained after long irradiation, is exemplified (Fig.1).

For the determination of the concentration of short lived elements short irradiations (5 minutes) in an air rabbit system of the reactor were performed; the samples were measured (2 minutes) using the same set up after 7 to 3o minutes of cooling time. The concentrations of Al, Mg, Mn, Na and K were determined using W-1, Soil-5 standard rocks and $KMnO_4$ solution. The gamma spectrum obtained after short irradiation of Bryopsis plumosa is exemplified (Fig.2).

V was found in two samples and Ti in one sample.

The concentration of elements determined in ashed material is expressed in % or in ppm.

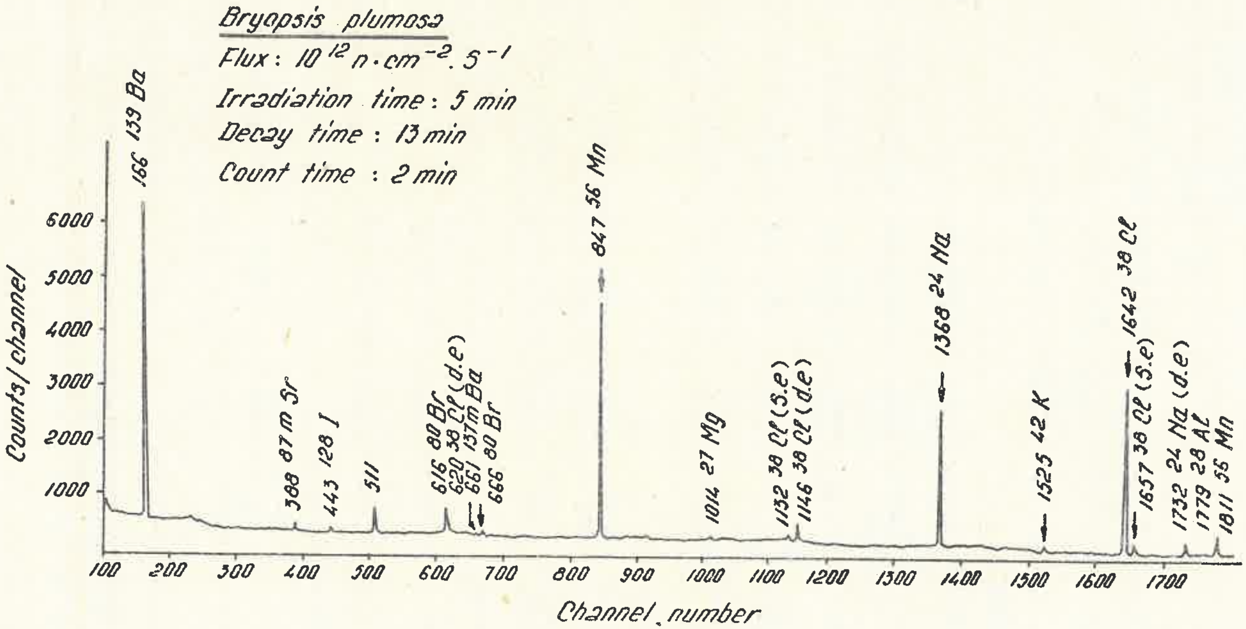

Fig.1 - Gamma spectrum of <u>Bryopsis plumosa</u>

Concentration of major elements of marine algae and phanerogams

Species	Locality	Sampling date	Al (%)	Ba (%)	Ca (%)	K (%)
CHLOROPHYTA						
Enteromorpha linza	Agigea	Aug., 1978	0.43±0.02	-	4.2±0.6	9.6±0.6
Ulva lactuca	Jupiter	May, 1978	0.51±0.02	0.033±0.006	8.2±0.6	10,4±0.5
Bryopsis plumosa	Agigea	May, 1978	1.70±0.07	11.1±0.9	3.6±0.5	7.4±0.5
Cladophora vagabunda	Techirghiol	Aug., 1978	0.68±0.01	0.015±0.008	1.8±0.4	15.6±0.7
Cladophora sericea	Agigea	Apr., 1980	2.75±0.03	0.050±0.017	7.3±0.6	22.4±1.1
PHAEOPHYTA						
Cystoseira barbata	Jupiter	Aug., 1978	0.74±0.03	0.064±0.006	8.2±0.6	22.4±1.2
Scytosiphon lomentaria	Agigea	Jan., 1980	1.47±0.03	0.055±0.016	8.1±0.7	13.8±1.0
RHODOPHYTA						
Ceramium elegans	Agigea	Mar., 1980	2.3 ±0.05	-	4.3±0.4	9.5±0.5
Porphyra leucosticta	Agigea	Apr., 1980	1.41±0.06	-	4.0±0.5	13.5±0.7
PHANEROGAMAE						
Zostera nana	Eforie Sud	Aug., 1978	1.5 ±0.1	0.026±0.011	5.5±0.5	14.0±0.6
Zostera marina	Eforie Sud	Aug., 1980	0.58±0.01	0.026±0.008	11.5±1.0	12.0±0.6
$R = \frac{\text{maximum concentration}}{\text{minimum concentration}}$			6.4	740	6.4	3.0

