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Instrumental neutron activation analysis of Mytilus galloprovincialis from the Romanian Shore

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ABSRACT. Mytillus galloprovincialis specimens sampled from two sampling sites of the Rumanian shore of the Black Sea have been analysed by instrumental neutron activation analysis. 27 elements have been determined in shoft tissues and byssus. Higher elemental content has been found in the shoft tissues than in byssus.

INTRODUCTION. Mussels have the capacity to accumulate various pollutants, heavy metals or radionuclides from sea water and therefore are considered as suitable marine pollution indicators. It is of interest to get information about the variation of the trace element concentration in mussels from north to south of the Rumanian shore in Black Sea.

EXPERIMENTAL. Mytillus galloprovincialis specimens have been collected in October 1987: at 36 km offshore East Sulina and 7 km in the front of Serpents Islands on a silty clay facies, 38 m depth and at 7.3 km offshore East Mangalia on a rocky facies, 37 m depth. After rinsing with distilled water and removal of shells of M. galloprovincialis the shoft tissues and byssus have been separated dried and grounded into a fine powder. About 100 mg of each sample were irradiated along with an equal quantity of the IAEA standard reference material MA-M-2/TM, in the VVRS-2 nuclear reactor of Bucharest (thermal neutron flux 10exp12-13 n/cm*exp2*sec). All measurements were carried out by using a high resolution (2 kev) Ge(Li) detector coupled with a multichannel analyser.

TABLE 1 - Instrumental neutron activation analysis of *Mytilus galloprovincialis* sampled on the Black Sea, Romanian shore during 1987

Element	Location and date of sampling			
	East Sulina 8 Oct. 1987, 38 m depth.		Mangalia (Vama Veche) 13 Oct. 1987, 37 m depth.	
	Byssus	Soft tissue	Byssus	Soft tissue
Al ppm	168 ± 13	223 ± 20	364 ± 27	1470 ± 110
As ppm	5.1 ± 0.3	10.3 ± 0.4	4.3 ± 0.2	10.3 ± 0.4
Au ppb	10 ± 1	18 ± 2	10 ± 1	25 ± 2
Br ppm	105 ± 2	145 ± 3	104 ± 2	205 ± 5
Ca %	0.78 ± 0.09	1.89 ± 0.17	1.01 ± 0.10	0.73 ± 0.08
Ce ppm	0.5 ± 0.2	1.1 ± 0.3	0.7 ± 0.2	2.1 ± 0.3
Cl %	2.28 ± 0.06	2.40 ± 0.06	1.73± 0.04	2.31 ± 0.06
Co ppm	0.35 ± 0.04	0.45 ± 0.04	0.59± 0.06	0.89 ± 0.09
Cr ppm	0.6 ± 0.2	1.2 ± 0.3	1.4 ± 0.2	3.5 ± 0.5
Cs ppm	<0.13	<0.2	<0.13	0.36 ± 0.13
Fe ppm	128 ± 22	516 ± 40	426 ± 40	1460 ± 60
Hg ppm	0.03 ± 0.01	0.09 ± 0.03	0.3 ± 0.1	0.4 ± 0.1
I ppm	6.4 ± 2.4	12 ± 3	5.5 ± 2.5	10 ± 3
K %	0.14 ± 0.04	<0.19	0.16± 0.05	0.42 ± 0.10
La ppm	<0.14	0.23 ± 0.08	0.21 ± 0.06	0.89 ± 0.10
Mg %	0.38 ± 0.06	0.41 ± 0.08	0.50 ± 0.07	0.62 ± 0.11
Mn ppm	18 ± 1	40 ± 2	57 ± 3	140 ± 6
Na %	1.51 ± 0.015	1.65 ± 0.016	1.36 ± 0.014	1.56 ± 0.015
Rb ppm	<2.6	<1.5	2.3 ± 0.6	4.1 ± 1.2
Sb ppm	0.19 ± 0.06	0.14± 0.04	0.09 ± 0.03	0.16±0.05
Sc ppm	42 ± 8	81 ± 8	84 ± 8	305 ± 30
Se ppm	2.8 ± 0.5	5.0 ± 0.7	3.9 ± 0.1	5.2 ± 0.1
Sm ppm	≤0.01	0.05± 0.01	0.03 ± 0.01	0.15 ± 0.01
Th ppm	0.06 ± 0.02	<0.05	0.08 ± 0.03	0.22 ± 0.04
U ppm	<0.4	<0.6	<0.4	<0.5
V ppm	0.6 ± 0.2	0.7 ± 0.3	0.9 ± 0.2	5.5 ± 0.8
Zn ppm	2630 ± 65	2430 ± 60	2230 ± 60	2070 ± 50