Table 1

(% of ash) from 11 species
along the Romanian Black Sea shore

Fe (%)	Mg(%)	Mn (%)	Na (%)	Sr (%)	Zn (%)
0.51±0.03	6.4±0.7	0.139±0.002	10.1±0.3	0.13±0.02	0.027±0.005
0.27±0.01	6.9±0.7	0.048±0.001	6.6±0.2	0.13±0.02	0.006±0.001
1.15±0.04	1.5±0.4	0.106±0.002	6.8±0.2	1.90±0.06	0.011±0.004
0.40±0.02	1.6±0.3	0.043±0.001	10.8±0.2	0.09±0.02	0.021±0.004
1.63±0.05	1.9±0.3	0.104±0.002	5.0±0.1	0.14±0.03	0.030±0.006
0.57±0.02	3.6±0.4	0.035±0.001	6.3±0.2	1.20±0.04	0.005±0.001
1.40±0.05	2.3±0.3	0.033±0.001	6.7±0.2	0.52±0.05	0.042±0.009
1.70±0.04	2.0±0.4	0.215±0.002	6.2±0.2	0.08±0.04	0.015±0.003
1.07±0.03	2.6±0.5	0.036±0.001	11.6±0.3	0.17±0.03	0.038±0.008
0.99±0.03	6.7±0.7	0.628±0.010	9.0±0.3	0.19±0.02	0.018±0.004
0.38±0.01	2.3±0.3	0.119±0.002	9.8±0.3	0.67±0.04	0.010±0.002
6.3	4.6	19	2.3	23.8	7

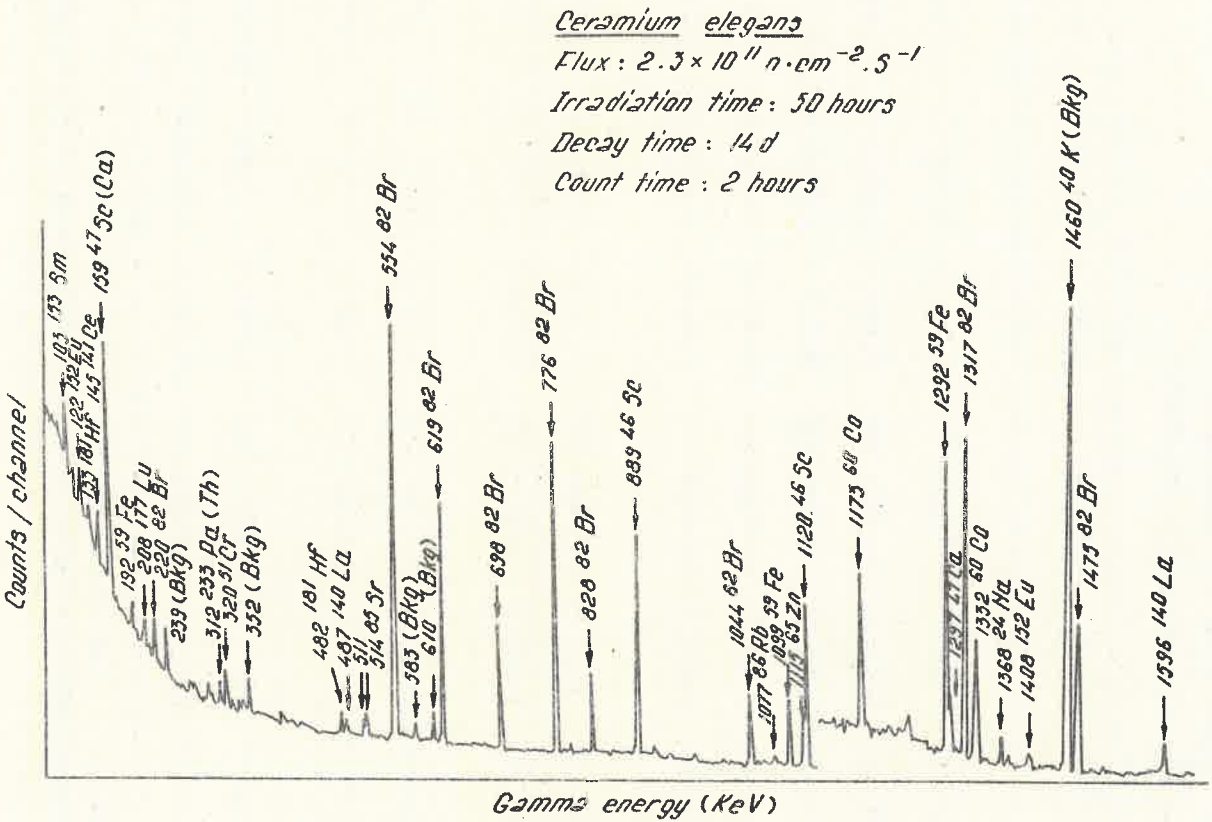

Fig.2 - Gamma spectrum of <u>Ceramium elegans</u>

RESULTS AND DISCUSSION

The concentrations of chemical elements are differently presented as major elements - % (Table 1) and trace elements- ppm (Table 2).

Beside the elements contained in the tables, the presence of V in Cystoseira barbata (12±4 ppm) and Ceramium elegans (29±6 ppm), and of Ti in Scytosiphon lomentaria (o.43±o.o4 %) is evinced.

In the tables, the ratio R means the coefficient between the highest and lowest concentration of an element. Generally, a variation within an order of magnitude of ratio R is observed. Exceptions concern the elements Ba, Sr, Eu, Mn, La, Hf and Th for which the ratios of 74o, 24, 2o, 19, 15, 13 and 11, respectively, show significant differencies among the analyzed species.

The element Ba, for which this ratio is very high (74o), is very concentrated in Bryopsis plumosa (11.1 %), as compared to Cladophora vagabunda with a minimum Ba content (o.o15 %), showing thus a variation of almost three orders of magnitude. Bryopsis plumosa is interesting also due to its high content of Sr(24 times higher than in Ceramium elegans), and of La (44.7 ppm) and Cs (2.4 ppm) as compared to Cladophora vagabunda (3 ppm) and Ulva lactuca (o.5 ppm), respectively.

But Bryopsis plumosa has the lowest concentration values concerning K and Mg as compared to the other species.

Other chlorophyceans, Enteromorpha linza and Cladophora vagabunda, do not evince a high concentration for none element, as compared to other species; they show the lowest concentrations for Al, Rb and Sc and for Ba, Ca, Ce, La, Lu, Rb, Sc, Sm, Th and Yb, respectively.

Cladophora sericea shows high concentrations for Al, K, Cr, Sc and a lowest value for Na concentration, and Ulva lactuca a high concentration of Mg and a lowest concentration for Fe, Zn, Co and Cs.

Among phaeophyceans, Scytosiphon lomentaria is interesting due to its high concentrations of several elements: Zn, Ce, Eu, Hf, Lu, Rb, Sm, Th and Yb, and low values for Mn and Cr.

Concentration of trace elements
of marine algae and phanerogams

Species	Ce (ppm)	Co(ppm)	Cr (ppm)	Cs(ppm)	Eu (ppm)	Hf(ppm)
CHLOROPHYTA						
Enteromorpha linza	6.8±1.5	7.4±0.4	18.5±2.5	1.0±0.2	0.31±0.12	0.9±0.2
Ulva lactuca	8.1±0.8	3.5±0.2	14.5±1.4	0.5±0.1	0.10±0.03	1.0±0.1
Bryopsis plumosa	21.4±2.0	7.6±0.3	30.7±3.0	2.4±0.2	0.39±0.12	3.0±0.2
Cladophora vagabunda	5.4±1.5	6.1±0.3	11.0±1.4	1.1±0.2	0.12±0.04	0.7±0.2
Cladophora sericea	26.5±2.5	9.6±0.4	40.7±3.2	1.9±0.2	0.50±0.10	2.5±0.3
PHAEOPHYTA						
Cystoseira barbata	6.4±0.7	6.0±0.2	14.2±1.0	1.0±0.1	0.05±0.02	0.6±0.1
Scytosiphon lomentaria	44±4	7.0±0.4	7.9±0.5	2.1±0.4	1.0 ±0.2	7.8±0.4
RHODOPHYTA						
Ceramium elegans	23.5±2.2	17.5±0.6	35.0±2.5	2.2±0.3	0.55±0.10	2.0±0.2
Porphyra leucosticta	17±2	6.2±0.3	30.3±3.0	2.3±0.3	0.32±0.08	2.5±0.3
PHANEROGAMAE						
Zostera nana	17.8±1.7	25.6±0.8	25.2±2.5	1.6±0.2	0.33±0.08	1.4±0.2
Zostera marina	6.7±1.0	9.2±0.3	11.2±1.1	1.1±0.2	0.18±0.04	0.6±0.1
$R = \frac{\text{max.conc.}}{\text{min conc.}}$	8.1	7.3	5.2	4.8	20	13