RESULTS AND DISCUSSION. The data concernig 27 elements determined in M. galloprovincialis collected from Sulina and Mangalia in Black Sea are given in TABLE 1. The following conclusions shoud be pointed out: a) Mineralisation is increasing from north to south in the Black Sea at about the same depth. b) Shoft tissues have higher concentration of trace element than byssus. c) The Hg content found in shoft tissue (0.09 ppm) and in byssus (0.03 ppm) from Sulina samples is four and ten times lower, respectively than in the corresponding samples collected from Mangalia.

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Distribution of trace elements in the hemolymphae of Mytilus galloprovincialis

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Summary. The concentration of 16 elements from the low molecular weight protein fraction of the hemolymphae of *Mytilus galloprovincialis* has been determined by the instrumental neutron activation method.
Resume. La fraction protéinique à petite masse moléculaire dans l'hémolyphe de la moule *Mytilus galloprovincialis* a été analysée par l'activation neutronique instrumentale. On a identifié 16 éléments.
Material and Method. Specimens of *Mytilus galloprovincialis* were collected in September 1987 from the Black Sea (North Constantza).

The spowning mussel was rinsed with the deionised water. After the shell opening the soft tissue was also thoroughly cleaned with deionised water. The hemolyphae was collected by long cuts of mussel body. The analysed fraction was prepared by deproteinisation and delipoidation with benzene. The aqueous fraction purified by vacuum evaporation of the benzene was dried. Two different concentrated samples extracted by the above method have been analysed.

The samples and reference material have been irradiated for two hours in a 2.10^{12} $n.cm^{-2}.s^{-1}$ flux. After 6 ÷ 30 days cooling time the measurements have been carried out making use by 65 cm^3 Ge(Li) detector with 2 keV energy resolution. The measurement time was 1 ÷ 7 hours.
Results and Discussion. The results expressed in g/ℓ, mg/ℓ or µg/ℓ are presented in Table 1.

Our method for hemolymphae preparation has concentrated the macroelements Na, K, Ca, Br. The samples are also high in Sr, Fe, Zn, Ba, Rb. The high strontium level in samples was associated with its role in shell formation [1]. The concentration of some oligoelements is also determined. The role of Se as an essential trace element in human and animal nutrition as well as its toxic effects at higher concentrations is well established [2].

The low molecular weight protein fractions isolated by our method are involved in the concentration of metals. Tolerance of mussels to increased tissue metals concentration may be related to the presence of detoxifying mechanisms. A process that may be important in metal detoxification in mussels is the binding of metals to low molecular weight proteins similar to metallothionein [3] and to the high molecular weight protein fraction which contains metalloenzymes [4].

TABLE 1 - Elemental composition of isolated low molecular protein fraction from the *Mytilus galloprovincialis* hemolymphae

Element		Concentration	
		Sample 1	Sample 2
Na	g/ℓ	1.19 ± 0.019	6.96 ± 0.139
K	g/ℓ	0.632 ± 0.063	2.537 ± 0.381
Ca	mg/ℓ	88 ± 9	158 ± 24
Br	mg/ℓ	12 ± 1	56 ± 2
Sr	µg/ℓ	1366 ± 260	2323 ± 63
Ba	µg/ℓ	607 ± 195	1161 ± 370
Fe	µg/ℓ	455 ± 108	1689 ± 370
Rb	µg/ℓ	347 ± 43	633 ± 53
Zn	µg/ℓ	195 ± 22	1267 ± 106
Cr	µg/ℓ	139 ± 7	259 ± 16
Ni	µg/ℓ	130 ± 43	264 ± 105
Se	µg/ℓ	39 ± 4	95 ± 11
Co	µg/ℓ	13 ± 1	42 ± 4
Hg	µg/ℓ	11 ± 2	9 ± 2
Sb	µg/ℓ	2.3 ± 0.4	5.9 ± 0.8
Au	µg/ℓ	0.14 ± 0.03	0.12 ± 0.05

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