Table 2

(ppm of ash) from 11 species
along the Romanian Black Sea shore

La(ppm)	Lu (ppm)	Rb(ppm)	Sc(ppm)	Sm(ppm)	Th(ppm)	Yb(ppm)
3.2±0.5	0.07±0.02	32±10	1.1±0.1	0.5±0.1	0.9±0.2	1.5±0.6
3.2±0.5	0.07±0.01	35± 9	1.1±0.1	0.9±0.1	1.2±0.1	0.5±0.2
44.7±2.7	0.10±0.02	36± 8	3.6±0.1	1.5±0.2	2.8±0.3	0.8±0.5
3.0±0.5	0.03±0.02	32± 8	1.0±0.1	0.5±0.1	0.7±0.2	0.4±0.3
15.3±0.7	0.18±0.03	65±20	5.7±0.1	2.5±0.2	4.0±0.3	1.5±0.6
3.5±0.4	0.05±0.01	84± 9	1.8±0.1	0.5±0.1	0.8±0.1	0.4±0.2
24.7±2.3	0.23±0.04	88±18	3.6±0.1	3.9±0.2	7.9±0.3	2.5±0.8
13.0±0.9	0.15±0.02	85±15	5.5±0.1	2.1±0.2	3.9±0.2	1.7±0.6
10.9±0.9	0.14±0.03	37±13	3.5±0.1	1.5±0.1	2.5±0.3	1.5±0.6
8.7±0.9	0.09±0.02	68±10	3.3±0.1	1.6±0.2	2.6±0.3	0.8±0.3
3.1±0.4	0.06±0.01	48± 7	1.1±0.1	0.7±0.1	0.9±0.2	0.4±0.2
14.9	7.7	2.8	5.7	7.8	11.3	6.3

Ceramium elegans, among rhodophyceans,evinces a highest concentration for Fe and a lowest value for Sr, and Porphyra leucosticta a highest concentration for Na.

Among phanerogams, Zostera nana has the highest concentration for Mn and Co, and Z.marina the highest concentration for Ca and lowest values for Yb and Hf.

Quite similar concentration values among species are visible from the tables concerning the major elements Na,K,Mg and even Fe,Ca and Al,and concerning the trace elements Rb,Cr and Sc.

Concerning the concentrations of Na,K,Ca and Mg, values of the same order of magnitude as previous ones obtained by chemical methods (14) resulted using neutron activation analysis; some differences occured only for Ca, consisting in lower values obtained using neutron activation analysis.

There are numerous references concerning the chemical composition of marine macrophytes,but less for a direct comparison with our results.

However, we exemplify some of other author's data concerning the same genus (species) from other marine areas.

Thus, among chlorophyceans, Enteromorpha linza evinced 1.55 mg Cr/kg dry weight (2), E.compressa 1o.9 mg Ni/kg d.w. (9), and E.proiifera concentrations especially of Mn, Co, Zn, Mo and Cr (15); in Cladophora glomerata 23.7 mg Zn/kg d.w. (1o); in Cladophora sp. high concentrations of Zn, Rb, Sc, Cr, Ba and Ni(16); in Ulva between 1.3 - 3.1 mg V/kg d.w. (4) and in U.fenestrata concentrations of Mn, Fe and Ni (15).

Among phaeophyceans,in Cystoseira barbata 1.42 mg Cr/kg d.w. were determined (2).

In Porphyra,among rhodophyceans,using the neutron activation analysis, 262 mg V/kg ash and 17 mg Mg/kg ash (3), or 1.2 mg As/kg d.w.and till 1.o mg Mb/kg d.w.(4),and in P.umbilicalis 66 mg Zn/kg d.w., 387 mg Fe, 29 mg Mn and 2.2 mg Ni (13) were found.

In the phanerogam Zostera asiatica concentrations of Ti, Mn, Ni and Mo were established (15).

The accumulation of rare earths in different marine organisms, including Ulva lactuca, Cystoseira barbata and Zostera marina, seems to be specific, suggesting the possibility of their use as indicator species; differences of one to two orders of magnitude were determined between the concentrations of some elements in the same algal species from the northern and southern Adriatic Sea (11).

It was established too that algae evince higher concentrations than terrestrial plants concerning Na,Fe and Mg, or much higher concentrations than sea water concerning Cr (8). Also, the Ni contents of limnetic algae are higher than those of seaweeds (9). But the data of different authors do not coincide always; thus, for example, higher concentrations of Fe were determined in chlorophyceans compared to phaeophyceans (8), or higher ones in phaeophyceans than in chlorophyceans (12).

CONCLUSIONS

1. The concentrations of 23 chemical elements were determined in the main species of algae and phanerogams along the Romanian Black Sea shore.

2. The concentration of chemical elements varied depending on the taxonomic belonging of species.

3. The species Cladophora sericea, Bryopsis plumosa and Scytosiphon lomentaria evinced numerous elements with the highest concentration as compared with other species.

4. The above mentioned species require further analyses of their chemical composition in order to precise their use as bioindicators in studies of marine pollution with metals.

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